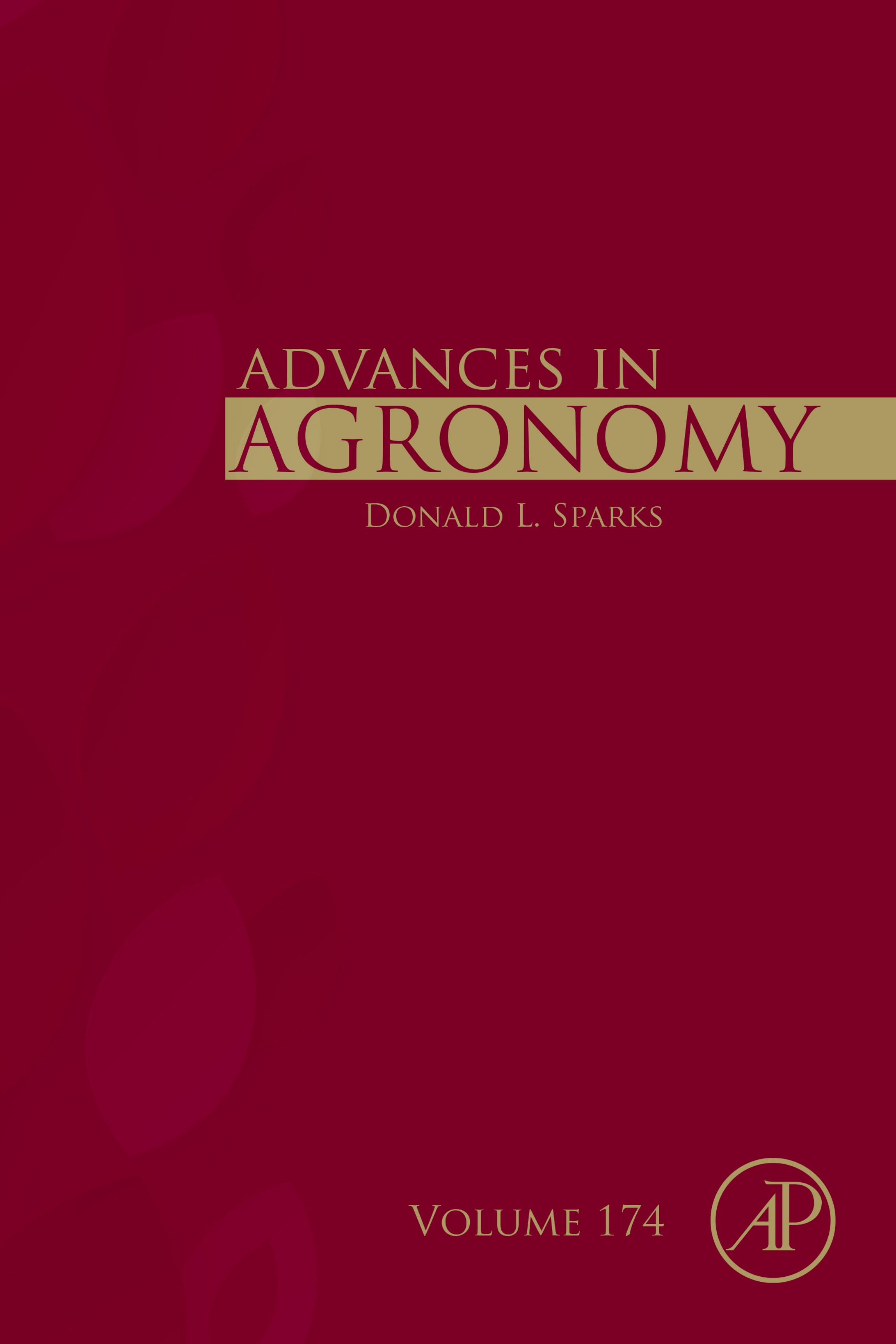

ADVANCES IN AGRONOMY

DONALD L. SPARKS

VOLUME 174

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Preface

Volume 174 contains five timely reviews that will be of interest to the readership. Chapter 1 covers soil nitrogen supply and nitrogen losses from fertilizers in Australian dryland grain cropping systems. Chapter 2 discusses the gaps in knowledge and methods in assessing environmental impacts of trace contaminants from organic waste recycling. Chapter 3 examines the relevance of the nutrient power buffer concept in quantifying plant nutrient bioavailability. Chapter 4 discusses the relationship of plasma membrane H^+-ATPase stimulation by auxins or fusicoccin and its relation to maize kernel setting, grain yield, and harvest index. Chapter 5 evaluates the application of the Mitscherlich equation and its extensions to estimate the soil nitrogen pool fraction associated with crop yield and nitrous oxide emission.

I greatly appreciate the outstanding contributions of the authors.

Donald L. Sparks
Newark, Delaware, USA

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CHAPTER ONE

Soil nitrogen supply and N fertilizer losses from Australian dryland grain cropping systems

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Abstract

There is a global imperative to satisfy the demand for grain production and minimize environmental impacts associated with applying nitrogen (N) fertilizers. Soil is critical to the regulation of N supply and loss from agricultural systems. We summarize field-based measurements of these pathways for Australian dryland (rainfed) grain cropping soils in three agroclimatic cropping regions. In situ net N mineralization rates have been widely reported from Australian dryland cropping soils, with up to 285 kg N ha^{-1} mineralizing during the growing season and up to 190 kg N ha^{-1} accumulating during the fallow between harvest and sowing of the next crop. Ammonia volatilization measurements are sparse and cover few Australian dryland cropping soils, with field-measured losses ranging from 0% to 34% of applied N. Nitrous oxide emissions have been quantified for all key Australian grain growing regions and the median annual rate is low (0.19 kg N ha^{-1} yr^{-1}). Dinitrogen losses via denitrification are poorly understood with evidence that they may be substantial (>50% of N fertilizer applied) from soils high in clay or organic carbon. Our understanding of nitrate leaching losses comes largely from coarse-textured, free-draining soils that have not received N fertilizer. Long-term studies investigating all key soil N supply and loss pathways and using a combination of field-based measurements, laboratory-based process studies, and modeling are required to advance our understanding of soil N supply and losses from contemporary and future dryland cropping systems in Australia.

1. Introduction

There is currently tension between satisfying global demand for grain production and minimizing the environmental impacts of applying nitrogen (N) fertilizers to produce these crops. Staple food crops need to increase by at least 1% per annum (relative to 2010) to maintain food security over the next two decades (Fischer et al., 2014), with some suggesting that this will be best achieved via intensification of production inputs such as N fertilizer (Hochman and Horan, 2018; Ladha et al., 2016; Pradhan et al., 2015). However, greater N fertilizer use could lead to increased losses of reactive forms of N such as ammonia (NH_3), nitric oxide (NO), nitrous oxide (N_2O), and nitrate (NO_3^-), from the soil to the environment; losses that need to be minimized if N fertilizer use is to be sustainable. This is a key challenge to crop production given that less than half of the N applied to agricultural land is currently assimilated by the crop in the first year of application (Angus and Grace, 2017; Gardner and Drinkwater, 2009; Ladha et al., 2016; Smith and Chalk, 2018).

Soil processes regulate the N supply from soil organic matter (SOM) and N fertilizers to agricultural crops, plus crop N utilization and soil N

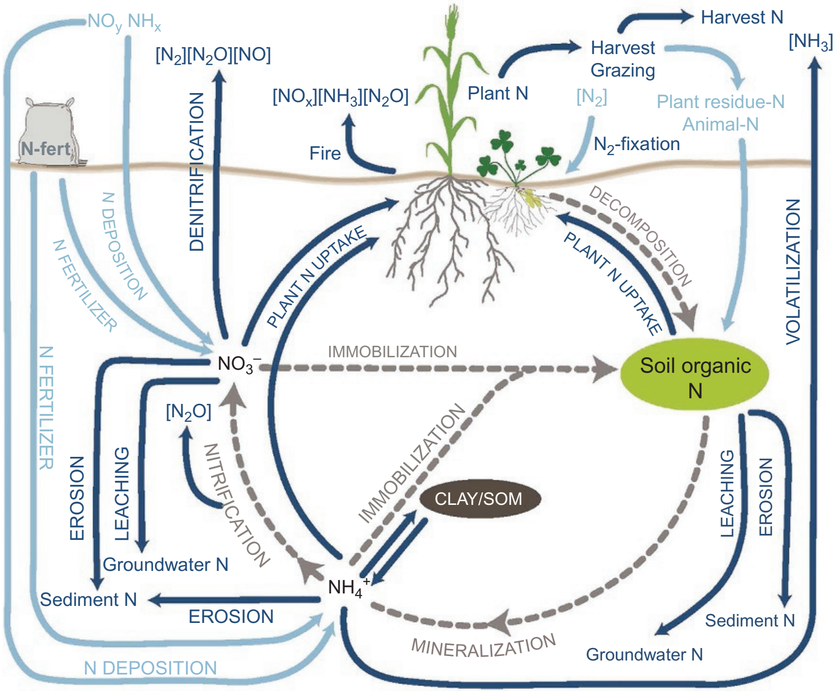
NO_y NH_x
$[N_2][N_2O][NO]$
N-fert
DENITRIFICATION
$[NO_x][NH_3][N_2O]$
Fire
Plant N
Harvest
Grazing
Harvest N
$[NH_3]$
$[N_2]$
Plant residue-N
Animal-N
N_2-fixation
DECOMPOSITION
PLANT N UPTAKE
N DEPOSITION
N FERTILIZER
PLANT N UPTAKE
VOLATILIZATION
NO_3^-
IMMOBILIZATION
Soil organic N
$[N_2O]$
NITRIFICATION
IMMOBILIZATION
CLAY/SOM
N FERTILIZER
EROSION
LEACHING
Groundwater N
Sediment N
NH_4^+
EROSION
N DEPOSITION
MINERALIZATION
LEACHING
EROSION
Sediment N
Groundwater N

Fig. 1 Terrestrial nitrogen (N) cycle showing pathways responsible for the supply and loss of N in soil and plants. Dashed lines indicate soil N transformations. Gases appear in square brackets. Abbreviations and chemical formulas: ammonia (NH_3), ammonium (NH_4^+), NH_3 + particulate NH_4^+ (NH_x), dinitrogen gas (N_2), nitrate (NO_3^-), nitric oxide (NO), nitrogen dioxide (NO_2), NO + NO_2 (NO_x), sum of all oxidized atmospheric odd-N species, e.g., NO_x + HNO_3 + HNO_2 (NO_y), nitrous oxide (N_2O), soil organic matter (SOM).

losses (Fig. 1). Soil organic matter is a reservoir of organically bound nutrients that must be mineralized to plant-available forms [e.g., ammonium (NH_4^+), NO_3^-] by soil microorganisms for crops to access the stored N (Robertson and Groffman, 2015). Nitrogen consumption via microbial immobilization, as well as loss pathways such as gaseous emissions, leaching and runoff, occur alongside N mineralization processes and collectively influence the amount of N available for plant uptake (Fig. 1). Gaseous N losses can occur through the volatilization of NH_3 from surface-applied fertilizer N (Freney et al., 1983; Pan et al., 2016), NO and N_2O emissions from the conversion of soil NH_4^+ to NO_3^- during nitrification (Wrage et al., 2001), and NO, N_2O and dinitrogen (N_2) gaseous emissions during denitrification of soil NO_3^- (Firestone and Davidson, 1989; Wrage et al., 2001).

Ideally, the timing and amount of N supply to crops via soil mineralization and N fertilizer additions are tightly coupled with crop assimilation to minimize the loss of surplus reactive N into the environment, an approach advocated by the "4R" nutrient stewardship concept (Johnston and Bruulsema, 2014). Meeting this challenge is overshadowed by the fact that global N input into crop production increased (+134%) faster than crop yields (+120%) between 1961 and 2007 (Conant et al., 2013), while the proportion of N recovered in grain or harvested crop parts remained relatively constant (approx. 40%) (Bouwman et al., 2017; Conant et al., 2013). This means that the ratio of crop N outputs to N inputs has fallen globally, causing reactive N to accumulate in the landscape and increasing the risk of N loss into the environment (Bouwman et al., 2017). However, N recovery trends in harvested components vary between countries, suggesting that balancing N inputs with crop requirements requires a local understanding of soil N transformations. This is consistent with the considerable variation in nature and the extent of soil N supply and loss mechanisms recorded in response to soil properties, climate, and land management (Conant et al., 2013; Zhang et al., 2015).

Australia is an important contributor to global food security, producing approximately 9% of global wheat (e.g., *Triticum aestivum*, *Triticum durum*) exports (Fischer et al., 2014). Crop production in Australia is largely conducted under "dryland" or "rainfed" conditions, relying only on natural rainfall without any form of irrigation. From 2014 to 2019, Australia's winter grain and oilseed production was dominated by wheat (average of 23,275 Kt yr^{-1}), followed by barley (*Hordeum vulgare*; 9844 Kt yr^{-1}) and canola (*Brassica napus*; 3378 Kt yr^{-1}), with grain sorghum (*Sorghum bicolor*) the most widely grown summer crop (1482 Kt yr^{-1}) (ABARES, 2020). Australia's N fertilizer usage rates were relatively low in comparison to global trends until the mid-1990s (Angus and Grace, 2017), but have increased significantly over the past three decades in response to a shift in land use toward higher cropping intensity, a decline in the proportion of arable area sown to leguminous crops or pastures, and improved yield responses to N fertilizer due to the adoption of improved agronomy and application technology (Angus and Grace, 2017; Seymour et al., 2012). The total amount of N fertilizer applied to Australian agricultural soils increased by 320% between 1989 and 2018 (Fig. 2), with nearly two-thirds of Australia's N fertilizer usage confined to the grains industry (including oilseeds) in 2014/15 (Heffer et al., 2017). During this period, the area of cropped land has remained relatively static, with an average of 20 M ha (Fig. 2). There have been extensive efforts over

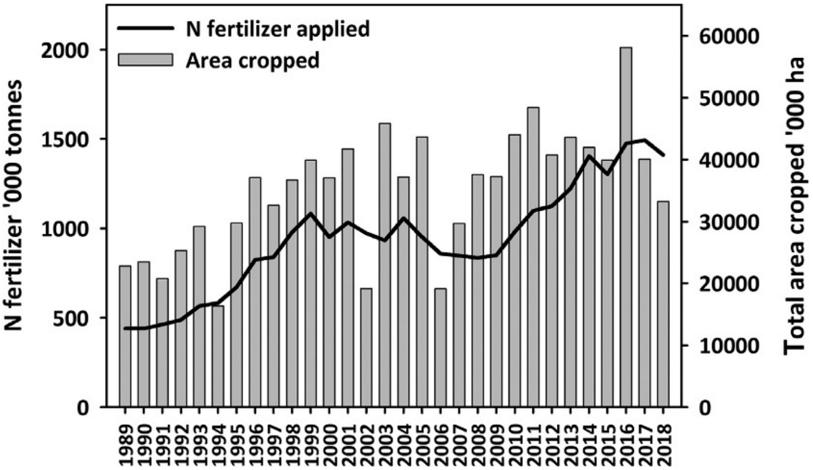

Fig. 2 Total area cropped to dryland grain crops and N fertilizer use by agriculture in Australia (1989–2018). Cropped areas include those sown to summer grains [maize (*Zea mays*), sorghum (*Sorghum bicolor)*, soybean (*Glycine* max), sunflower (*Helianthus annuus*)] and winter grains [barley (*Hordeum vulgare*), canola (*Brassica napus*), chickpea (*Cicer arietinum*), faba bean (*Vicia faba*), field pea (*Pisum sativum*), lentil (*Lens culinaris*), lupins (*Lupinus angustifolius*), oats (*Avena sativa*), triticale (X *Triticosecale*), wheat (*Triticum aestivum*, *Triticum durum*)]. Nitrogen fertilizer use is for all agricultural sectors, however two-thirds of Australia's N fertilizer usage is confined to the grains industry (including oilseeds) (Heffer et al., 2017). Data sources: Australian Bureau of Agricultural and Resource Economics and Sciences (ABARES, www.agriculture.gov.au/abares) and Food and Agriculture Organization of the United Nations (FAO, www.fao.org/home/en/).

the past two decades to quantify the extent of N supply and losses from the major soils of Australia's dryland grain growing regions and to improve NUE and limit off-site impacts (e.g., Angus and Grace, 2017; Mielenz et al., 2016a), providing valuable insights into the regulation of soil N supply and losses from Australian dryland cropping systems.

This review summarizes current knowledge on the extent, timing, and regulation of soil N supply and loss pathways from Australian dryland grain cropping systems. We focus specifically on N sources resulting from SOM mineralization and N losses via volatilization, nitrification, denitrification, and leaching. Nitrogen supply from the mineralization of plant residues and symbiotic N_2-fixation, and soil N losses from erosion and harvested crop products, are not included in the review. We identify limitations in our current understanding of soil N supply and losses and outline prospects for decreasing soil N losses from Australian dryland grain-growing regions.

2. Australian agroclimatic cropping regions

The Australian continent includes 27 million ha of land used for dryland cropping across five distinct climatic zones and a diverse range of soils (www.agriculture.gov.au/abares/aclump/land-use/land-use-of-australia-2010-11). Australian dryland grain cropping predominantly occurs between the 300 and 700 mm rainfall isohyets (Fig. 3), with farm sizes relatively large by world standards, often exceeding 2000 ha (Anderson et al., 2017). For this review, we divided the Australian dryland grains industry into three agroclimatic cropping regions based on geographical location and climate (Fig. 3; Table 1) and briefly describe each below.

The "South-West" dryland grains cropping region is the largest region in Australia and is located entirely within Western Australia. A high frequency of small rainfall events occurs from autumn (fall) to spring, confining

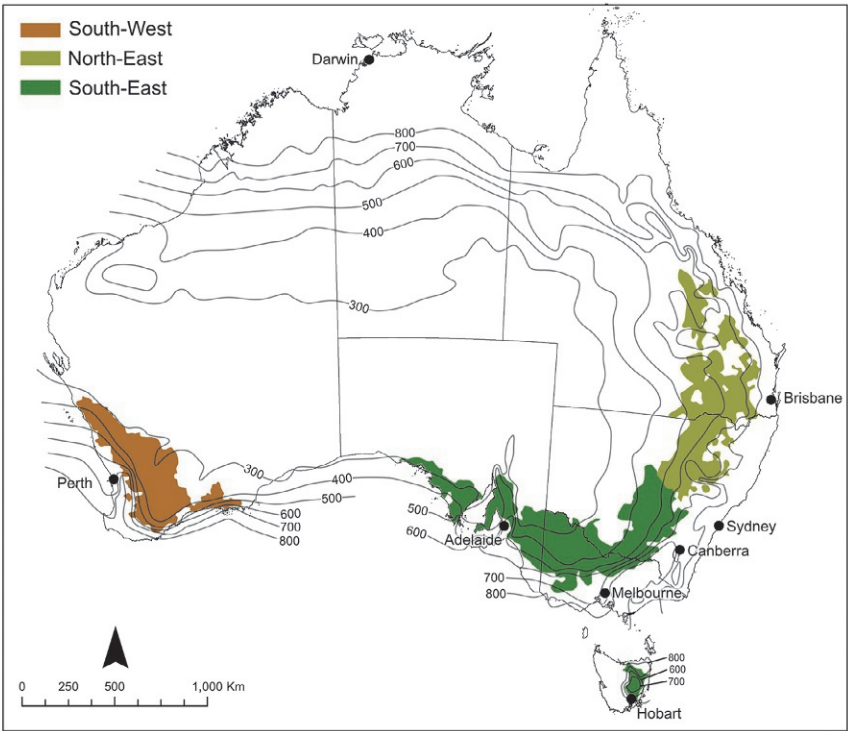
South-West
North-East
South-East
Darwin
800
700
600
500
400
300
Brisbane
Perth
300
400
500
600
700
800
500
600
Adelaide
Sydney
Canberra
700
800
Melbourne
800
600
700
Hobart
0 250 500 1,000 Km

Fig. 3 Location of South-West, South-East, and North-East dryland grain cropping regions in Australia and annual rainfall isohyets (mm yr^{-1}).

Table 1 Description of key agroclimatic dryland cropping regions of Australia.

Region[a]	Climates[b]	Annual rainfall[c] (mm)	Dominant WRB Soil Group[d,e]	Growing season[f]	Crops[g]	Wheat yield (t ha^{-1})
South-West	BSh, BSk, Csa, Csb	<250–750	Arensols, Luvisols, Planosols, Solonetz	Winter dominant cropping Yield dependent on winter and spring rainfall N fertilizer rates reflect yield potential and mineral N in the soil profile in the preceding fallow (average of 37 kg N ha^{-1} yr^{-1} for cereals, 48 kg N ha^{-1} yr^{-1} for canola)[h]	Barley, canola, lupin, wheat	1.5–2.5
South-East	BSh, BSk, Cfa, Cfb, Csa, Csb	<325–700	Calcisols, Histosols, Luvisols, Planosol, Solenetz, Vertisols	Winter dominant cropping Yield dependent on autumn to spring rainfall (and extent of waterlogging during winter for HRZ) N fertilizer rates reflect yield potential and mineral N in the soil profile in the preceding fallow (<40 kg N–150 kg N ha^{-1} yr^{-1})	Barley, canola, chickpea, field pea, lentil, wheat	0.5–8
North-East	BSh, Cfa, Cfb	450–750	Calcisols, Histosols, Luvisols, Nitisols, Solonetz, Vertisols	Summer and winter opportunity cropping (winter dominant in drier western areas) Yields dependent on storage of soil water during fallow (6–18 months) N fertilizer rates reflect yield potential and mineral N in the preceding fallow (< 40–150 kg N ha^{-1} yr^{-1})	*Winter:* barley, canola, chickpea, faba bean, wheat *Summer*: maize, mung bean, sorghum	1.5–5

[a] See Fig. 3 for details of geographical location of each region in Australia.

[b] Köppen–Geiger climate classification (Peel et al., 2007): BSh, hot semiarid; BSk, cold semiarid; Cfa, humid subtropical climate; Cfb, temperate oceanic climate; Csa, temperate (hot-summer Mediterranean climate); Csb temperate (warm-summer Mediterranean climate).

[c] Australian Bureau of Meteorology (http://www.bom.gov.au).

[d] WRB, World Reference Base for Soil Resources.

[e] Identified using Teng et al. (2020).

[f] HRZ high-rainfall zone (>500 mm yr^{-1}).

[g] Botanical names: barley, *Hordeum vulgare*; canola, *Brassica napus*; chickpea, *Cicer arietinum*; faba bean, *Vicia faba*; field pea, *Pisum sativum*; lentil, *Lens culinaris*; lupin, *Lupinus angustifolius*; maize, *Zea mays*; mung bean, *Vigna radiate*; sorghum, *Sorghum bicolor*; wheat, *Triticum aestivum*.

[h] Harries et al. (2021).

cropping primarily to winter and spring. Total annual rainfall generally declines from west to east across the region, and temperatures decrease from north to south (Fletcher et al., 2020). Summer rainfall is sporadic and coincides with warm to hot temperatures; rainfall and temperature are predicted to increase due to climate change (Alexander et al., 2007). The soils tend to be coarse-textured and relatively infertile, with a recent survey finding the average soil organic C (SOC) content lower in the northern and central parts of the region (0.95%) than the southern parts (2.4%) (Harries et al., 2015). This includes free-draining deep sands with a low capacity to store plant available water (40–140 mm; Lawes et al., 2009) and texture-contrast soils with an underlying clayey subsoil that limits the rate of water infiltration (<0.01–0.21 m day^{-1}; Moore et al., 1998). Annual legume-based pastures and grain legumes (especially narrow-leafed lupins, *Lupinus angustifolius*) were a significant part of the cropping rotation and acted as "break crops" to provide weed management, N inputs and disease breaks for wheat and barley—the dominant winter cereal crops. However, the collapse of wool prices in the early 1990s saw a move toward "continuous cropping" and a decline in the use of pasture legumes, as well as a shift from grain legumes to oilseed break crops (Harries et al., 2015; Robertson et al., 2010). This resulted in an increased reliance on N fertilizers (urea or urea ammonium nitrate), with growers decreasing the amount of N fertilizer applied before or at sowing. Instead, N fertilizer is tactically applied during the growing season (mainly by topdressing with granular urea) once there is greater certainty about likely crop N demand in response to the growing season (winter) rainfall outlook (Harries et al., 2015). Soil conservation practices that minimize soil disturbance are widely promoted, with minimum tillage and crop residue retention widely adopted (Llewellyn et al., 2012). Between cropping seasons, the soil remains "fallow," with weed growth controlled by herbicides to maximize the accumulation of plant available water for use by the next winter crop.

The "South-East" dryland grain cropping region includes land in South Australia, Victoria, Tasmania, and southern New South Wales. It is characterized by cool, wet winters and warm–hot, dry summers. The South-East region is typically subdivided into three zones based on rainfall: low rainfall zone (LRZ; <325 mm annual rainfall), medium rainfall zone (MRZ; 325–500 mm), and high rainfall zone (HRZ; >500 mm). Annual rainfall variability is high in all zones with frequent droughts, while areas of the HRZ regularly experience waterlogging damage to crops. The South-East region includes a diverse range of soils (Table 1), with most containing neutral–alkaline clay subsoils. Up to the late 1990s much of the region was characterized by "mixed farming"—phased rotations of wheat or barley with leguminous pastures such as annual subterranean clover (*Trifolium subterraneum*) and/or medic (*Medicago* spp.). The mineralization of SOM during the fallow following the termination of a pasture legume minimized the need for N fertilizer application to one or more cereal crops. Like the South-West dryland grain region, there has been a shift toward continuous cropping since the 1990s (especially in the MRZ) resulting in an increased reliance on N fertilizers, with an increasing proportion tactically applied during the growing season in response to projected yield. There has also been a widespread move away from mechanical cultivation and increased use of long fallows for minimum tillage and residue retention practices in this region.

The "North-East" dryland grain cropping region encompasses areas of inland northern New South Wales and southern and central Queensland. Annual rainfall in this region ranges from 500 to 750 mm but can be erratic (Webb et al., 1997). Seasonal rainfall distribution ranges from summer-dominant in the north to a more uniform distribution across the year in the southern extremities, with rainfall totals generally declining from east to west across the region (Webb et al., 1997). A large proportion of the cropping soils are heavy-textured (clay content 50–70%), have high soil water holding capacities (>150 mm), and crack freely due to swelling/shrinking clay minerals. The success of summer and winter cropping depends on soil water accumulating over the preceding fallow period, with the fallow duration determined by seasonal rainfall (Freebairn et al., 1997). Cropping programs vary from opportunistic summer or winter plantings in the eastern, higher rainfall areas to more conservative, winter-dominated crop rotations using soil water stored over summer. There are few mixed farming enterprises, with most soils continuously cropped at a frequency determined by achieving stored soil water targets. Minimum- and no-tillage systems predominate, with retention of ground cover a necessity during summer fallow when rainfall often occurs in intense storms. Residue cover reduces the risk of soil erosion and maximizes water infiltration and retention in the soil profile for use during the next cropping phase (Freebairn et al., 1997; Silburn et al., 2007; Thomas et al., 2007). The dominant winter and summer crops are wheat and sorghum, respectively. This cropping system presents several challenges for N management, with the high soil temperatures promoting SOM mineralization in moist soil during the summer fallow. The lack of pasture rotations and low frequency of grain legumes in crop rotations promote greater reliance on synthetic N fertilizers. The highly variable in-season rainfall leads to uncertainty about the timing and yield expectations of a future crop and limits opportunities to apply additional N during the growing season. As a result, fertilizer N is mostly applied in the weeks and months preceding sowing, after the soil water accumulation targets are met and a planting window approaches.

Nitrogen fertilizer management across Australia's diverse grain cropping systems has evolved in response to extreme variability in environmental and economic conditions (Anderson et al., 2017; Kirkegaard et al., 2011). The shift to continuous cropping and declining soil fertility has seen N fertilizer progressively become a large expense for Australian grain producers, contributing 20–25% of the variable costs (2006–2009; http://anz.ipni.net/article/ANZ-3133). This is despite Australian grain yields being relatively low and quite volatile by international standards, which is partly due to increasing season-to-season variability in rainfall (Anderson et al., 2017). Government support to Australian grain production contributed just over 2% of Australian farmer revenues in from 2017 to 2019 and consisted of research, biosecurity, and drought-related support (OECD, 2020). Understanding the extent of soil N supply (and losses) from Australian dryland grain production is important for the environment and to manage economic risk.

3. Soil nitrogen supply pathways

Up to 80% of the N needs of cereal crops in low input dryland farming systems in Australia were estimated to be derived from SOM mineralization (Angus, 2001); however, these values were typically derived from cereals grown after legume pasture leys in mixed farming systems in the South-East region. In such situations, non-leguminous grain crops rely heavily on the decomposition of SOM and previous crop and/or pasture residues for N (Angus et al., 2006; Angus and Grace, 2017; Smith et al., 2000), with only small annual inputs of N generated from free-living N_2-fixation (Gupta et al., 2006) or deposited in rainfall/dust (Angus and Grace, 2017). Soil organic matter stores approximately 95% of the N held in soils (total N), with the average turnover of topsoil N stores in Australian dryland cropping systems estimated to be 23 years or just over 4% per annum (Angus and Grace, 2017), although this fraction will vary depending on soil depth, water content, and temperature (Xu et al., 1996).

Soil N supply varies both spatially and temporally. In many Australian soils (particularly no-tillage farming systems), SOM and associated soil biota are concentrated in the surface soil (0–10 cm), with soil N mineralization potential decreasing with increasing depth (Murphy et al., 1998b; Purnomo et al., 2000a). In the South-East dryland grain region (MRZ) of Australia, over 90% of the N mineralized within the surface 20 cm of a soil profile occurred from 0 to 10 cm in a cropping soil, with most occurring from 0 to 6 cm soil depth (Purnomo et al., 2000a,b). Therefore, the surface horizon of cropping soils is a primary source of mineralized N, and maintaining the labile organic N in this profile layer is critical to soil N supply. Mineralization of soil N is strongly influenced by substrate availability and abiotic factors such as temperature and soil water content (Hoyle et al., 2006; Paul et al., 2003). Labile carbon (C) substrates such as root exudates can also regulate the activity of soil organisms (Schroth and Hildebrand, 1964) and foster continued slow release of N for plant uptake (Fisk et al., 2015a). During summer, SOM is mineralized rapidly when soils are moist and temperatures are high. Depletion of labile C substrate can constrain N release (Wang et al., 2004). In contrast, SOM mineralization rates often slow under the cool, moist winter growing conditions in the South-West and South-East dryland grain-growing regions.

Nitrogen supplied from Australian cropping soils has been primarily assessed by measuring "net" N mineralization rates, with few studies measuring "gross" rates. "Net" N mineralization measures accumulated inorganic soil N (as $NH_4^+ + NO_3^-$) and represents the net balance between N supply (i.e., SOM turnover, plant residue decomposition, N_2-fixation, excluding fertilizer N where applied) and N losses due to both biotic (e.g., immobilization, denitrification) and abiotic processes (e.g., leaching, volatilization). In contrast, gross N mineralization reflects the rate at which SOM is converted to NH_4^+ and excludes consumption processes, generally making this method less variable than net N mineralization in arable soils (Cookson et al., 2008; Fisk et al., 2015b; Hoyle et al., 2006; Murphy et al., 2000). Similar net N mineralization values may result from the summation of very different gross N mineralization and abiotic and biotic N losses (Murphy et al., 1998a). The following sections summarize net and gross N mineralization rates reported for Australian dryland cropping soils. We only report in situ net N mineralization rates, as these have been measured widely, and rates determined in the laboratory are likely to differ from in situ rates due to temporally variable rainfall patterns and diurnal temperature fluctuations that occur in the field. Gross N mineralization rates have not been measured extensively in Australian cropping soils, so both field (in situ) and laboratory (under controlled conditions) measurements are discussed.

3.1 Net nitrogen mineralization

In situ net N mineralization rates have been measured in all mainland Australian dryland grain cropping regions when cropped (growing season) and in the subsequent fallow (Table 2). Growing season methods generally use the incubation of intact cores (Raison et al., 1987; Stein et al., 1987) or a variation of this method (Anderson et al., 1998b) to varying soil depths (0.1–2.0 m) (Table 1a in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Net N mineralization rates during fallow are usually determined as the difference between soil mineral N at harvest and the subsequent break of the season, using cores extracted to various depths to 2.0 m (Table 1b in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Much of the research reviewed was conducted between 1986 and 2005, with only three studies in the past 10 years: two in the South-West region (Craig, 2016; Flower et al., 2012) and one in the South-East region (Dunsford et al., 2015).

Rates of in situ net N mineralization during the cropping season ranged from −0.20 to 1.26 kg N ha^{-1} d^{-1} (median, 0.33 kg N ha^{-1} d^{-1}) in Australian dryland cropping soils, culminating in either net N immobilization of up to 36 kg N ha^{-1} or net N accumulation of up to 285 kg N ha^{-1} during the growing season (Fig. 4; Table 2). These studies have been mainly conducted on acidic soils (pH[a] <6.5) with relatively low SOC contents (<2.0%) and a range of clay contents (<5–70%) (Table 1a in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). The greatest rates of accumulation were reported for winter crops in the MRZ and HRZ of the South-East region (Table 1a in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Only a limited number of studies have measured net N mineralization in both fallow and the subsequent growing season in each grain-growing region, with the amount mineralized during the growing season representing 7 to 75% of the total N mineralized (Anderson et al., 1998a; Angus et al., 2000; Armstrong et al., 1996).

Previous crop rotation, tillage, residue (stubble) retention, and N fertilizer management have had small but variable impacts on growing season net N mineralization rates across soil types and environments through their influence on substrate availability and soil water content (Table 1a in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Growing season net N mineralization rates tended

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[a] Soil pH measured using either water or 0.01 M $CaCl_2$ depending on study.

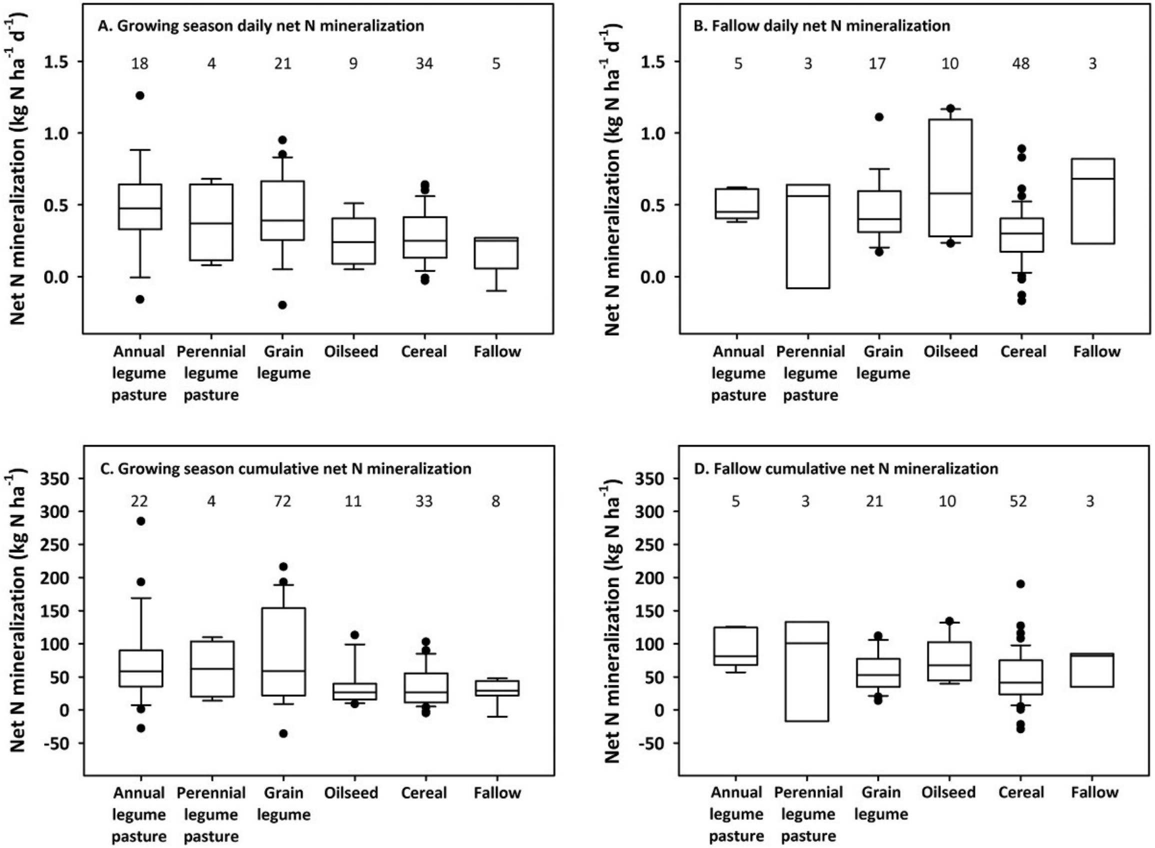

Fig. 4 See figure legend on next page.

to be greater following canola and grain legume crops than wheat for all Australian dryland cropping regions (Heenan and Chan, 1992; McNeill et al., 2000; Murphy et al., 1998a). The inclusion of pasture species in cropping rotations in the MRZ and HRZ of the South-East region often increased growing season net N mineralization rates during the cropping phase (Dunsford et al., 2015; Heenan and Chan, 1992; Ladd et al., 1994), depending on the choice of pasture species and length of time since the pasture phase was terminated (Angus et al., 2006; Dunsford et al., 2015). For example, growing season net N mineralization in dryland cropped soils averaged over 4 years was up to 35% greater after annual pasture (0.44 kg N ha^{-1} d^{-1}) and a mix of lucerne and perennial grasses (0.41 kg N ha^{-1} d^{-1}) than after lucerne (0.32 kg N ha^{-1} d^{-1}) or perennial grasses (0.32 kg N ha^{-1} d^{-1}) alone (Angus et al., 2006). These positive mineralization responses to the inclusion of pasture phases contrasts with findings from the South-West region, where the effect of including pastures in rotations on growing season net N mineralization rates has been inconsistent (Anderson et al., 1998a; McNeill et al., 2000; Murphy et al., 1998a).

Growing season net N mineralization rates have been positively influenced by soil temperature and extended periods of high soil water content, and associated with crop duration, cultivation, and residue management (Anderson et al., 1998a; Angus et al., 1998). In the South-East region, residue management ("stubble" retention) and tillage (direct drill)

Fig. 4 Distribution of (A and B) daily net N mineralization (kg N ha^{-1} d^{-1}) and (C and D) cumulative net N mineralization (kg N ha^{-1}) rates for growing season and fallow and in response to dryland crops and pastures grown in the previous season. Figure compiled from data extracted from peer-reviewed scientific literature on Australian dryland grain cropping soils (Table 1 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Crop and pasture category composition: Oilseed [canola (*Brassica napus*), linseed (*Linum usitatissimum*), mustard (*Brassica juncea*)], fallow, grain legume [chickpea (*Cicer arietinum*), faba bean (*Vicia faba*), field pea (*Pisum sativum*), lathyrus (*Lathyrus odoratus*), lupin (*Lupinus angustifolius*)], annual pasture [cocksfoot (*Dactylis glomerata*), purple pigeon grass (*Setaria incrassata*), lucerne (*Medicago sativa*), annual medics (*Medicagoa scutellata, M. truncatula*), phalaris (*Phalaris aquatia*), rhodes grass (*Chloris gayana*), subterranean clover (*Trifolium subterraneum*), vetch (*Vicia sativa*)], perennial pasture (lucerne, lucerne + perennial grasses), cereal [barley (*Hordeum vulgare*), oats (*Avena sativa*), sorghum (*Sorghum bicolor*), triticale (X *Triticosecale*), wheat (*Triticum aestivum*)]. Composition of crop and pasture categories varies with growing season and fallow datasets. Boxes are 50% of the observations, with the median shown as a horizontal line within the box, and bars indicate 1st and 99th percentiles. Outliers are shown as solid circles (●). Number of observations per category listed above each box.

Table 2 A summary of soil nitrogen (N) supply and loss processes measured in Australian dryland[a] grain cropping soils.

Soil N process	Period	Units	Median (range)[b]	No. values	Climate[c]	No. of publications[d]
Gross N mineralization	Growing season	$\mathrm{mg\,N\,kg\,soil^{-1}\,d^{-1}}$	0.7 (0.6–0.9)	3	Csa	1
	Fallow	$\mathrm{mg\,N\,kg\,soil^{-1}\,d^{-1}}$	0.8 (0–2.0)	47	Csa	1
Net N mineralization	Growing season	$\mathrm{kg\,N\,ha^{-1}\,d^{-1}}$	0.3 (−0.2 to 1.3)	91	BSh, BSk, Cfa, Cfb, Csa	15
	Fallow	$\mathrm{kg\,N\,ha^{-1}\,d^{-1}}$	0.4 (−0.2 to 1.2)	86	BSh, Cfa, Cfb, Csa	9
Ammonia volatilization[e]		% of N applied	6.7 (0.1–34)	91	BSk, Cfa, Cfb, Csa	6
Nitrous oxide emissions	Annual[f]	$\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$	0.2 (0–48)	87	BSh, Cfa, Cfb	14
	Growing season	$\mathrm{kg\,N\,ha^{-1}}$	0.3 (−0.1 to 16)	92	BSh, Cfa, Cfb	13
Denitrification	Growing season[g]	% of N applied	28 (0–54)	61	BSh, Cfa, Cfb	10
Nitrogen leaching	Annual	$\mathrm{kg\,N\,ha^{-1}}$	6 (4–14)	3	Cfa, Csa	2
	Growing season	$\mathrm{kg\,N\,ha^{-1}}$	34 (4–72)	10	Cfa, Csa	3

[a] Supplementary irrigation provided in some instances to establish or maintain crop when rainfall below average (see Supplementary material for details).
[b] Specific values listed in Supplementary material.
[c] Köppen–Geiger climate classification (Peel et al., 2007): BSh, hot semiarid; BSk, cold semiarid; Cfa, humid subtropical climates; Cfb, temperate oceanic climate; Csa, temperate (hot-summer Mediterranean climate).
[d] Publications listed in Supplementary material.
[e] Summarizes results for both surface and subsurface soil applied N fertilizer.
[f] Authors who report annual losses did not necessarily calculate growing season losses.
[g] Strong et al. (1992) values are for fallow plus growing season.

practices—which conserved soil water—increased net N mineralization rates in a growing season where soil water content limited net N mineralization (Angus et al., 2006). However, in other instances in the South-East and North-East regions, tillage treatments had inconsistent or no effect on net N mineralization rates (Angus et al., 2006; Armstrong et al., 1996; Heenan and Chan, 1992; Stein et al., 1987).

Fallow net N mineralization rates have been reported for all Australian dryland grain cropping regions across a broader range of soil properties (soil pH[a] 4.8–8.5; SOC 0.7–5.8%; clay contents 4–70%) and greater variety of previous crops (e.g., cereals, grain legumes, oilseeds) and pastures than growing season net N mineralization rates (Table 1b in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). In situ net N mineralization rates during the fallow ranged from −0.17 to 1.17 kg N ha^{-1} d^{-1} (median, 0.36 kg N ha^{-1} d^{-1}), culminating in net accumulation >100 kg N ha^{-1} between harvest and sowing of the next crop in many situations (Table 1b in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). A few studies have reported net N immobilization (22–29 kg N ha^{-1}) during the fallow and in the South-East and North-East regions (Angus et al., 2006; Armstrong et al., 1996). Across all grain growing regions, median net daily net N mineralization rates tended to be greater in the fallow (0.36 kg N ha^{-1} d^{-1}) than the growing season (0.33 kg N ha^{-1} d^{-1}) (Fig. 4). This trend was consistent across southern and northern grain growing regions and could be due to short-lived periods of rapid N mineralization associated with high temperature during sporadic summer rainfall events in the South-West and South-East regions (where winter rainfall dominates) or over more prolonged fallow periods in the North-East region (where profile moisture reserves accumulate). Both situations can strongly influence the accumulation of profile mineral N before sowing.

The contribution of fallow mineralization to annual net N mineralization is strongly influenced by prior cropping history (rotation), rainfall amount between cropping seasons, and the length of fallow between cropping phases (Table 1b in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Studies investigating the effect of cropping rotation on fallow net N mineralization show greater rates following oilseeds and grain legumes than cereal crops (Anderson et al., 1998a; Dalal et al., 1994; Kirkegaard et al., 1999; Marcellos et al., 1998; Ryan et al., 2006; Strong et al., 1986), except when grain legumes were poorly nodulated (Strong et al., 1986). There is no consistent ranking between oilseeds and grain legumes (Kirkegaard et al., 1999; Ryan et al., 2006; Strong et al., 1986). Angus et al. (2000, 2006) determined changes in net N mineralization per unit rainfall of 0.37 to 0.62 kg N ha^{-1} mm^{-1} and 0.51 kg N ha^{-1} for each additional mm of available water during the fallow period in the South-East region. Residue retention and tillage practices did not affect fallow net N mineralization rates in continuously cropped Australian soils (Angus et al., 2006; Armstrong et al., 1996; Dalal et al., 1994), although changes in mineral N accumulation were sometimes associated with decreased plant growth and N uptake, or increased available soil water (Angus et al., 2006).

Finally, soil N accumulated via soil mineralization does not always result in enhanced plant N uptake sufficient to meet crop requirements, particularly in contemporary Australian rotations where the soils are continuously cropped. This can be due to either asynchrony between supply and demand (Anderson et al., 1998a), insufficient supply to meet the demands of the subsequent crop (Marcellos et al., 1998), or soil constraints to crop water and N uptake (Dang et al., 2006; Unkovich et al., 2020). The powerful influence of climate drivers and generally inconclusive results regarding the effect of management on net N mineralization rates described above suggests that understanding the timing and magnitude of N mineralization rates and the factors affecting differences between gross and net N mineralization (i.e., N loss processes) are important for improving soil and fertilizer N utilization.

3.2 Gross nitrogen mineralization

Gross soil N mineralization rates have been reported only for dryland grain cropping soils in Australia's South-West region. In situ rates ranged from 0 to 2 mg N kg $soil^{-1}$ d^{-1}, while laboratory-based measurements under controlled temperatures (5–60 °C) ranged from 0 to 13 mg N kg $soil^{-1}$ d^{-1} (Fig. 5), as determined by measuring the rate of ^{15}N dilution over 24 h due to newly mineralized NH_4^+. The studied soils varied in texture (2–26% clay), but all were acidic (pH^a <6.5) and had SOC <2% (Table 2 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001).

Laboratory studies of gross N mineralization rates and using soils collected from a range of field experiments reported no measurable effect of land management factors such as tillage (Cookson et al., 2008), residue retention (Hoyle and Murphy, 2006), or use of nitrification inhibitors

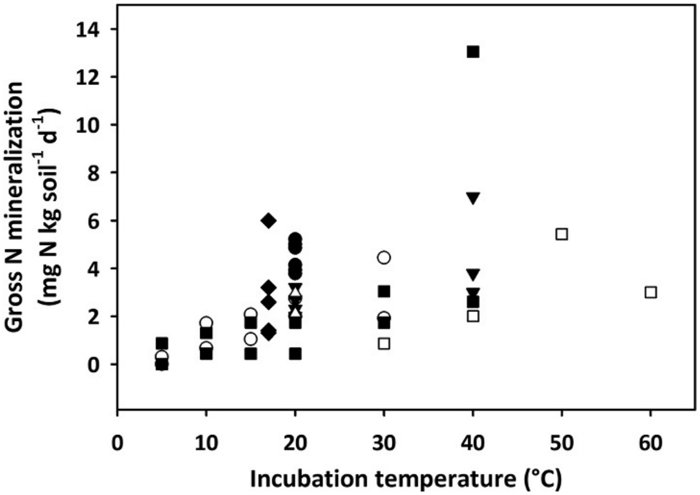

Fig. 5 Relationship between gross N mineralization (mg N kg soil^{-1} d^{-1}) and incubation temperature (°C). Gross N mineralization rates determined in the laboratory using ^{15}N isotopic dilution under controlled temperature and soil water content. Figure compiled from data extracted from peer-reviewed scientific literature for Australian dryland grain cropping soils (Table 2 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001): ● Cookson et al. (2008), ○ Fisk et al. (2015a), ▼ Fisk et al. (2015b), △ Hoyle and Murphy (2006), ■ Hoyle et al. (2006), □ Luxhøi et al. (2008), ◆ Osler et al. (2004).

(Fisk et al., 2015b). However, N mineralization rates increased in response to repeated addition of crop residues to deep sand over 8 years (Fisk et al., 2015a). Gross N mineralization measured under controlled conditions (non-water limited) often show a linear increase as temperatures rise from 5 °C to 30 °C; in some instances, rates continued to increase substantially from 30 °C to 50 °C (Fig. 5). Thus, N mineralization is primarily controlled by organic inputs, climate, and soil attributes that influence microbial activity, rather than agricultural management practices such as tillage, rotation, and residue management (Murphy et al., 2003).

The fate of mineralized N is determined in part by controls on the rates of other N processes. Limited laboratory studies measuring gross nitrification from field experiments in the South-West region suggest that the rate of conversion of NH_4^+ to NO_3^- increases with increasing temperature (Hoyle et al., 2006), but microbial immobilization rates are not affected, leading to the accumulation of mineral N at higher (>30 °C) temperatures (Cookson et al., 2002; Fisk et al., 2015a; Hoyle et al., 2006; Luxhøi et al., 2008). This suggests that, in the South-West region, rapid mineralization of

SOM during the summer fallow in response to infrequent but often significant rainfall events (e.g., >5 mm) can lead to the accumulation of mineral N at risk of being lost via NO_3^- leaching or gaseous emissions (N_2O, N_2) due to nitrification/denitrification during subsequent rainfall events (Anderson et al., 1998b; Austin et al., 2004; Barton et al., 2008; Fillery, 2001; Fisk et al., 2015a). This contrasts with the cooler winter months when there is little to no build-up of NH_4^+ or NO_3^- due to low soil temperatures and the depletion of available N via active winter crop growth (Anderson et al., 1998b; Hoyle et al., 2006). The applicability of these findings to other Australian grain-growing regions has not been investigated.

In addition to temperature effects, N transformation rates are regulated by the source of C used by heterotrophic soil microorganisms. For example, Fisk et al. (2015a) showed that root exudate C was more effective at decreasing the risk of N loss than adding crop residues to a sandy soil low in SOM. Exudate compounds increased the potential for microbial immobilization relative to nitrification by providing a more readily available C substrate than that from crop residues.

4. Nitrogen losses

^{15}N fertilizer studies have demonstrated that, on average, 28% of the N applied to Australian dryland grain crops remains unaccounted for up to 1 year after application (Fig. 6). The unaccounted N is assumed lost via NH_3 volatilization, denitrification, or leaching. However, unaccounted N ranged from 0% to 94% of the applied ^{15}N fertilizer, highlighting that the extent of N losses varies considerably within Australian dryland grain cropping systems. The following sections review N losses measured from field-based studies, focusing on gaseous losses via NH_3 volatilization, denitrification, and nitrification (N_2 and N_2O), plus losses of soluble N (NO_3^-) in leachate.

4.1 Ammonia volatilization

Ammonia losses ranged from 0.1% to 34% (median 6.7%) of the N fertilizer applied (surface and subsoil) to Australian dryland grain cropping systems (Table 2) or up to 34 kg N ha^{-1} (Table 3 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Studies have largely investigated losses under typical N fertilizer practices for the study area and how these losses are influenced by fertilizer type, placement, and timing (Table 3 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Research has been

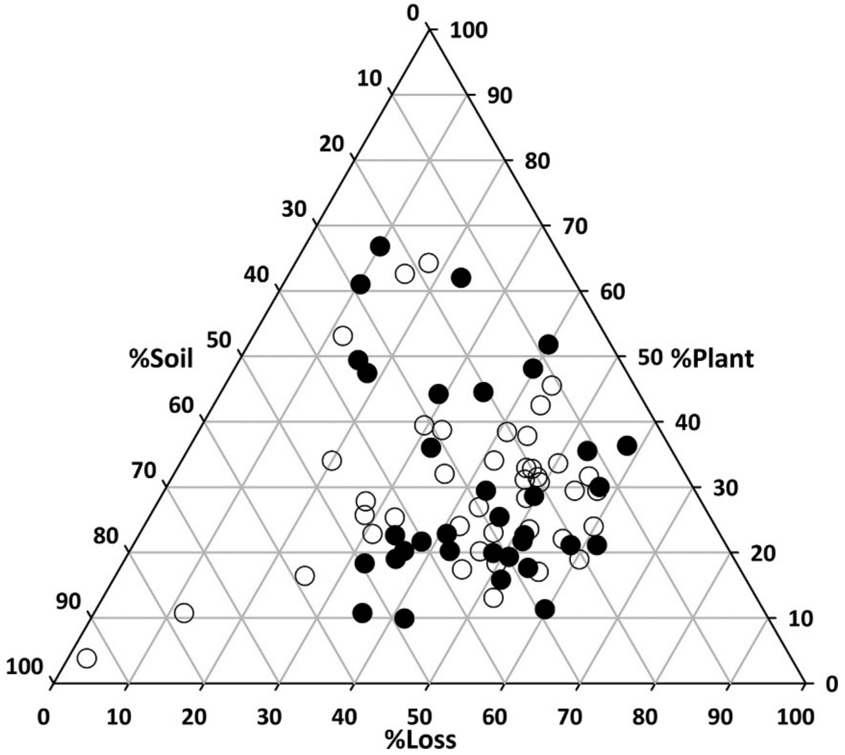

Fig. 6 Proportion (% of total) of ^{15}N labeled fertilizer applied to Australian dryland grain cropping systems measured in aboveground plant parts at harvest, soil at harvest (or before sowing the next crop), or unaccounted for and reported as a loss. Figure compiled from data extracted from peer-reviewed scientific literature for Australian dryland grain cropping soils: Armstrong et al. (1996), Bell et al. (2015), Fillery and McInnes (1992), Harris et al. (2016a), Ladd and Amato (1986), Li et al. (2016), Robertson et al. (1997), Schwenke and Haigh (2019a,b, 2016), Smith and Whitfield (1990), Strong et al. (1992), Wallace et al. (2019). Symbols: North-East region (●), South-East region (○).

predominantly conducted on neutral to alkaline soils cropped to wheat, using either urea or NH_4-based N fertilizers broadcast onto the soil surface at rates of up to 100 kg N ha^{-1}, with losses mostly estimated using non-intrusive micrometeorological methods (Table 3 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). The dataset is dominated (68%) by a series of studies conducted on neutral–alkaline clay soils in the North-East region, where fertilizer products were applied to bare-fallow (pre-seeding) or during the growing season (Schwenke et al., 2014). Values reported from Australian studies are consistent with global estimates, being 10 to 18% of N lost from mineral fertilizers via volatilization (Bouwman et al., 2002; de Klein et al., 2006; Pan et al., 2016).

The greatest NH_3 losses from Australian dryland grain cropping soils occurred when N fertilizer was applied to the surface of alkaline soils or soils with low pH-buffering capacity (Bacon et al., 1986; Fillery and Khimashia, 2016; Schwenke et al., 2014). For example, 29% of N fertilizer applied was volatilized from an acidic soil with a low pH-buffering capacity in the South-West region (Fillery and Khimashia, 2016), while 34% of ammonium sulfate was volatilized when applied to a fallow soil with >10% calcium carbonate (Schwenke et al., 2014). In the latter case, the low solubility of the calcium sulfate formed (along with unstable ammonium carbonate–bicarbonate) was the catalyst for the NH_3 production reaction, which also produced a high solution pH—conditions that favor the presence of NH_3 gas in equilibrium with NH_4^+ cations (Freney et al., 1983).

Applying N fertilizer to fallow soil or immediately before seeding appears to increase the risk of NH_3 losses (mean, 10.4%; median, 8.4%), relative to applying during the growing season (mean, 7.5%; median, 5.2%), if we only consider data where the fertilizer was applied to the soil surface ($n=84$; Fig. 7). Actively growing crops can directly absorb volatilized NH_3 before it reaches the bulk atmosphere. The crop canopy also reduces wind movement in the boundary layer above the soil surface—a driving force for NH_3 release from the soil (Sommer et al., 2004). Ammonia volatilization does not appear to vary greatly between fertilizer types when applied to the soil surface. However, it is important to note that only urea or NH_4-based N fertilizers have been investigated due to expectations that these fertilizer types would be most susceptible to NH_3 volatilization (Fig. 7). The temporal patterns of NH_3 losses vary among studies depending on soil and environmental conditions at the time of N fertilizer application (e.g., Schwenke et al., 2014; Turner et al., 2012) and fertilizer type and method of application (e.g.,Schwenke et al., 2014; Turner et al., 2010). Consequently, while some losses became negligible within a few days after N fertilizer application (Angus et al., 2014; Fillery and Khimashia, 2016), others took between 11 and 30 days to return to baseline values (e.g., Bacon and Freney, 1989; Schwenke et al., 2014). This highlights the crucial importance of timing and intensity of subsequent rainfall on quelling or prolonging NH_3 losses after fertilizer application.

Using urea coated with N-(n-butyl) thiophosphoric triamide (NBPT) to inhibit the urease enzyme has been investigated as a strategy for decreasing

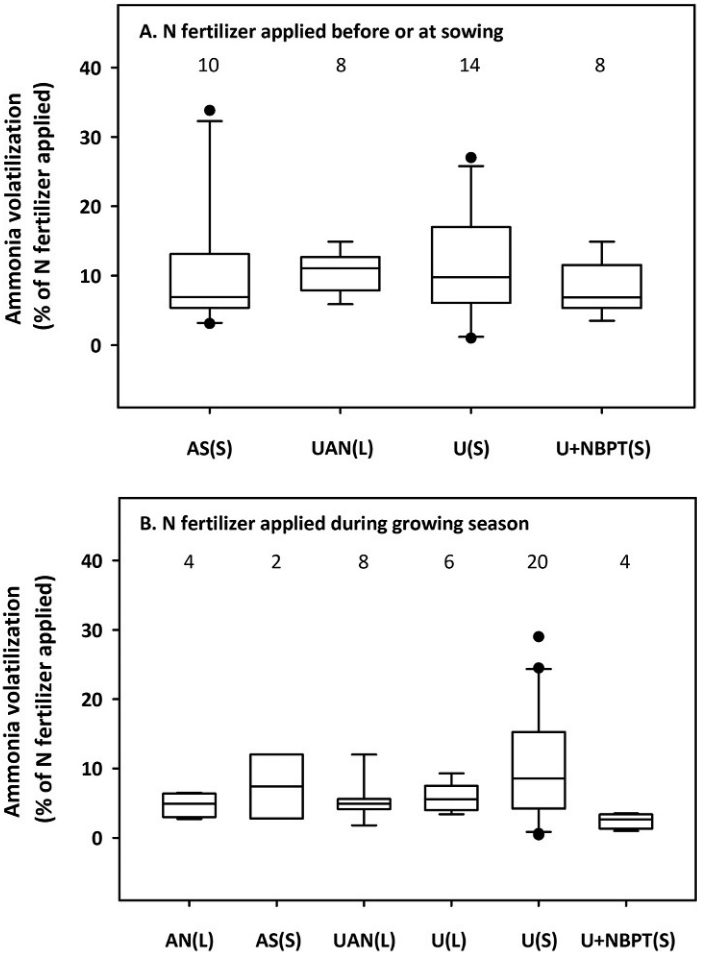

Fig. 7 Distribution of ammonia (NH_3) volatilization fluxes (% of N applied) for different N fertilizer types applied to the soil surface at (A) before or at sowing and (B) during the growing season. Figure compiled from data extracted from peer-reviewed scientific literature for Australian dryland grain cropping systems (Table 3 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Fertilizers types are: ammonium nitrate (AN), ammonium sulfate (AS), urea ammonium nitrate (UAN), urea (U), and urea coated with N-(n-butyl) thiophosphoric triamide (U + NBPT) in solid (S) or liquid (L) form. Boxes are 50% of the observations, with the median shown as a horizontal line within the box, and bars indicate 1st and 99th percentiles. Outliers are shown as solid circles (●). Number of observations per category listed above each box.

NH_3 losses from Australian dryland grain cropping soils (Bacon and Freney, 1989; Schwenke et al., 2014; Turner et al., 2010). Applying NBPT-coated urea to the soil surface decreased NH_3 losses by up to 89% compared to applying urea, but the results were not consistent across all Australian studies (Schwenke et al., 2014; Turner et al., 2010). A global evaluation of mitigation strategies for NH_3 volatilization identified several potential approaches to minimize losses from Australian dryland cropping systems, including the use of non-urea-based fertilizers, urease inhibitors and controlled release fertilizers (Pan et al., 2016); strategies that decreased NH_3 losses by 54–75% on average. However, while the use of non-urea-based fertilizers avoids localized increases in soil pH during urea hydrolysis (promoting NH_3 volatilization), the authors warn that the use of some non-urea-based fertilizers may contribute to soil acidification (Pan et al., 2016).

4.2 Nitrous oxide emissions

Nitrous oxide is emitted from soils in response to a range of biological (and abiotic) soil processes, but microbial nitrification and denitrification contribute approximately 70% to worldwide emissions (Butterbach-Bahl et al., 2013). Globally, N_2O emissions from cereal crops range from 0 to 56 kg N ha^{-1} (Shcherbak et al., 2014; Stehfest and Bouwman, 2006). Nitrous oxide emissions from Australian dryland grain cropping soils are relatively low by international standards and represent only a small proportion of the N fertilizer applied. Annual N_2O emissions from Australian dryland grain cropping soils ranged from 0 to 48 kg N ha^{-1} yr^{-1} (median, 0.19 kg N ha^{-1}), representing up to 1.8% of applied N (median, 0.2%) when N fertilizer was applied. Losses occurring during the growing season ranged from -0.1 to 16 kg N ha^{-1} (median, 0.30 kg N ha^{-1}) and represented up to 8.9% of applied N (median, 0.4%) when N fertilizer was applied (Table 2, Fig. 8). Losses have been reported from many areas within Australia's dryland grain-growing regions, with measurements undertaken using manual (daily/weekly measurements) and automated (subdaily measurements) chambers. Studies differed in crop grown (grain legumes, cereals and oilseeds), climate, rainfall (<300–776 mm yr^{-1}), N fertilizer rates (0–240 kg N ha^{-1} per crop), tillage practices, clay content (<3–81%), and SOC (<1.0–3.9%) (Fig. 8, Table 4 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001).

Australian field-based studies have largely investigated the influence of N fertilizer management on N_2O emissions from dryland grain cropping, with

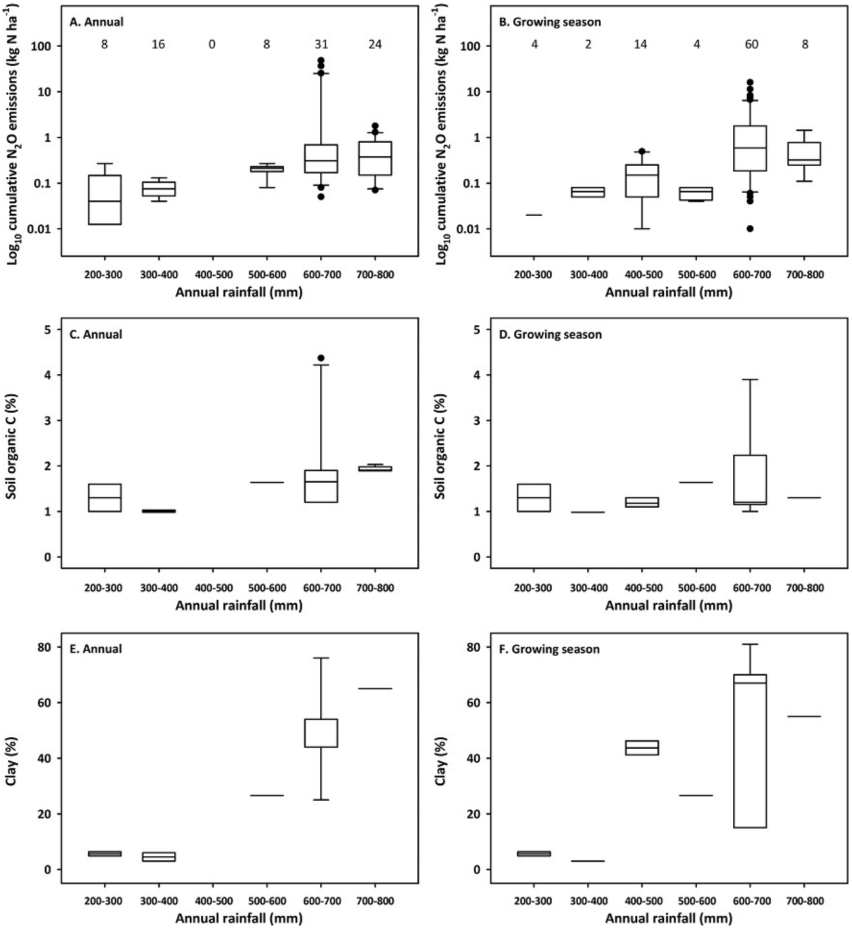

Fig. 8 Distribution of (A and B) log$_{10}$ nitrous oxide (N_2O) emissions, (C and D) soil organic C (%), and E and F) clay content (%) for Australian dryland grain cropping systems against long-term annual rainfall (mm) for studies where N_2O emissions were measured for a year ("annual," kg N ha^{-1} yr^{-1}) or a growing season ("growing season," kg N ha^{-1} growing season^{-1}). Long-term annual rainfall as reported by authors or downloaded from the Australian Bureau of Meteorology (http://www.bom.gov.au). Figure compiled from data extracted from peer-reviewed scientific literature for Australian dryland cropping systems (Table 4 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Boxes are 50% of the observations, with the median shown as a horizontal line within the box, and bars indicate 1st and 99th percentiles. Outliers are shown as solid circles (●). Number of N_2O observations per annual rainfall category listed above each box.

a limited number of studies examining the effects of other agronomic practices (e.g., liming, residue management, crop sequencing) on losses (Table 4 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Applying N fertilizer (often as urea) tended to increase N_2O losses above "background" levels in all Australian dryland cropping systems (Table 4 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001), particularly when there was a temporal "mismatch" between N fertilizer and crop N demand. This mismatch, and resultant N_2O emissions, has been widely observed in high-rainfall areas when N fertilizer application rates have exceeded crop requirements, N fertilizer has been applied well in advance of peak crop demand, or when N fertilizer has been placed at depth (De Antoni Migliorati et al., 2016; Harris et al., 2016b; Schwenke et al., 2016; Schwenke and Haigh, 2016). Increased N_2O emissions can occur because the elevated pool of soil mineral N in the surface soil coincided with high-rainfall events, providing ideal conditions for denitrification. For example, the cultivation of long-term pastures in the HRZ of the South-East region resulted in N_2O emissions ranging from 23 to 48 kg N_2O-N ha^{-1} yr^{-1} in the subsequent cropping year (Mielenz et al., 2017); the greatest annual losses reported from an Australian dryland grain cropping soil (Fig. 8). Similarly, the greatest growing season loss (16 kg N_2O-N ha^{-1} yr^{-1}) from Australian dryland cropping soils was reported for a waterlogging-prone soil from the HRZ of South-East region (Harris et al., 2016b) (Fig. 8).

Nitrous oxide emissions resulting from N fertilizer application to Australian dryland grain cropping systems have been partly mitigated by either splitting N applications or deferring N fertilizer applications to immediately before peak N demand (Schwenke and Haigh, 2019b), thus avoiding the creation of a pool of mineral N at sowing when crop growth is insufficient to fully use the available N (Schwenke et al., 2016; Wallace et al., 2018). Globally, and as discussed by Schwenke et al. (2016), the effectiveness of splitting N applications as a strategy for decreasing N_2O emissions varies and is often dependent on the timing of rainfall events in relation to N fertilizer applications. Using enhanced efficiency N fertilizers (e.g., urea plus nitrification or urease inhibitors, polymer-coated fertilizers) has decreased cumulative N_2O losses by up to 83% from dryland grain crops in high-rainfall zones ($\geq$600 mm yr^{-1}) of Australia, relative to conventional fertilizers, by controlling the rate of fertilizer N release and thus the size of the mineral N pool (De Antoni Migliorati et al., 2016; Harris et al., 2016b; Scheer et al., 2016; Schwenke and Haigh, 2019a). However, the effectiveness of enhanced efficiency N fertilizers for decreasing N_2O emissions from cropped soils where annual rainfall is $<600\,mm\,yr^{-1}$ has not been investigated widely in Australia. One study in the South-East region (MRZ) showed that applying urea coated with 3,4-dimethylpyrazole phosphate (DMPP) decreased peak N_2O emissions on five sampling dates during winter, whereas urea coated with a urease inhibitor (NBPT) did not significantly alter N_2O emissions, relative to the non-amended urea (Wallace et al., 2018).

Growing grain and pasture legumes in rotation with cereal crops could be a strategy for decreasing N_2O emissions from Australian dryland cropping soils (e.g., Barton et al., 2013b; Schwenke et al., 2015). This approach can decrease N_2O emissions by (i) growing a legume in place of crop requiring N fertilizer and (ii) adjusting (lowering) N fertilizer applications to account for the N supplied through mineralization of the legume residue. However, results from such a strategy remain inconclusive in Australia. For example, growing a grain legume in place of an N-fertilized crop emitted a similar amount of N_2O as a fallow soil in a 1-year study in the South-West region (Barton et al., 2011), up to five times less than N-fertilized canola crops (Schwenke et al., 2015) in a 1-year study in the North-East region, but trebled hourly emissions immediately after simulated rainfall in a short-term study in the South-West region (Manalil and Flower, 2014). The greatest N_2O losses in year-long studies investigating the inclusion of grain legumes in cropping rotations occurred during the post-harvest fallow after rainfall (Barton et al., 2011; Schwenke et al., 2015). This highlights that mineralization of legume residues following harvest, rather than biological N_2-fixation during the growing season, was mainly responsible for N_2O emissions from grain legume crops.

Growing cereal crops following a grain or pasture legume has had mixed effects on N_2O emissions from Australian dryland grain cropping soils. For example, growing a cereal crop following a legume pasture either decreased cumulative N_2O emissions in the South-East region when compared to growing N-fertilized wheat following a non-legume crop (canola) in a year where growing season rainfall was significantly below average (Officer et al., 2015) or had no effect in the North-East region when N fertilizer applications were lowered to account for the N mineralized from pasture legume residues (De Antoni Migliorati et al., 2015a). However, and as noted previously, converting pasture to cropping has resulted in some of the greatest annual N_2O emissions from Australian dryland grain cropping soils (Mielenz et al., 2017). Incorporating grain legumes in the cropping rotation and adjusting N fertilizer inputs to the subsequent wheat crop has decreased cumulative N_2O emissions from 2-year cropping sequences by up to 80%, relative to cropping sequences that have not included a grain legume, in both the South-West and North-East regions (Barton et al., 2013b; Schwenke et al., 2018).

Collectively, these Australian field-based studies have demonstrated that the effectiveness of including legumes in cropping rotations to lower cumulative N_2O emissions is dependent on (i) sufficiently lowering N fertilizer inputs to the following non-legume crop, (ii) the amount of biomass produced (N_2 fixed) and N retained (not harvested) from the legume phase, (iii) good synchrony between N mineralized from legume residues and N uptake by the following non-legume crops, (iv) absence of rainfall (or elevated soil water contents) during the post-harvest fallow period to stimulate mineralization of legume residues in the absence of an actively growing crop, and (v) the extent to which labile C released from the crop residue stimulates denitrification.

Globally, management practices that directly or indirectly increase labile soil C can influence the extent and timing of N_2O emissions from cropped soils (e.g., Helgason et al., 2005; Liu et al., 2014; Six et al., 2004). Directly increasing soil C content by adding crop residues (chaff) in the South-West region increased N_2O emissions during a 2.5-year study (Barton et al., 2016). In contrast, retaining crop residues did not affect N_2O emissions during a 1-year study in the South-East region (LRZ) (Barker-Reid et al., 2005) or enhanced N_2O emissions when annual precipitation was greater than the long-term average in a 3-year study in the North-East region (Wang et al., 2011). Where cumulative N_2O emissions were enhanced by adding or retaining crop residues, N_2O losses were still relatively low ($0.14–0.27\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$; Barton et al., 2016) or offset by a slowed decline in SOC (Wang et al., 2011). Only a limited number of Australian studies have investigated the effects of indirectly increasing soil C via no-tillage practices on N_2O emissions. No-tillage largely did not affect annual N_2O emissions in the South-East region (Barker-Reid et al., 2005; Li et al., 2016), but decreased N_2O emissions in the North-East region (Wang et al., 2011). Wang et al. (2011) concluded that the relative differences between conventional and no-tillage treatments resulted from the promotion of denitrification losses under conventional tillage, rather than any inherent decrease in N_2O emissions under no-tillage, with the mechanical disruption of soil structure in the conventional tillage treatments leading to slower soil water movement and poorer aeration. Overall, we have a limited understanding of the influence of crop residue management and tillage practices on N_2O emissions from Australian dryland grain cropping systems. Some studies have shown that the effects are likely to be site- and soil-specific and will therefore require frequent measurements across several years to assess the effects on N_2O emissions.

Various studies in Australian dryland grain cropping regions have demonstrated the risk of elevated N_2O emissions in response to summer–autumn rainfall during the summer fallow period in southern regions (Barker-Reid et al., 2005; Barton et al., 2008; Manalil et al., 2014). At these times, the soil is warm, and summer–autumn rainfall enhances soil mineralization and increases the soil mineral N pool in the absence of plant growth (e.g., Barton et al., 2008, 2013b, 2016). Raising the pH of acidic soils is one approach for mitigating N_2O losses that are not directly related to N fertilizer application (Barton et al., 2013b). Applying lime decreased N_2O emissions during a 2-year cropping sequence (wheat–wheat) with a history of annual N fertilizer applications in the South-West region but had no effect when the cropping rotation included a grain legume (lupin–wheat). A subsequent ^{15}N laboratory study found that increasing soil pH only decreased N_2O emissions from an acidic soil when the losses resulted from nitrification (Barton et al., 2013a).

4.3 Denitrification

Denitrification in anaerobic soils proceeds via chemical and microbial reactions that produce NO, N_2O, and N_2, with the dominant emitted gas dependent on soil depth, aeration status, temperature, NO_3^- concentration, soil pH, and soil structure (Butterbach-Bahl et al., 2013). Measurements of in situ N_2 emissions from rainfed cropping soils are uncommon due to the methodological challenge of measuring relatively small emissions of N_2 against a large background of N_2 in the atmosphere (78%). Instead, total N losses via denitrification tend to be indirectly estimated during a growing season using a ^{15}N mass balance approach with labeled fertilizer—this method does not identify the amounts of each form of N lost, although N_2O measured directly may be subtracted from the total N loss to estimate N_2 if NO is negligible. Our review of denitrification losses from dryland cropping systems does not include data where the authors were not confident in attributing unrecovered ^{15}N to denitrification (e.g., Fillery and McInnes, 1992; Saffigna et al., 1985) or attributed some of the unaccounted ^{15}N losses to other pathways (e.g., Craswell, 1979; De Antoni Migliorati et al., 2014; Robertson et al., 1997; Wallace et al., 2019). We found 61 estimates of total gaseous N loss via denitrification, with all reports from the eastern grain-growing regions and most from humid subtropical climates in the North-East region (Table 2; Fig. 9).

Denitrification losses from Australian dryland cropping soils ranged from 0% to 54% of applied fertilizer N (median, 28%; Table 5 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001) or up to 78 kg N ha^{-1}; representing much greater losses than directly measured N_2O alone. Some of the greatest losses occurred in the North-East region when N fertilizer was applied to clay-textured soils well before sowing (Armstrong et al., 1996; Bell et al., 2015; Strong et al., 1992). The contribution of denitrification to N losses from cropping soils in the South-West grain region is inconclusive (Fillery and McInnes, 1992). Direct measurements of gaseous N_2 and N_2O from intact soil cores investigated under controlled environmental conditions indicated that waterlogged texture-contrast soils of the South-West region had greater N fertilizer losses

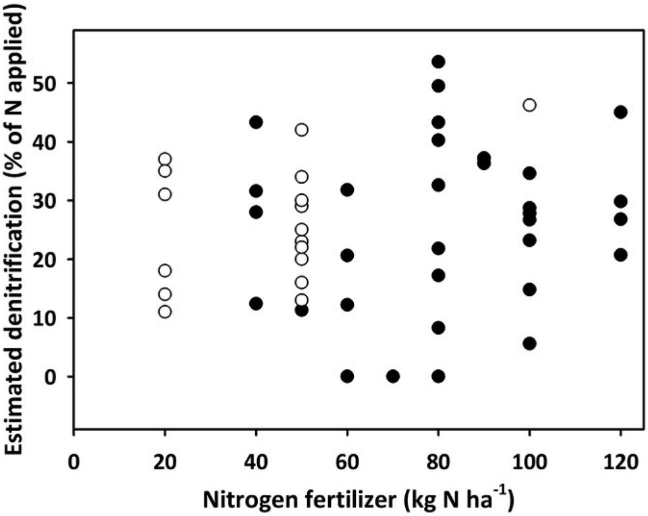

Fig. 9 Relationship between estimated denitrification [% of nitrogen (N) fertilizer applied] during the growing season and N fertilizer rate (kg N ha^{-1}) for Australian dryland grain cropping systems. Figure compiled from data extracted from peer-reviewed scientific literature (Table 5 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Contribution of denitrification was estimated indirectly using a ^{15}N mass balance approach with isotopically labeled fertilizer. Only data where unrecovered ^{15}N was attributed to denitrification is included. Symbols: North-East region (●), South-East region (○).

from denitrification (3.1–9.4% of applied urea-N) than from leaching (3.1–5.3%) (Bronson and Fillery, 1998).

Australian field-based ^{15}N mass balance studies in dryland grain cropping systems have largely investigated the influence of N fertilizer management, including rate, fertilizer type, placement, timing, and use of inhibitors, on denitrification losses (Table 5 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Increasing the N application rate did not affect the estimated denitrification losses from cropped soils in both low rainfall and high-rainfall regions (Li et al., 2016; Schwenke and Haigh, 2016) or decreased the proportion lost from a high-rainfall region (Schwenke and Haigh, 2016). In the latter study, the increased N recovery rate at the greatest application rate ($200\,\mathrm{kg\,N\,ha^{-1}}$) was attributed to C availability limiting denitrification (Schwenke and Haigh, 2016). Consequently, there is no clear relationship between N fertilizer rate and the proportion of loss attributed to denitrification (Fig. 9). Instead, the timing and placement of N fertilizer are critical in terms of decreasing the risk of N losses via denitrification. Applying N fertilizer months in advance of sowing has at least doubled estimated N losses via denitrification from heavy clay soils in the North-East region, which were partly mitigated by deeper placement of N fertilizer into subsoils with lower denitrification potential (Strong et al., 1992). Refining the timing of growing season N fertilizer application to synchronize N supply with crop demand has decreased losses via denitrification in some instances (Fillery and McInnes, 1992; Schwenke and Haigh, 2019b; Wallace et al., 2019), but the results are not consistent (Fillery and McInnes, 1992; Schwenke and Haigh, 2019b; Smith and Whitfield, 1990). The use of DMPP-coated urea appears to decrease denitrification losses during wheat production in the South-East (Harris et al., 2016a; Wallace et al., 2019) and North-East (De Antoni Migliorati et al., 2014; Schwenke and Haigh, 2019a) grain regions when both soil and seasonal conditions were conducive to denitrification.

4.4 Nitrogen leaching

Nitrogen leaching is the removal of N via drainage of soil solution below the active crop rooting zone. It is often assumed that NO_3^- is more susceptible to leaching than other forms of N as the solid phase of most soils has a net negative charge, and so repels negatively charged anions such as NO_3^-. However, organic N leaching can also be significant from agricultural soils (Macdonald et al., 2017; Murphy et al., 2000), and all forms of applied N are at risk of being leached once in a soluble form (Barton et al., 2006). Nitrogen leaching from soils is best quantified directly in the field, with measurements made throughout the year to account for seasonal changes in soil N availability. Techniques such as soil lysimeters fitted with anion exchange resin traps at the base or porous (suction) cup lysimeters, combined with soil hydrological models, have been commonly used to directly measure N leaching from Australian dryland cropping soils (Table 3).

Australian field-based studies investigating N leaching from dryland grain cropping soils have only measured NO_3^- leaching. These investigations were mainly confined to deep sands (Arenosols; IUSS Working Group WRB, 2015) in the South-West region that were cropped to wheat following a grain legume and largely in the absence of N fertilizer application (Tables 2 and 3). Nitrate leaching losses beyond the rooting zone (0.9–1.5 m, depending on the study) were highly episodic, ranging from 4 to 72 kg N ha^{-1} during the growing season, while other studies have reported annual losses of 4 to 14 kg N ha^{-1} (Table 3). The greatest losses were reported for deep sands cropped to wheat following a grain legume (lupin), with no N fertilizer applied (McNeill and Fillery, 2008). In a single study where NO_3^- leaching losses were measured from N-fertilized and non-N-fertilized soils, losses represented 1.2% of the N fertilizer applied (Poss et al., 1995). In southern Australia, the risk of N leaching is greatest at the commencement of late autumn or winter rains (i.e., the "break" of season) when soil mineral N contents are elevated and the capacity for crop N uptake by young crops is limited (Anderson et al., 1998b; Smith et al., 1998). This risk is mitigated when soil mineral N contents are low and/or soil water content remains below the drainage limit at the break of season, or where soil texture favors a high capacity to retain water in the rooting zone and minimizes drainage (Smith et al., 1998).

Monitoring changes in mineral N through the soil profile over time can demonstrate the susceptibility of crop management systems and soil types to N leaching. Ideally, the applied N fertilizer is differentiated using ^{15}N so that changes in mineral N can be specifically attributed to the fertilizer applied. Although these measurements do not necessarily quantify N leaching losses with time, they can demonstrate whether N has leached beyond the crop rooting zone. This approach has shown the limited downward movement of N fertilizer in texture-contrast soils planted to cereals (Fillery and McInnes, 1992) on "cracking clays" (Vertisols; IUSS Working Group WRB, 2015) cropped to grain sorghum in the North-East region and northern Western Australia (Armstrong et al., 1996, 1998; Schwenke and Haigh, 2016, 2019a,b; Wright and Catchpoole, 1985). However, N leaching has

Table 3 Nitrate leaching (NO_3-N ha^{-1}) reported from Australian dryland grain cropping soils.

Location, climate, and annual rainfall (mm)[a,b,c]	**Soil texture and clay content (%)**[d]	**Soil pH**[e]	**Nitrogen fertilizer type and amount (kg N ha^{-1})**	**Method (depth, m)**	**Study period and duration (days)**	**Nitrogen leached (kg N ha^{-1})**	**References**
Lupin (wheat)[f]							
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Anion exchange resin (1)	Jun. 1994–Sep. 1994 (97)	24	Anderson et al. (1998b)
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Ceramic suction cup (1.5)	Apr. 1995–Aug. 1995 (125)	35	Anderson et al. (1998b)
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Ceramic suction cup (1.5)	Jun. 1996–Aug. 1996 (58)	23	Anderson et al. (1998b)
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Anion exchange resin (1)	Jun. 1995–Jun. 1996 (353)	14	McNeill and Fillery (2008)
Wheat (lupin)[f]							
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Ceramic suction cup (1.5)	Apr. 1995–Aug. 1994 (125)	59	Anderson et al. (1998b)
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Ceramic suction cup (1.5)	Jun. 1996–Aug. 1996 (58)	42	Anderson et al. (1998b)
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Anion exchange resin (1)	Jun. 1996–Nov. 1996 (161)	72	McNeill and Fillery (2008)

Wheat (pasture)[f]							
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Ceramic suction cup (1.5)	Apr. 1995–Aug. 1994 (125)	34	Anderson et al. (1998b)
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Ceramic suction cup (1.5)	Jun. 1996–Aug. 1996 (58)	43	Anderson et al. (1998b)
Wheat (wheat)[f]							
Moora, WA; Csa; 460	Sand, 3.6–9.4	5.0–5.7	0	Anion exchange resin (1)	Jun. 1994–Sep. 1994 (97)	24	Anderson et al. (1998b)
Wagga Wagga, NSW; Cfa; 539	Clay, 23–55	4.5–5.8	157, diammonium phosphate, urea	Ceramic suction cup (0.9)	Mar. 1993–Feb. 1994 (362)	4	Poss et al. (1995)
Wagga Wagga, NSW; Cfa; 539	Clay, 23–55	4.5–5.8	0	Ceramic suction cup (0.9)	Mar. 1993–Feb. 1994 (362)	6	Poss et al. (1995)
Wagga Wagga, NSW; Cfa; 539	Clay, 23–55	4.5–5.8	17, diammonium phosphate	Ceramic suction cup (0.9)	Jul. 1993–Nov. 1993 (143)	4	Smith et al. (1998)

[a] Australian States: NSW, New South Wales; WA, Western Australia.
[b] Long-term annual rainfall as reported by authors.
[c] Köppen–Geiger climate classification (Peel et al., 2007): Cfa, Temperate, hot summer; Csa, Temperate, hot-summer Mediterranean climate.
[d] Clay content varied depending on soil depth, range presented.
[e] pH measured in 1:5 $CaCl_2$, pH varied depending on soil depth (range presented).
[f] Current crop (previous crop).

occurred in Vertisols due to increased soil mineral N concentrations resulting from N fertilizer applications and the burning of crop residues, or enhanced infiltration rates after introducing no-tillage (Turpin et al., 1998). Targeting N fertilizer applications to match crop demand has decreased N leaching from clay soils in high-rainfall cropping systems in the South-East region (Harris et al., 2013) and in years characterized by abnormally high drainage (Smith et al., 2000).

The extent of annual NO_3^- leaching losses reported for Australian cropping soils is conservative relative to those reported for arable cropping systems elsewhere, which could reflect the Australian cropping systems, rainfall amount and distribution, or more simply, the lack of measurements. For example, in a review of soil N cycling in temperate agricultural systems, Cameron et al. (2013) reported that 4 to 107 kg NO_3^-N ha^{-1} yr^{-1} leached below the root zone of arable crops, with rate-influencing factors including the rate of N fertilizer applied, soil type and crop rotation system.

5. Knowledge gaps and research priorities

Substantial knowledge gaps in our understanding of specific N supply and loss pathways from Australian dryland grain cropping soils require attention, particularly where our understanding is limited to specific locations, climates, or soil types. Here, we identify these gaps and recommend future areas of study.

5.1 Quantifying soil N supply and loss pathways

5.1.1 Soil nitrogen supply via mineralization

Our understanding of soil N mineralization rates largely comes from dryland cropping systems that no longer reflect Australia's current practices. Additional experimental studies are required that elucidate the mechanisms responsible for mineral N supply within current land management practices and under varying soil and environmental conditions to improve our understanding of contemporary Australian dryland cropping systems. Soil N mineralization is linked to total soil N, which exists in different SOM fractions with variable composition and turnover rates, and the soil microbial community (Phillips et al., 2015). Future studies should consider using improved SOM fraction measurement techniques and investigating the potential of molecular techniques for examining functional genes/traits instead of non-specific fingerprinting techniques to understand the rate-limiting factors responsible for SOM turnover (Finn et al., 2017; Phillips et al., 2015). This should include spatial and temporal soil N mineralization responses to varying rainfall (soil water content), temperature, and residue management in contrasting soil types. For example, in southern Australian grain-growing regions, low soil temperatures during winter often limit soil N mineralization in the early part of the cropping season, with one study suggesting that crop N demand exceeded supply by as much as two to three times, with a maximum soil N supply occurring several weeks later than peak demand (Angus, 2001). However, the relevance of this finding needs investigating in other grain-growing areas in southern Australia.

An improved understanding of the processes leading to mineral N accumulation before sowing in southern Australian dryland grain cropping soils is needed. Studies have focused on approaches to manipulate the soil N cycle during a winter cropping season in southern Australia, where low soil temperatures during the winter often limit soil N mineralization in the early part of the cropping season. However, as outlined in previous sections, soil mineral N can accumulate in appreciable amounts in response to sporadic rainfall during "typical" summers and "atypical" extended drought fallows. This highlights the need to better predict N mineralization during summer fallows, for developing effective management responses that minimize soil N losses during these periods. Laboratory-based research has identified that stimulating soil microbial N immobilization in preference to nitrification could limit net N mineralization and improve N availability to crops at sowing (Fisk et al., 2015a; Hoyle and Murphy, 2006; Phillips et al., 2015), but this requires field verification across a greater range of soil types and agroclimatic cropping regions. Similar studies need to be done in the North-East region to understand the balance between soil N mineralization during the fallow vs the growing season.

5.1.2 Ammonia volatilization

Understanding the extent of NH_3 volatilization from a broader range of soil types, N fertilizer types, and application methods within each of Australia's dryland grain cropping regions warrants further attention, as N fertilizers are still commonly broadcast in all regions. Applied N losses as great as 30% have been reported from Australian dryland grain cropping soils; however, a large proportion of the measurements have been confined to a single area dominated by alkaline, medium to heavy clay soils (Schwenke et al., 2014) (Table 3 in Supplementary material in the online version at https://doi.org/10.1016/bs.agron.2022.03.001). Future research needs to extend the current understanding of NH_3 volatilization to all dryland cropping regions throughout Australia. This is particularly critical in southern grain-growing regions given the increasing shift to surface applications of N during the growing season instead of direct drilling or incorporation at or before seeding (Harries et al., 2015; Kirkegaard et al., 2011). Our review has highlighted that the risk of NH_3 volatilization is not confined to alkaline soils, as poorly-buffered neutral–acidic soils may be at risk of substantial N losses, particularly when the hydrolysis of applied urea creates a highly alkaline microenvironment that converts some of the urea-derived NH_4^+ into NH_3 gas. Consequently, NH_3 volatilization studies should include measurement of soil pH-buffering capacity, cation exchange capacity, and $CaCO_3$ content—soil properties that can significantly influence the volatilization loss process (Sommer et al., 2004). Furthermore, given that this review has highlighted that losses can occur for a few days to 30 days after N fertilizer application, field-based measurements with complementary weather data are needed to define how long N fertilizer is at risk of being volatilized following N fertilizer application under different scenarios.

5.1.3 Nitrous oxide and dinitrogen gas emissions

Nitrous oxide emissions from Australian dryland grain cropping soils have been researched extensively in many field situations, with results confirming that this loss pathway typically represents a small percentage of the N fertilizer applied. Further research on minimizing N_2O emissions is not justified for refining N fertilizer decisions and budgets unless there are changes to land management practices that have not been investigated (e.g., re-introduction of crop-pasture rotations). In such situations, the effects are likely to be region- and soil-specific and require continuous measurements across several years, i.e., the whole crop sequence.

In contrast, gaseous N_2 losses from Australian dryland cropping soils are rarely directly quantified. This is particularly concerning for clay and texture-contrast soils, especially those with poor soil structure or elevated soil C status (e.g., cropped after a pasture phase), which are likely to experience significant denitrification losses following intense rainfall events. Indeed, extrapolation from ^{15}N mass balance studies shows denitrification losses greater than 30% of applied N are not unusual (Fig. 9). The current dearth of direct measurement of N_2 losses from Australian cropping soils needs addressing to develop mitigation strategies in those cropping systems where losses are of significant economic and environmental concern. Novel analytical methods have been developed recently to quantify the fate of applied N in agricultural soils, including the fate of native soil N through the mineralization of SOM and residues (Warner et al., 2019).

5.1.4 Nitrogen leaching

The extent to which N fertilizer is leached from Australian dryland grain cropping soils has been quantified to a limited extent in the field. Only 2 of the 13 field measurements of N leaching included an N fertilizer treatment. The greatest leaching losses occurred for non-N-fertilized, coarse-textured soils cropped to wheat following lupins (Anderson et al., 1998b). Monitoring changes in soil mineral N with depth in other soil types reinforced that coarse-textured soils are more susceptible to N leaching than other soils. However, the assumption that N leaching does not occur in fine-textured soils is challenged by reports of NO_3^- leaching losses from Australian dryland grain cropping soils containing up to 55% clay (Table 3; Poss et al., 1995; Smith et al., 1998). Nitrate leaching losses, estimated by measuring soil NO_3^- concentrations at depth, were "surprisingly" high from a "cracking" clay soil (Vertisol) after 20 years of continuous cropping ($19\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$, or up to $377\,\mathrm{kg\,N\,ha^{-1}}$ in total) (Turpin et al., 1998), a similar magnitude to that reported for non-fertilized coarse-textured soils (Table 3). Therefore, there is a need to quantify the proportion of N fertilizer leached in coarse-textured soils and in soil types prone to preferential flow pathways in all Australian dryland grain cropping regions.

5.2 Improving simulation modeling of soil N dynamics

Future N process research should incorporate targeted field and laboratory experiments that address current weaknesses in our understanding and simulation modeling capacity of soil N mineralization and N loss pathways. Crop–soil simulation models, such as the Agricultural Production Systems Simulator (APSIM) (Holzworth et al., 2014), have been used to develop N management strategies across a wide range of the Australian dryland cropping environment (e.g., Anwar et al., 2009; Asseng et al., 2012; Hochman and Waldner, 2020; Lawes et al., 2019; Meier et al., 2021; Mielenz et al., 2016a,b; Monjardino et al., 2015). While structurally sound in terms of linking soil, plant, and water processes, the underlying algorithms in APSIM for simulating soil N transformations are potentially outdated. For example, the N mineralization module in APSIM was created in the late 1990s (Probert et al., 1998) and incorporated a single equation for denitrification from the original CERES model (Godwin et al., 1984). Useful modifications to the denitrification simulation module were incorporated by Mielenz et al. (2016b) and Thorburn et al. (2010) but require further testing in a wider range of cropping soils. Ammonia volatilization is not simulated by APSIM (Salo et al., 2016). The use of measurable pools of soil C and N, in contrast to the original conceptual pool approach, to simulate SOM dynamics has been tested within APSIM but resulted in an over-estimation of soil N content (Luo et al., 2014).

Modeling the extent and timing of net N mineralization is critical for managing N supply and loss from Australian dryland cropping soils. Nitrogen loss events are directly related to, and sometimes stimulated by, the availability of soil mineral N, which in turn is often regulated by the extent of net N mineralization in cropping systems. We provided various examples where soil N mineralization resulted in soil mineral N accumulation followed by significant N losses via leaching, nitrification or denitrification (e.g., Anderson et al., 1998b; Barton et al., 2008, 2013a). However, the ability to accurately model and predict net N mineralization in dryland cropping soils is poor in Australia and globally and for a range of simulation models (Salo et al., 2016; Smith et al., 2020). This means we are not currently able to confidently predict the rates of N mineralization or the size of mineralizable N pools in response to changes in farming systems that inevitably occur with time due to changing management and climate. Smith et al. (2020) suggested that simulation of soil N mineralization by APSIM could be improved by (i) redefining the SOM fractions used, and therefore modifying the conceptual representation of C and N cycling in the model by measuring the size and dynamics of the active soil C pools; (ii) explicitly simulating the effect of the microbial population on net fluxes between soil C pools; and (iii) better describing the interaction between C and N pools. The issue of conceptual soil C/N pools and their definition, and the degree to which they can (or should) be measured to initialize simulations, is an on-going problem for all soil C/N models. Our capacity to predict N losses from nitrification (N_2O), denitrification (N_2O and N_2), and N leaching (NO_3^-) will ultimately hinge on our ability to simulate soil N mineralization processes adequately.

The capacity of process-based models to predict N_2O and N_2 losses from Australian dryland cropping soils requires refining the existing denitrification algorithms or developing alternatives. Mielenz et al. (2016a) found APSIM to be reasonably accurate in estimating the total seasonal emissions of N_2O from subtropical cereals but failed to predict daily emissions. Subsequently, Mielenz et al. (2017) implemented routine accounting for N_2O transport through the soil profile in APSIM that significantly improved the simulation of daily N_2O emissions. Alternative modeling approaches, such as DayCent (De Antoni Migliorati et al., 2015b), DNDC (Ma et al., 2018), and WNMM (Li et al., 2012, 2013), can estimate N_2O emissions from cereal crops in subtropical or semiarid regions. Efforts to refine denitrification algorithms are hampered by our lack of accurate measurements of the partitioning of gaseous fluxes resulting from denitrification (Smith et al., 2020), as previously highlighted. This could be overcome by employing novel high enrichment ^{15}N-fertilizer techniques to directly measure N_2, N_2O, and NO emissions (Warner et al., 2019), coupled with new algorithms that better simulate daily changes in soil aeration, substrate availability (i.e., NO_3^-, dissolved organic C) for denitrifying microorganisms, and gas diffusion from depth.

The suitability of current modeling approaches for predicting the extent of N leaching from Australian dryland cropping soils needs to be reconsidered for several reasons. First, while APSIM is widely used for simulating the fate of N applied to agricultural soils, its calibration in cereal systems is limited to data collected from free-draining, coarse-textured soils at a relatively small scale (<1 ha) and in the absence of N fertilizer application (Asseng et al., 1998a,b). Second, modeling N leaching in Australia has focused on point-scale measurements, which may not adequately represent losses at the spatial scales relevant to agronomic and economic management (Robertson et al., 2008). Capturing the impact of spatial variation in soil properties on N leaching requires high resolution spatial measurements to parameterize process-based models (Djurhuus et al., 1999) or the adoption of alternative statistical approaches (e.g., White and Magesan, 1991). Third, simulation models used to estimate N leaching often assume that water infiltrates uniformly through soil (i.e., equilibrium water flow) (Asseng et al., 1998a), yet it is well known that preferential flow and transport occurs in a range of soil types (Clothier et al., 2008). For example, Anderson et al. (1998b) queried the assumption of uniform water flow in coarse-textured soils following a leaching event in autumn, where leaching from a sandy cropping soil was greater than that expected under uniform infiltration of rainfall. Indeed, the assumption of equilibrium flow in coarse-textured soils may not be valid considering these soils are susceptible to water repellence (Guo and Lin, 2018; Roper et al., 2015). The impact of water repellence on water infiltration and redistribution in soil has been explored with simulation modeling (Brown et al., 2018; Kramers et al., 2005), but its impact on soil N dynamics and use efficiency of applied N does not appear to have been investigated. Conducting ^{15}N mass balance field studies in partnership with soil water monitoring and application of an inert tracer (e.g., bromide), and in response to a range of rainfall intensities (McLeod et al., 1998) and contrasting soil profile water contents, will enable better scrutiny of modeled N leaching losses from a range of soil types. Finally, our ability to simulate N leaching will continue to be hampered while soil N mineralization processes that produce NO_3^- are not adequately modeled.

The publication of a specific model for predicting NH_3 losses from moist, N-fertilized agricultural soils provides the opportunity to strategically investigate and verify the risk of NH_3 losses from Australian dryland grain cropping systems using current fertilizer management practices (Fillery and Khimashia, 2016). The modeling approach starts with a maximum potential NH_3 volatilization loss (65% of applied N), which is decreased using scaling factors; the model generally provided estimates that closely agree ($r^2 = 0.85$) with measured values from a limited number of Australian and international studies. The authors of the model note that it could be further refined by investigating the effect of N fertilizer application on NH_3 volatilization at different crop stages, assessing the impact of the amount and type of crop residue on losses, and including additional scaling factors for soil water content at the time of N fertilizer application for a range of soil textures (Fillery and Khimashia, 2016). The latter factors explained much of the variance in cumulative NH_3 loss from dryland grain cropping soils in the North-East region (Schwenke et al., 2014). Studies that include soil types with contrasting properties and fertilizer placement options are also needed to investigate the relative impact of specific factors on resultant NH_3 volatilization losses. This includes examining the case for defining a critical cation exchange capacity for Australian cropping soils below which NH_3 volatilization occurs (Bouwman et al., 2002; O'Toole et al., 1985).

5.3 A systems perspective for future land management and climate scenarios

This review confirms widespread recognition of the fragmentary nature of N research in Australian dryland grain cropping systems, with reported studies typically focusing on a single supply process or loss pathway without broader consideration of other co-occurring processes (including crop utilization) and losses. Quantifying the complete soil N cycle is not often attempted for Australian dryland cropping systems, which is problematic as mitigating one loss can increase another. For example, a global analysis revealed that while applying nitrification inhibitors to agricultural soils decreased direct N_2O emissions by up to 57%, they simultaneously increased NH_3 emissions by up to 65% (Lam et al., 2017). There is also a lack of integrated, long-term field studies investigating SOM mineralization and the interactions between fertilizer application strategies, nutrient losses, crop recoveries, and system nutrient budgets. The results of nutrient balances are often at odds with more quantitative isotope studies (Smith et al., 2020) and suggest that an "apparent" nutrient balance for a locally relevant N fertilizer rate may occur by mining the SOM pool of nutrients, rather than balancing matching nutrient inputs to removal rates (Angus and Grace, 2017).

It is also critical that the understanding of N supply and loss pathways remains relevant for current and future dryland grain cropping land management. While considerable research and modeling has been conducted on soil N supply processes nationally, many of the field measurements (including model calibration) were conducted in mixed farming systems that are no longer practiced in many areas and are therefore not representative of the more intensive, continuous cropping systems that are currently used. Similarly, noticeable shifts in temperatures and rainfall patterns (Alexander et al., 2007) have occurred in at least some parts of Australian dryland cropping regions, which we expect will increasingly impact the relative importance of fallow and growing season soil N dynamics. Changing temperatures and rainfall patterns alter the relative importance of fallow and growing season SOM mineralization in some areas, with implications for both the timing and availability of mineralized nutrients for crop uptake and the development of complementary fertilizer management strategies. Crop simulation modeling, combined with simulated climate data, is needed to explore rotation and N fertilizer scenarios to build SOM and reduce the risk of N losses. Currently, approaches to decrease the risk of N loss are implemented reactively, including not applying N fertilizer immediately before heavy rainfall, split applications, or applying additional fertilizer after loss events. The overall long-term effectiveness of these approaches, including that on crop N utilization, remains unclear.

6. Conclusions

Our knowledge of the extent of soil N supply and loss from Australian dryland grain cropping systems is incomplete. While significant research has been conducted on soil N supply processes nationally, much of the work has occurred in mixed farming systems that no longer represent the current, more intensive cropping systems. Quantifying each of the N loss pathways has been undertaken in a limited number of regions, often without considering other potential losses that can occur simultaneously or later in the same growing season. The exception is N_2O emissions, where an extensive database of measurements has been amassed across multiple years and regions as part of three national research programs. Measurements of gaseous losses of NH_3 are largely confined to alkaline soils in a single region, while N_2 losses from Australian dryland cropping soils have not been quantified. We are deficient in our knowledge of N leaching from Australian dryland cropping soils as field-based studies have been largely conducted in the absence of N fertilizer and under an incorrect assumption that N leaching is confined to coarse-textured, free-draining soils. Where fertilizer N mass balances have been undertaken using ^{15}N, losses of greater than 30% during the growing season have been reported in many instances, highlighting the need to better understand these N loss pathways. The findings could have major economic (and environmental) implications for the Australian grains industry in the longer term.

Australia's increasing reliance on fertilizer N to meet the demands of dryland grain crops requires an improved understanding of pathways for rebuilding SOM and the fate of applied N, both within the cropping season and in the subsequent fallow. Using more adaptive management responses to climatic events will become increasingly important if Australia is to meet international expectations on effective N fertilizer management, especially with the changing climate. The key to this success will be the ability to place loss pathways in context with soil N supply processes, accurately model soil N transformations in current and future cropping systems, and develop management strategies that either decrease the risk of N losses or respond retrospectively to a loss event while maximizing crop N utilization.

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CHAPTER TWO

Trace contaminants in the environmental assessment of organic waste recycling in agriculture: Gaps between methods and knowledge

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Abstract

Agricultural recycling of organic waste (OW) derived from urban, agricultural and agroindustrial sources is an essential sustainable development strategy. Yet repeated application of nutrient-laden OW in crop fields can also drastically boost contaminant levels in soil. This review focuses on the consideration of three categories of OW-borne contaminants, namely trace elements, organic contaminants and pathogens (including antibiotic resistance), in environmental assessments, chiefly involving life cycle assessment (LCA) and risk assessment (RA). The in-depth discussion also focuses on gaps between empirical knowledge and the models underlying these frameworks. Potential improvements to fill the identified gaps are proposed, including novel approaches and uses of existing approaches, while also featuring various levels of "readiness." Finally, a comprehensive theoretical framework to assess OW recycling scenarios, combining complementary approaches and models, is proposed and exemplified.

1. Introduction

1.1 Treatment and agricultural recycling of organic waste

There is a global consensus among scientists, economists, politicians and civil society on the need to recycle resources, engage in industrial symbioses whereby wastes are transformed into resources, while closing material loops in circular economies as a pathway to sustainable development (Costa et al., 2010; Frosch and Gallopoulos, 1989; Ghisellini et al., 2014; Gontard et al., 2018). The waste-agriculture nexus is particularly relevant in this context (Kurian and Ardakanian, 2015), especially from the bioeconomy perspective (EC, 2012; Loiseau et al., 2016). First, the ever-increasing waste production pattern has prompted the need for more sustainable waste management, from economic, environmental and human health standpoints (Morrissey and Browne, 2004; Singh et al., 2014) and secondly, the rising food demand is exerting additional pressure on agriculture and other food production systems that are expected to feed the growing population in more sustainable ways despite increased resource constraints (EC, 2011; Moreau et al., 2012). Both concerns could—and perhaps should!—be jointly addressed, but they are often studied separately. When addressed alone, waste management is generally viewed as a costly disposal activity, whereas agriculture consumes large quantities of finite resources while generating environmental burdens (e.g., emissions).

Agricultural recycling can allow for effective synergistic use of **organic waste** (OW), i.e., any organic biogenic waste (residue) derived from urban, agricultural, and agroindustrial sources, including crop residue, animal effluents, agroindustrial residue, landscaping residue, organic fraction of municipal solid waste, and sewage sludge (Avadí, 2020). These OWs contain nutrients that could become substitutes for mineral fertilizers and thus contribute to soil fertility. OWs also contain organic matter whose application on soils could contribute to increasing soil organic matter contents and help mitigate climate change—a mechanism that is currently being put forward to cope with this key concern (Minasny et al., 2017). These OWs are applied to agricultural soils in raw form or after processing for stabilization, volume reduction, hygienisation, etc. Aerobic (composting) and anaerobic digestion are the most obvious operational processes for OW treatment prior to soil application from a waste management perspective (see Fig. 1 for OW, treatments and recycling pathways considered in this study). Source separation of the organic fraction of municipal waste followed by composting is considered to be an effective method for diverting organic material from landfills and incineration, while reducing the waste volume, eliminating pathogens and creating a stable product suitable for crop field application. The use of anaerobic digestion has also significantly increased in recent decades in several European countries, while representing an opportunity to convert OW into biogas and organic fertilizer (digestate). Both treatments have been found to produce stable fertilizing materials by effectively retaining macronutrients and converting certain nutrients to phytoavailable forms (Houot et al., 2014). However, it is essential to take the organic, biologic and inorganic contaminants contained in waste and their environmental and human health impacts into account when studying the waste-agriculture nexus (Houot et al., 2014).

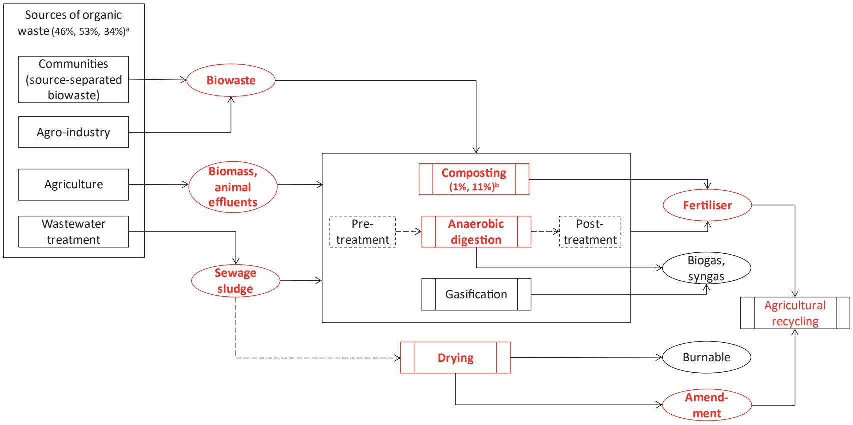
Sources of organic waste (46%, 53%, 34%)a
Communities (source-separated biowaste)
Agro-industry
Agriculture
Wastewater treatment
Biowaste
Biomass, animal effluents
Sewage sludge
Composting (1%, 11%)b
Pre-treatment
Anaerobic digestion
Post-treatment
Gasification
Drying
Fertiliser
Biogas, syngas
Agricultural recycling
Burnable
Amend-ment

Fig. 1 Main global organic waste sources and disposal routes. Treatments and products studied here are highlighted. Less common/optional routes and treatments are dashed. Statistical sources: Hoornweg and Bhada-Tata (2012); UNEP (2015). Notes: ^{a} Contribution of organic waste to total waste composition for the world, low income and high income countries, respectively. ^{b} Contribution of composting to total waste management for low income and high income countries, respectively.

1.2 Contaminants in organic waste and effects of its agricultural recycling on soil

Many studies have highlighted that repeated OW application in crop fields can drastically boost contaminant levels in soil, regardless of their origin (urban, agricultural, etc.), the type of OW (raw, digestate or compost) or the pedoclimatic conditions (Achiba et al., 2009; Börjesson et al., 2015; Formentini et al., 2015; Roig et al., 2012; Udom et al., 2004). Moreover, the contaminants borne by this raw or treated OW may have potential impacts on ecosystem functions and ultimately on human health.

Several national monitoring programs have revealed that **trace elements**[a] are quantitatively the main type of contaminants spread on agricultural soils (Benoît et al., 2014; Senesi et al., 1999). Mean inputs typically range from $2\,\mathrm{g\,ha^{-1}\,year^{-1}}$ for Cd to $1500\,\mathrm{g\,ha^{-1}\,year^{-1}}$ for Zn (Belon et al., 2012; Eckel et al., 2005; Luo et al., 2009; Nicholson et al., 2003). While atmospheric deposition is the major source of trace elements in the most industrialized countries, OW remains a major, if not the main source of trace elements in agricultural soils. Zn and Cu input is typically—by several orders of magnitude—the highest among trace elements. This is particularly due to agricultural recycling of livestock effluents that exhibit high concentrations in Cu and Zn, two animal feed supplements. OW transformation by anaerobic digestion or composting usually tends to increase the total trace element concentration in OW due to organic matter mineralization and/or liquid phase elimination (Bożym and Siemiątkowski, 2018; Gusiatin and Kulikowska, 2014; Knoop et al., 2017). Accordingly, Kupper et al. (2014) recently calculated that fertilization with compost or digestates results in higher trace element loads than application of equivalent nutrient inputs through raw OW. It has also been found that dilution of the trace element concentration following anaerobic digestion or composting may occur when organic matter degradation during the thermophilic phase prompts the release of leachates containing some trace element complexes (Amir et al., 2005), or when substantial amounts of solid organic substrate containing lower trace element concentrations than in the initial raw OW are added to enable liquid OW composting (e.g., animal slurry and sewage sludge). Trace elements are usually: (i) more concentrated in OW than in most soils, (ii) not biodegradable, and (iii) strongly bound to the soil solid-phase. Hence these substances tend to almost irreversibly to gradually accumulate in topsoil, with a residence time in soil typically much longer than 100 years (Benoît et al., 2014; Senesi et al., 1999). Cd, Cu, and Zn accumulation in agricultural soils is particularly worrisome since the estimated time needed to increase the soil concentration of these substances from the natural background level to regulatory limits is the shortest among all trace elements, while OW contributes substantially to this incremental pattern (Luo et al., 2009; Nicholson et al., 2003). Most of risk assessment methodologies point out trace elements as the type of contaminants that dominates the impacts on human health and, even more so, on aquatic and terrestrial ecotoxicity (Pettersen and Hertwich, 2008; Pizzol et al., 2011a, 2011b; Tarpani et al., 2020). The robustness of these methodologies has, however, been questioned as they do not account for the speciation and bioavailability which are essential factors in determining the toxicological and ecotoxicological impacts of trace elements (Plouffe et al., 2015a, 2015b, 2016; Sydow et al., 2020). It would therefore be essential to develop robust risk assessment methodologies specifically focused on the input of trace elements from raw and transformed OW in agricultural soils to ensure the sustainability of agricultural recycling of OW.

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[a] Trace elements usually refer to chemical elements in soil that occur at lower than $100\,\mathrm{mg\,kg^{-1}}$ concentration. The term 'trace elements' encompasses metals, metalloids, and non-metals and was herein preferred over the many other unsatisfactory synonyms commonly found in the literature (e.g. heavy metals, potentially toxic metals, etc.) (Duffus, 2002).

Organic contaminants have been documented in a diverse range of OWs, and OW recycling is a possible gateway for these contaminants in agricultural soils (Hargreaves et al., 2008; Verlicchi and Zambello, 2015) and connected ecosystems (Balderacchi et al., 2013). An extensive review of the available data has nevertheless revealed that knowledge on this complex issue is highly heterogeneous depending on the origin and type of OW, as well as on the class of organic pollutant targeted (Houot et al., 2014). Contrary to trace elements, waste treatment involving composting or anaerobic digestion can partly reduce organic pollutant concentrations via dilution (mixtures with co-substrates), leaching (during composting), transformation (biotic or abiotic), volatilization or non-extractable residue formation. The extent of involvement of these processes largely depends on the type of treatment and on-site conditions. Yet these treatments seldom fully eliminate the contamination. In particular, transformation products and non-extractable residues are usually formed during OW decomposition and biodegradation (Benoît et al., 2014). Following OW spreading onto soil, organic compounds not removed during OW treatment can undergo physicochemical and biological processes that may alter their chemical forms and availability. These compounds may then pose a risk to humans upon their transfer to crops, water or air and to the environment via their impacts on terrestrial and aquatic organisms (Langdon et al., 2010; Thomaidi et al., 2016). Most available data concern organic contaminants in sewage sludge monitored for regulatory purposes, such as pesticides, polyaromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB). Data are also available on other yet to be regulated compounds, including nonylphenol ethoxylates, linear alkylbenzene sulfonate, polychlorinated dibenzodioxins, furans and bis(2-ethylhexyl) phthalate (Olofsson et al., 2012). Over the last 10 years, pharmaceuticals and personal care products (PPCP) have drawn greater attention due to their potential impacts on human health (Clarke and Smith, 2011; Sarmah et al., 2006). However, few field studies have focused on the fate of these PCPP in the agricultural OW recycling setting. OW treatment influences the concentration and availability of organic contaminants in soil, their persistence and leaching but the impacts of these substances largely depend on their chemical class (Bourdat-Deschamps et al., 2017). Scant data is available on the transfer of many different organic contaminants and OW to plants, although some plant uptake and transport models have been designed for ionic chemicals, for instance (Trapp, 2004).

OWs can be vectors for the transmission of all categories of infectious agents, **pathogens**, ranging from viruses to parasites. Enteroviruses, adenoviruses, polyomaviruses, astroviruses, noroviruses and hepatitis A and E viruses have, for instance, been detected in raw and treated biosolids (Bofill-Mas et al., 2006; Chapron et al., 2000; Laverick et al., 2004; Sidhu and Toze, 2009). Biosolids from wastewater treatment plants have been shown to be major vectors of human enteric viruses (USDA—NASS, 2012) and other wastewater treatment plant-related pathogens, including standard waterborne pathogens, e.g., *Cryptosporidium*, *Salmonella* and *Pseudomonas aeruginosa* (Lagriffoul et al., 2009). Higher numbers of pathogens have also been reported in digestates and composts (Fradkin et al., 1989; Nell et al., 1983). Similarly, but to a lesser extent, livestock manure can also substantially contribute to the transmission of human infectious agents (so-called zoonotic agents). The main zoonotic microorganisms are *Salmonella enterica*, *Campylobacter jejuni, Listeria monocytogenes*, *Staphylococcus aureus*, the Shiga toxin-producing *Escherichia coli* and *Coxiella burnetii* (Q fever) and are involved in disease outbreaks. The microbiological safety of OW treatment products (i.e., digestate and compost) is controversial and hard to assess because of significant differences between the technologies used and the varied sanitary quality of the waste prior to treatment. It would be essential to gain insight into the number of pathogens in the initial OW—as reviewed for instance in Zhao and Liu (2019)—to help select appropriate treatments for the defined end uses. However, this would be difficult to achieve because of the high cost of such microbial source tracking analyses and the lack of background regarding the pathogens potentially found in these OW. Indicator bacteria such as *E. coli* and intestinal *Enterococci* are generally used to monitor the microbiological quality of digestate. Several knowledge gaps would need to be filled to be able to predict the survival and fate of pathogens in digestate applied on agricultural soils. In fact, pathogens may survive in the environment for days to months, and their transport can occur naturally via wild uncontrollable animals or by insect or worm movements (Moore and Gross, 2010). Pathogen die-off in soils also depends on a number of factors, including the applied OW-bound nutrients, microbial species, and soil parameters such as moisture and pH (Girardin et al., 2005; Lepeuple et al., 2004; Pourcher et al., 2007). Indeed, no cultivable forms of *Salmonella* or *E. coli* were detected a month after manure and digestate application on soils, whereas the *Listeria* count in soil was only reduced by one order of magnitude 3 months after digestate application (Goberna et al., 2011). *E. coli* survival periods of more than 99 days in bovine manure amended pastures have nevertheless been reported for pathogenic serogroups (Bolton et al., 1999). These die-off datasets thus appear to depend upon the nature of the *E. coli* phylogroup considered. Microbial competition with the native soil microbiota is likely a key factor driving the survival of such pathogens in soils (Goberna et al., 2011), as also is predation. Microbial competition between native bacteria and pathogens generally occurs through antimicrobial production, and chelator-mediated nutrient deprivation (Buchanan and Bagi, 1999; Galia et al., 2017; Goberna et al., 2011; Haas and Défago, 2005; Sidhu et al., 2001). Unc and Goss (2004) emphasized that digestate application on soils can have negative environmental effects even when it has a low pathogen concentration, i.e., given its low solid content, any digestate-bound microbe could have higher mobility and thereby more readily colonize deeper soil layers and groundwater. Agricultural runoff may carry and transfer human pathogens from amended sites to water bodies (Barbarick and Ippolito, 2007; Bibby et al., 2011; Palmer et al., 2005).

Over 70% of antibiotics consumed by humans or animals are excreted un-metabolized (Kümmerer, 2009a,b) and enter wastewater treatment plants or slurry lagoons —this can create suitable environments for resistance development and horizontal gene transfer of resistance between bacteria (O'Neill, 2016). Similarly, around 30–90% of antibiotics used for animal production end up in manure (Sarmah et al., 2006) which, when applied as fertilizer in fields, can potentially lead to antibiotic contamination of the soils (Fahrenfeld et al., 2014; Hou et al., 2015; Qiao et al., 2018; Sun et al., 2018). **Antibiotic resistant bacteria (ARB)**, **antibiotic resistance genes (ARG)** and/or **mobile genetic elements (MGE)** are also abundant in animal and human fecal materials that end up in agricultural and urban waste treatment systems. These systems are designed to reduce total fecal organism numbers in effluent before discharge into the environment, but they are not specifically designed for ARB, ARG and MGE removal. Wastewater treatment plants have been identified as potential hotspots for resistance development and ARG transmission between pathogenic and non-pathogenic bacteria. Indeed, bacteria from different sources (municipalities, hospitals and industries) are present at high density and in close contact during the purification process—this includes a diverse range of species across bacterial phyla. Many studies aimed at determining the extent of resistome changes throughout the treatment process have involved comparisons of influent and effluent contents. The conclusions of a meta-analysis (Harris et al., 2012) indicated that wastewater treatment led to a reduction in the total bacterial count but an increase in the ARB percentage, thereby highlighting that resistance-oriented selection pressure may prevail in wastewater treatment plants. Recently, Goulas et al. (2020) documented the extent of ARB, ARG and MGE reduction possible following wastewater processing in treatment plants, yet these markers were still found in both treated effluents and sewage sludge. Youngquist et al. (2016) compiled data on the effects of composting and anaerobic digestion on ARB and ARG persistence and reported that "some ARB and ARGs persist during mesophilic anaerobic digestion," and that "thermophilic treatments are more effective at decreasing ARB and ARGs." They observed more inconsistent results regarding composting as some studies even revealed increased ARG levels after treatment. Goulas et al. (2020) showed that treatments could decrease ARB amounts, and variations in the observed reduction rates could possibly be related to differences in initial ARB abundances between studies. They also reported a significant effect on ARG/MGE relative abundance during composting. Treated or not and irrespective of the treatment process, OW are a source of ARB, ARG and MGE when applied on soils. Most studies on OW-amended soils have focused on animal manure, generally investigating ARG and MGE persistence in soil and potential dissemination in vegetables. They were conducted at various scales (microcosms to experimental fields) and targeted antibiotic resistance markers (Chee-Sanford et al., 2009; Ghosh and Lapara, 2007; Heuer et al., 2011; Ji et al., 2012; Munir and Xagoraraki, 2011; Muurinen et al., 2017). Manure (Graham et al., 2016; Heuer et al., 2011; Heuer and Smalla, 2007; Marti et al., 2013) or biosolid (Rahube et al., 2014) fertilization modifies the soil resistome, and increases in ARB and ARG levels in agricultural soils have been detected shortly after spreading and after repeated long-term applications. Antibiotic resistance may trickle down the food chain. Recent studies revealed that ARG were more abundant in vegetables harvested in soil fertilized with manure (Marti et al., 2013; Tien et al., 2017) or sewage sludge (Rahube et al., 2014) as compared to control soil. Human or animal consumption of these contaminated vegetables represents a potential route of ARG exposure (Zhu et al., 2017).

1.3 Scope and objectives of this review

The advantages of using raw OW materials, compost or digestate as fertilizer and soil amendment need to be assessed alongside the potential environmental and toxicological impacts due to the presence of contaminants. This review focuses on three categories of contaminants—trace elements, organic contaminants and pathogens (including antibiotic resistance[b])—regarding their consideration in environmental assessments. In this review, "environmental assessment" is broadly understood as *ex ante* (thus model-based) estimation of environmental impacts and risk indicators for decision support. This review thus aims to identify: (1) limitations in existing environmental assessment frameworks for agricultural recycling of OW, regarding the absence or inadequate consideration of some biophysical processes governing the fate of contaminants; and (2) suitable approaches for assessing contaminants involved in agricultural recycling of OW, such as complementary analytics, methods, and models. This review seeks to fulfill its objectives by highlighting the state of the art with regard to the consideration of contaminants in environmental assessment frameworks applied to OW treatment, products and their recycling in agriculture (Section 2), followed by a discussion on gaps between empirical knowledge and the two most widely used environmental assessment frameworks, namely life cycle assessment (LCA) and risk assessment (RA), including potential improvements (Section 3). The state of the art is presented per framework and per type of contaminant. In the LCA context, the state of the art focuses on trace elements (Section 2.3), because toxicity modeling in LCA does not yet consider pathogens, and terrestrial ecotoxicity models are not yet available for organic contaminants. The discussion on limitations of and potential improvements to assessment frameworks is also organized per type of contaminant (Section 3), as approaches, methods and models are generally contaminant-specific for both frameworks.

2. Environmental assessment of organic waste treatment and agricultural recycling—State of the art: Consideration of contaminants

2.1 Environmental assessment frameworks

Various environmental assessment frameworks have been applied to OW treatments and agricultural recycling of treated and raw OW. They are either procedural (focused on societal and decision-making aspects) or analytical (focused on technical aspects), according to the classification of Finnveden and Moberg (2005). Table 1 briefly defines the most common

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[b] Other contaminants present in organic waste, such as toxins (i.e. toxic substances produced by living entities) and particulate matter, were excluded from this review, mainly because their study is beyond the coauthors' scope of expertise. In LCA, particulate matter formation is treated as an impact category separate from toxicity (Huijbregts et al., 2016; Humbert et al., 2011). There is abundant literature on toxin (e.g. Böhnel and Lube 2000; Ibelings and Chorus 2007; Then 2010; Brown et al. 2011) and particulate matter (e.g. US EPA 2005; Levy 2016) consideration in risk assessment. Toxins are not taken into account in LCA.

Table 1 Main frameworks for environmental assessment of waste treatments and their products

Procedural frameworks	**Focus/level**	**Pros**	**Cons**
• Environmental impact assessment (EIA): Multi-tool framework aimed at explicitly considering environmental and social impacts associated with new project developments. Often required by legislation in public projects.	Micro (site)	Possibility of learning from previous projects and reducing mitigation costs of unforeseen impacts, improves long-term viability[a]	Exclusive focus on biophysical issues[a], some at the local scale and some at the global scale
• Strategic environmental assessment: Multi-tool framework similar to EIA but oriented towards policy instrument evaluation, often in situations of high uncertainty.	Meso, macro (policy)	Identify potentially unsustainable development alternatives at an early stage[a]	Perceptions of increased costs (work, time, resources); absence of a single step-by-step approach[a]
• Multi-criteria decision analysis: A collection of decision support methods aimed at comparing alternatives based on a set of decision criteria. Suitable for conflicting decision situations.	Micro to macro (project, policy)	Evaluation of alternatives against multiple, often opposing criteria[b]	Subjective weighting scores, lack of a coherent universal framework[b]
Analytical frameworks	**Focus/Level**		
• Material flow assessment/analysis/accounting (MFA): Systematic accounting of flows and stocks of materials and energy prevailing within an economic system, often a whole region or country.	Macro (policy, plan)	Multiple applications: industrial ecology, environmental management, resource management	No impacts are calculated, only environmental pressure indicators are provided

Continued

Table 1 Main frameworks for environmental assessment of waste treatments and their products—cont'd

Procedural frameworks	Focus/level	Pros	Cons
○ Substance flow analysis (SFA): MFA-type assessment focused on the fate of specific substances at regional or national levels.	Micro, macro (production systems, regions)	Similar to MFA, focused on details pertaining to specific substances of interest	Similar to MFA
○ Material input per service unit (MIPS): Estimation of the environmental pressure associated with products and services expressed as a life cycle-wise ratio of natural resource consumption to benefit provided.	Micro (product, service)	Simple and intuitive cost (in terms of environmental pressure) to benefit ratios	Similar to MFA
• Energy/exergy/emergy analysis: Group of methods aimed at accounting for energy flows in the studied system, usually a process or product system. Exergy refers to energy of a certain quality (useful to produce work).	Micro (process, product, service)	Multiple resource consumption issues are expressed in common intuitive units	Reliance on energy-related impact categories at the expense of other relevant environmental impact categories
○ Energy return on investment: A ratio of industrial energy embedded in a product vs. the energetic content of the product, representing energy efficiency.	Micro (process, product, service)	Similar to MIPS, very relevant in energy intensive systems	Similar to energy analyses

• Risk assessment (RA): Assessment toolset aimed at evaluating human health, environmental and safety-related risks associated with projects or product systems (chemicals, hazardous substances, and industrial facilities). An emerging research area is HERA: Health and ecological risk assessment, also known as Environmental risk assessment (i.e., health + ecological).[e]	Micro (site, chemicals)	Highly regulated framework, mainly focused on human health; allows for absolute quantitative comparisons; considers casual mechanisms affecting health	Lack of full environmental impact assessment, often focuses on toxicity; high data requirements; emphasis on expert knowledge
○ Ecological risk assessment (ERA): a process that evaluates the likelihood that adverse ecological effects may occur or are occurring to ecosystems exposed to one or more stressors (risk factors).[c]	Organism to socioecological system	Provides a system-oriented perspective for holistic risk evaluation and management[c]	Lack of model integration, which complicates the selection and application of the most suitable models for each assessment scale, subjective weighting scores[c]
○ Human health risk assessment: a process intended to estimate the risk to a given target organism, system or (sub)population, including the identification of attendant uncertainties, following exposure to a particular chemical, biological or physical agent, taking into account the inherent characteristics of the agent of concern as well as those of the specific target system.[d]	Organism to socioecological system	Similar to ERA	Lack of model integration and modeling challenges, especially regarding hazard characterization (description of inherent properties of the agent) and exposure assessment (evaluation of the concentration or amount of a particular agent that reaches a target population)

Continued

Table 1 Main frameworks for environmental assessment of waste treatments and their products—cont'd

Procedural frameworks	Focus/level	Pros	Cons
• Eco-efficiency analysis: Concept aligned with the growing environmental concerns in economic sectors, which can be defined as a management philosophy encouraging business to search for more environmentally-sound alternatives producing similar economic benefits.	Micro (product, service)	Developed and used by companies (e.g., BASF), balances economic and environmental concerns of alternatives	Lack of full environmental impact assessment
• Life cycle assessment (LCA): Life-cycle tool aimed at accounting for the environmental impacts, expressed in a number of impact categories, associated with the provision of a good or service over its whole life cycle. Various existing "footprints" are related to LCA, but focused on single issues/indicator categories:	Micro (process, product, service), macro, meso (footprints, experimental regional LCA)	Highly standardized framework, immense body of knowledge (theory and application), ample coverage of impact categories; prevents burden transfer among life cycle stages or impact categories; allows comparative assessments of multiple pathways with equivalent functions	Data intensive, controversial design/methodological details and schools of thought (e.g., system boundaries, allocation of impacts among co-products, uncertainty management, descriptive vs prospective, inclusion of market data, carbon modeling, etc.)
○ Carbon footprint (CFP): Can be considered as an LCA subset focused on the global warming potential.	Similar to LCA	Similar to LCA	Focused on a single impact category

○ Ecological footprint (EF): Accounts for land use associated with the provision of a product. It can be complemented by human appropriation of net primary production (HANPP), which studies the proportion of original primary production that remains on a spatially-specifically defined land area with given specific land use practices.	Similar to LCA	Similar to LCA	Similar to CFP
○ Water footprint (EF): Accounts for freshwater resource appropriation (including fresh, rain and polluted water volumes affected) associated with the provision of a product, in a spatiotemporally explicit fashion.	Similar to LCA	Similar to LCA, regionalizable	Focused on a single impact category, multiple competing approaches

[a] http://www.environmental-mainstreaming.org/, [b] Velasquez and Hester (2013), [c] Chen et al. (2013), [d] WHO (2010), [e] SETAC (2018).

Adapted from Jeswani, H.K., Azapagic, A., Schepelmann, P., Ritthoff, M., 2010. Options for broadening and deepening the LCA approaches. J. Clean. Prod. 18, 120–127. https://doi.org/10.1016/j.jclepro.2009.09.023 and Avadí, A., 2014. Durabilité de la filière d'anchois du Pérou, de la mer aux rayonnages (Sustainability of the Peruvian anchoveta supply chains from sea to shelf: towards a new strategy for optimal resource use). PhD thesis. Université Montpellier 2, Doctoral School SIBAGHE.

ones, indicates their usual application level (i.e., system size), and their main associated pros and cons. Among these frameworks, material and substance flow analysis (an accounting approach to flows and stocks of materials, often in a regional system) considers contaminants only in terms of flows and stocks. Other frameworks, such as environmental impact assessment (a project analysis toolbox), exergy (an indicator of useful energy) and emergy (a measure of quality differences among different energy forms) analyses, eco-efficiency analysis (ratio between socioeconomic benefits and environmental burdens) and strategic environmental assessment (policy analysis toolbox), often do not explicitly consider specific contaminants (Allesch and Brunner, 2014, 2015). Only **life cycle assessment (LCA)** and **risk assessment (RA)** consider contaminants explicitly in terms of their impacts on human and/or ecosystem health, via toxicity impact categories.

LCA (Sections 2.2 and 2.3) is an accounting framework geared towards documenting all resource consumption and emissions associated with the provision of goods or services, throughout the whole life cycle from raw material extraction to the construction, use, maintenance and end of life/ final disposal of production means. LCA is formalized by an ISO standard (ISO, 2006a), and several guidelines are focused on its theory and practice (EC-JRC, 2010; EC, 2018). LCA estimates impacts under a range of impact categories, including human toxicity and environmental ecotoxicity. Human toxicity is often split into cancer and non-cancer effects, while ecotoxicity is further subdivided into freshwater aquatic, marine and terrestrial ecotoxicity. Toxicity assessment in LCA deals with huge numbers of substances in minimal detail, which results in high model and data uncertainty regarding environmental mechanisms and characterization factors[c] (Fantke et al., 2018; Rosenbaum et al., 2013).

RA (Sections 2.4 and 2.5) is mainly a human health-related framework while also featuring ecological/ environmental elements, such as the set of models used in ecological risk assessment (ERA) (Roast et al., 2007). In practice RA involves mandatory procedures, usually published by authorities, such as the different technical guidelines issued by the European Union and the United States Environmental Protection Agency. The two main branches of RA focus on ecological and human health risks. A variety of models and empirical tests are used in RA for identification and characterization of (mainly toxicity-related) hazards, dose responses, exposure assessment and risk characterization of chemicals, as comprehensively reviewed in the literature (Roast et al., 2007; Thoeye et al., 2003; WHO, 2010). RA addresses a very limited number of substances in detail.

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[c] Characterization factor: a factor applied to convert a given flow of a given substance, assigned to an impact category, into a 'potential impact' expressed in the common unit of all flows contributing to that impact category (ISO, 2006a). Generally, this common unit corresponds to that of one of the substances potentially contributing to the category at hand, such as CO_2 for all greenhouse gases.

LCA and RA are complementary methods (Flemström et al., 2004), i.e., the first is comprehensive but not detailed whereas the second is the opposite.

Combined LCA and RA for joint ecological and human health assessment is a promising option for agriculture and food production research (Jolliet et al., 2014; Notarnicola et al., 2017; Tukker et al., 2011), while providing a means to inform robust multicriteria decision-making (Huang et al., 2011; Linkov and Seager, 2011). Various studies have, for instance, attempted to integrate exposure RA with LCA of wastewater treatments on the basis that both frameworks yield endpoint indicators on human health (Harder et al., 2016, Harder et al., 2015, 2014; Heimersson et al., 2014; Jolliet et al., 2014). The scope of such joint assessments could encompass OW treatment and agricultural use. Combined RA-LCA studies, despite their fundamental differences regarding aims and conceptual background (Olsen et al., 2001), often express chemical and pathogen exposure risk in terms of DALY (Harder et al., 2015, Harder et al., 2014), i.e., a common unit to express impacts on human health (Gao et al., 2015; Kobayashi et al., 2015).

Various studies have also advocated and demonstrated the efficacy of material flow analysis and substance flow analysis for tracking different trace contaminants (e.g., trace elements) through waste management systems, in addition to the modeling of downstream processes (e.g., agricultural use) (Laurent et al., 2014a, 2014b; Wassenaar et al., 2015). Combined substance flow analysis and LCA has also been put forward as a means for mapping pollutant flows in the urban environment (Arena and Di Gregorio, 2014; Azapagic et al., 2007), which could also be tailored to agricultural recycling scenarios.

Table 2 lists representative reviews on environmental, life cycle and risk assessments regarding OW treatment and the impacts of contaminants.

Toxicity models used in LCA are usually based on RA, yet they differ in terms of metrics (e.g., health impacts vs. chemical concentrations), scope (all emissions from global life cycles vs. all local emissions including background concentrations), parameterization (e.g., thousands vs under 10 chemicals), modeling choices (average vs. worst case), compartments (e.g., sediment) and mechanisms (Table 3). These modeling principles, illustrated with

Table 2 Recent reviews on environmental and risk assessment of organic waste treatments, including the consideration of contaminants.

Publication: No. of studies reviewed	**Assessment frameworks considered**	**Waste streams and treatments**	**Nutrients, contaminants and impacts considered**	**Main findings and recommendations**
Bernstad and la Cour Jansen (2012): 25	Life cycle assessment	Food waste, various treatments	Environmental impacts	• Assumptions on the content of toxic compounds in treated waste vary largely • Mass-flows of carbon, nutrients and trace elements are often not respected in life cycle assessments due to cut-offs and the use of published values rather than transfer coefficients throughout the treatment chain
Bopp et al. (2016): 21	Human and ecological risk assessment	Surface and groundwater, wastewater treatment	Pharmaceuticals and personal care products, VOCs, PPPs, trace elements, pesticides, etc.; chemical mixtures	• Several factors might lead to an underestimation or overestimation of the potential risk, e.g., uncertainty in reference values used, incompleteness of monitoring data, etc. • It would be relevant to improve data sharing regarding toxicity and exposure information
Gallagher et al. (2015): 10 studies, 5 issue papers	Cumulative risk assessment	Various industrial streams and impoundments, including wastewater treatment sludge	Single chemicals and chemical mixtures	• An iterative approach is essential; a tiered approach is particularly useful • Vulnerable populations need to be considered • Early involvement of multiple stakeholders facilitates the process • New methods are required for multiple exposure routes, pathways, and chemicals • The spatial scale affects the methods used, data needs, and types of risk management questions that can be addressed

Harder et al. (2015): 30[a]	Combined life cycle and risk assessment	Water and wastewater treatment	Pathogens	• Environmental assessment case studies based on elements taken from RA and LCA can be designed in many different ways (combination, integration, combined use, or hybridization) • There are a number of implications and pitfalls at the model structure level, which analysts should be aware of (e.g., the potential asymmetry between the handling of local risks and impacts in the immediate sphere of interest to the decision maker and elsewhere)
House and Way (2014): 88	Human and ecological risk assessment	Industry, agroindustry, agriculture, wastewater treatment	Sewage and septic tank sludge, manure, waste plant matter, food waste, abattoir waste, molasses, compost, paper waste	• For many organic materials little organic chemical data are available • Widely used veterinary medicines, such as antiparasitic treatments, are likely to be of greatest concern in cattle due to the greater active ingredient quantities required for treatment • Monitoring the concentrations of veterinary chemicals in organic materials, and the carbon contents of the soils to which they are being applied would greatly reduce uncertainty in environmental risk assessment
Laurent et al. (2014a,b): 222	Life cycle assessment	Solid waste management systems (non-organic, biowaste, sludge), various treatments	Environmental impacts (non-toxic, toxic, resources, energy)	• There is generally little decisive agreement among studies: the strong dependence of each system on its local context hampers a consistent generalization of life cycle impact assessment results • A number of recommendations are provided to improve future life cycle assessments of waste management systems
Zang et al. (2015): 44	Life cycle assessment	Wastewater treatment plants, activated sludge	Environmental impacts, trace elements, pharmaceuticals and personal care products	• Life cycle assessments of wastewater treatments should include spatial differentiated characterization methods, considering the emission location, spatial dimensions (transfer between environmental compartments) and pollutant properties

[a] Most studies were on contaminated site remediation; we refer here to three studies on water and wastewater treatment.

Table 3 Models for human toxicity and ecotoxicity in LCA (USEtox) and RA (REACH)

	Life cycle assessment (USEtox) [a]		**Risk assessment (REACH, quantitative)** [b]	
Factors	**Human**	**Ecosystem**	**Human**	**Ecosystem**
Fate (LCA) Hazard (RA)	• Measurements and models, to determine emission rates and intermedia transfers of chemicals using a mass balance differential equation for each compartment (indoor air, urban air, continental rural air, continental freshwater, continental seawater, continental agricultural soil, continental natural soil, and crop residues) due to various processes (deposition, volatilization, degradation). The initial transfer rate matrix is then inverted to determine the time-integrated, steady state cumulative transfer rates (the fate of a chemical in the long term, across all compartments).[c] • Data required includes partition coefficients (air-water, octanol-air and octanol-water) • The mass balance equation system consists of a matrix of transfer rates among compartments.[c]		• Measurements, to determine the derived no-effect level (DNEL). • Measurements and models to determine toxicity.	• Measurements to determine the predicted environmental concentration (PEC) and predicted no-effect-concentration (PNEC). • Measurements and models to determine the toxicity.
			• Measurements for hazard: in vitro tests. • Models for toxicity (in silico): quantitative structure-activity relationship (QSAR)[d], read-across, virtual screening, quantum chemical, molecular dynamics, docking.	
Exposure (LCA and RA)	• Human exposure factors are ratios between the intake by the population of a polluted medium (direct: air, water; indirect: food) via an exposure pathway; and the bulk density and volume of the medium[c]: ○ General direct exposure pathways = direct intake of a polluted medium * population / bulk density	• The environmental exposure factor for freshwater ecotoxicity is the fraction of a chemical dissolved in freshwater, depending on the water-suspended solids and water-dissolved organic carbon partition coefficients, suspended matter concentration, bioconcentration factor in	• Measurements and models (when no measured data exists), to determine inhalation, dermal and oral exposure by workers (occupational), consumers and humans in general via the environment.	• Measurements and models (when no measured data exists), to determine exposure of life forms in pelagic water, sediment, aquatic food chain, sewage treatment and air compartments.
			• Models for occupational exposure: ○ Tier 1: ECETOC-TRA[h], EMKG-Expo-Too ○ Tiers 2–3: Stoffenmanager[i], RISKOFDERM, Advanced REACH Tool (ART)	

	of the medium * volume of the medium ○ General indirect exposure pathways = biotransfer and accumulation of a contaminant in a substrate * individual ingestion rate of a polluted substrate * population/bulk density of the medium * volume of the medium • Indirect exposure pathways include bioaccumulation factors, a plant uptake model and a pesticide model (inspired from the dynamiCROP[e] model, which accounts for exposure via crop residues and crop to soil transfers).	fish and concentration of biota in water: ○ Exposure factor for freshwater ecotoxicity = dissolved mass of chemical in freshwater / total mass of chemical in freshwater ○ Partition coefficients are determined with the WHAM7 model[f]; bioaccumulation factor for fish are from databases. • For terrestrial ecotoxicity, a preliminary USEtox model separates exposure into accessibility and bioavailability factors: ○ Accessibility (reactive fraction in soil) and Bioavailability (free-ion fraction of the reactive fraction in soil) are determined from empirical regression models[g].	• Models for environmental exposure: chemical assessment and reporting tool (CHESAR), which contains ECETOC and EUSES tools, and which integrates functions to calculate PEC values; probabilistic material flow modeling (PMFA) for establishing exposure scenarios.

Continued

Table 3 Models for human toxicity and ecotoxicity in LCA (USEtox) and RA (REACH)—cont'd

	Life cycle assessment (USEtox) [a]		Risk assessment (REACH, quantitative) [b]	
Factors	**Human**	**Ecosystem**	**Human**	**Ecosystem**
Effect (LCA) Risk characterization (RA)	• Effect factor: change in the lifetime disease probability due to a change in lifetime intake of a chemical) = 0.5/ED_{50} • Effect data rarely exist for humans, and are often extrapolated based on relative body weight from animal data. ED_{50} are listed in various databases.	• Effect factor: change in the potentially affected fraction of species (PAF) due to a change in concentration of a chemical, for freshwater aquatic or terrestrial ecosystems = 0.5/HC_{50}	Risk characterization ratio (RCR) = exposure/DNEL	RCR = PEC/PNEC
Damage (LCA)	• The damage factor is the effect factor expressed as disability-adjusted life years (DALY) per number of cases of a specific disease caused by exposure to a contaminant. ○ Different factors are applied to cancer effects and non-cancer effects, with the former being >4 times higher than the latter.	• The damage factor is the effect factor expressed as the potentially disappeared fraction of species (PDF), achieved by a factor of 0.5 (i.e., PDF/PAF = 0.5).[j]	N/A	N/A

Indicator definitions:

- DALY: years of healthy life lost to premature mortality in the population and loss of quality of life (disability) due to health issues (Fantke et al., 2017). It is a World Health Organization metric. DALYs measure the health condition in a population, accounting for the sum of years of life lost (YLL) due to premature death and years lost due to disability (YLD): DALY = YLL + YLD. One DALY represents one lost year of "healthy" life. Calculation of YLL requires information on the number of people who died from a disease and their life expectancy at age of death. YLD incorporates the number of incident cases, symptom duration, and disability weight (symptom severity) (Solberg et al., 2017).
- DNEL: is the maximum permissible level of exposure to a substance, as mandated by the REACH legislation.
- ED$_{50}$: the daily dose per kg body weight that causes a disease probability of 50% on a species, per exposure route.
- HC$_{50}$: the geometric mean of chronic EC$_{50}$s for freshwater or soil species.
- NOEC: the no observed effect concentration is the dose, determined by toxicity tests, which will not cause harm on the tested species. It is an expression of the No effect concentration (NEC).
- PAF: the fraction of a species exposed to a concentration above their NOEC.
- PEC: the concentration of a substance in the environment, as determined by exposure models such as EUSES (Vermeire et al., 2005).
- PNEC: the maximum concentration of a substance at which an ecosystem may be exposed without adverse effects.

Sources: [a] Fantke et al. (2017), [b] REACHnano (2015), [c] Rosenbaum et al. (2007), [d] Gadaleta et al. (2016), [e] http://dynamicrop.org/model.php, [f] https://www.ceh.ac.uk/services/windermere-humic-aqueous-model-wham, [g] Owsianiak et al. (2015), [h] http://www.ecetoc.org/tra, [i] http://nano.stoffenmanager.nl, [j] Jolliet et al. (2003).

examples of their application for OW-borne contaminant assessment, are outlined in the following subsections.

2.2 Toxicity modeling in LCA

2.2.1 General principles

The LCA framework consists of four phases (ISO, 2006a,b): (1) goal and scope, where the objectives and limits of the study are decided, including the system boundaries and other fundamental choices; (2) life cycle inventory (LCI), where all data regarding resource consumption and direct emissions from the studied system are compiled; (3) life cycle impact assessment (LCIA), where all LCI factors are multiplied by characterization factors so as to express them in a common unit per impact category, i.e., where the potential impacts are estimated; and (4) interpretation, where the quantitative results of both LCI and LCIA are interpreted and explained, and environmental hotspots of the process are identified.

LCA involves the use of toxicity models to assess the toxic effects of substances on human health and both aquatic and terrestrial ecosystems. Note that in most models terrestrial and marine ecotoxicity data considered in LCA are generally extrapolated from freshwater ecotoxicity data, thereby increasing the uncertainty associated with toxicity modeling. It has been pointed out that differences among LCIA methods regarding toxicity impacts are related to the characterization phase (e.g., the inclusion or not of specific substances, the type of multimedia model[d]) (Geisler et al., 2005; Pizzol et al., 2011a,b). None of these toxicity models take the combination of trace elements, organic contaminants and pathogens in OW into account, or all of the dynamics determining their fate following their soil application. Their uncertainty is high regarding characterization factors, which are usually based on total concentrations and are not regionalized. Moreover, many substances potentially present in OW—notably PAH, hydrocarbons and non-methane volatile organic compounds—lack characterization factors, which are only available across models for a limited set of substances out of the >30,000 most frequently used chemicals (Fantke et al., 2017; Huijbregts, 2000; Saouter et al., 2017). Moreover, these models disregard contaminant transformation, degradation and combination products after emission and within the period taken into account in the studies, i.e., usually a year and seldom longer. Lastly, toxicity models developed to date do not assess pathogens, genetic material (e.g., antimicrobial resistant genes), or other forms of contamination, such as toxins and particulate matter, that negatively impact health.

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[d] Multimedia model: a type of model used in environmental chemistry that expresses the diffusion of a substance between environmental media/compartments based on the chemical properties of the concerned substance (e.g. partition coefficients, etc.).

The Uniform System for the Evaluation of Substances adapted for Life Cycle Assessment (USES-LCA, current version 2.0), is a global nested multimedia fate, exposure, and effects model to calculate characterization factors for terrestrial, freshwater and marine ecotoxicity, as well as for human toxicity, on both midpoint and endpoint levels (Van Zelm et al., 2009). It is based on empirical equations (Guinée et al., 2002; Huijbregts et al., 2000) and a class of risk assessment models for EU applications, i.e., the European Union System for the Evaluation of Substances (EUSES) toolkit, a harmonized quantitative risk assessment tool to calculate predicted environmental concentrations of chemical substances (Vermeire et al., 2005). It currently has a database of 3396 (organic and inorganic) chemicals, with 10 emission compartments, including urban air, rural air, freshwater and agricultural soil. Based on three scales, i.e., regional (original USES-LCA only), continental and global, it calculates human-toxicological effect and damage factors per chemical with information related to intake route (inhalation and ingestion) and disease type (cancer and non-cancer). Moreover, it calculates endpoint ecotoxicological effect factors expressed in terms of changes in overall toxic pressure due to chemical concentration changes. These ecotoxicological effect factors consist of a slope factor and a chemical-specific toxic potency factor reflecting the average environmental toxicity of given chemicals (based on single species toxicity data).

The Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI, current version 2.0), is an LCIA method featuring toxicity models for human health cancer, non-cancer, and ecotoxicity (Bare, 2011). TRACI uses the CalTOX toxicity model for these impact categories (CalTOX is a collection of multimedia transport and transformation, exposure scenario and multiple-pathway exposure models incorporating uncertainty and population-distribution data (Mckone, 1993). For toxicity, TRACI only characterizes chemicals included in the US EPA Toxics Release Inventory (https://www.epa.gov/toxics-release-inventory-tri-program/tri-listed-chemicals).

The EDIP programme and the Danish LCA Methodology Development and Consensus Creation Project, produced two LCIA methods, respectively EDIP97 and EDIP2003. The latter is an update of the former regarding the extent to which the characterization factor modeling takes the causality chain into account for all non-global impact categories: EDIP97 encompasses emissions, their fate and degradation, while EDIP2003 includes exposure, impacts and damage (Hauschild and Potting, 2005). Characterization factors in EDIP2003 are spatially resolved at the country level. EDIP includes human and ecotoxicity impact categories, whose characterization factors are based on "some-fate" modeling rather than on multimedia "full-fate" modeling. For human toxicity, EDIP97 characterization factors express "the volume of environmental compartment (air, water, soil) which can be polluted up to the human reference concentration or dose, the level not expected to cause effects on lifelong exposure" ($m^3 \cdot g^{-1}$), while EDIP2003 characterization factors represent "the reciprocal of a fate-corrected human reference dose or concentration." Legacy models such as EcoSense and empirical equations are used to calculate characterization factors. Otherwise, ecotoxicity is assessed in aquatic and terrestrial ecosystems, as well as in wastewater treatment plants, through "simplified fate modelling based on a modular approach where redistribution between the environmental compartments and potential for biodegradation are represented as separate factors." Characterized substances include those compiled in the Danish Environmental Protection Agency List of Undesirable Substances and List of Effects.

IMPACT 2002+ is an LCIA method featuring damage factors, including human toxicity and ecotoxicity impact categories that take intake fractions, best estimates of dose-response slope factors, as well as severities, into account (Jolliet et al., 2003). IMPACT 2002 (without the "+," also known as Impact Assessment of Chemical Toxics) models risks and potential impacts per emission for several thousand chemicals. It proposes generic characterization factors for Western Europe and spatially explicit characterization factors for 50 catchments and air cells in Europe based on fate, exposure, dose-response and severity modeling (via models and empirical equations).

USEtox, current version 2.0 (Fantke et al., 2017), is a scientific consensus toxicity model and collection of human toxicity and aquatic freshwater ecotoxicity characterization factors developed under the auspices of the United Nations Environment Programme (UNEP) and the Society for Environmental Toxicology and Chemistry (SETAC) Life Cycle Initiative (Rosenbaum et al., 2008). The consensus process culminating in the development of USEtox included the developers of previous CalTOX, IMPACT 2002, USES-LCA, BETR, EDIP97, WATSON and EcoSense models. It was based on a quantitative comparison of these models on 45 organic substances, and on their underlying fate, exposure and effect modeling

(Hauschild et al., 2008; Rosenbaum et al., 2008). The consensus-building process was carried out between 2003 and 2008 (Hauschild et al., 2008), partially based on previous toxicity assessment harmonization initiatives (De Koning et al., 2002; Molander et al., 2004). USEtox development and refinement is ongoing and, for instance, the model was recently implemented in the LC-IMPACT regionalized life cycle impact assessment method (Verones et al., 2020).

2.2.2 USEtox: The consensus fate, exposure and toxicity model

USEtox features over 29,000 characterization factors for over 3000 substances emitted in all ecosystem compartments, including trace elements (Ag, As, As, Ba, Be, Cd, Co, Cr, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Sb, Se, Sn, Tl, V and Zn) and organic contaminants (e.g., alkylbenzene, PCB, nonylphenol and phthalates). Certain substance groups are still excluded, namely PAH, hydrocarbons, non-methane volatile organic compounds and particulate matter, because the models is best equipped for modeling "non-dissociating and non-amphiphilic organic substances" (Fantke et al., 2017). USEtox characterization factors are calculated on the basis of the cause-effect chain linking emissions to impacts through environmental fate, exposure and effects. It uses continental and global scales and relies on chemical property, ecotoxicity impact and physicochemical data, along with environmental multimedia and multi-pathway models to account for environmental fate and exposure processes, as well as impacts (damage). Compartments (air, soil, fresh water, etc.) are modeled as homogenous well-mixed boxes, and the inventory of a contaminant in each box depends on the concurrent processes determining whether or not it will remain in the box, be transferred to another box (by dispersive and advective cross-media transfers), degraded (by oxidation, etc.) or removed (by leaching or burial). Fate modeling is thus based on a mass balance equation taking these processes into account. Exposure modeling transforms the amount of a chemical found in a given compartment into human intake via direct and indirect (via bioaccumulation in animal tissues) pathways, but this presently excludes intake by dermal contact and dust inhalation. Effect modeling is based on statistics for cancer and non-cancer effects (for human toxicity) and on species sensitivity distribution modeling (for freshwater ecotoxicity). USEtox does not consider speciation, aging and weathering (UNEP, 2019), complexation with organic matter (Weng et al., 2002) and other transformative dynamics of chemicals following emission, yet it does consider environmental conditions (temperature, rain, etc.) during the fate and exposure modeling process (Fantke et al., 2017).

Human toxicity characterization factors, expressed in comparative toxic units ($\mathrm{CTUh \cdot kg^{-1}}$), represent the estimated increase in morbidity in the total human population per unit mass of an emitted chemical, expressed in $\mathrm{cases \cdot kg^{-1}}$ (assuming equal weighting between cancer and non-cancer effects). **Aquatic ecotoxicity** characterization factors, expressed in comparative toxic units ($\mathrm{CTUe \cdot kg^{-1}}$), estimate the potentially affected fraction of species (PAF, see Table 3) integrated over time and volume per unit mass of an emitted chemical ($\mathrm{PAF\ m^3 \cdot day \cdot kg^{-1}}$). Freshwater aquatic ecotoxicity is defined as the comparative toxicity potential (CTP, i.e., equivalent to CTUe defined above) of the total concentration of a chemical emitted to any compartment and reaching the freshwater body. USEtox is currently being expanded to include near-field exposure (Fantke et al., 2016; Jolliet et al., 2014) and terrestrial ecotoxicity of trace elements (Owsianiak et al., 2015, Owsianiak et al., 2013; Verones et al., 2020), along with the development of a dynamic version of the model (the current steady-state version features an infinite time horizon) (Fantke et al., 2015). Discussions are also under way regarding developments in aquatic ecotoxicity of effluents, human toxicity of pesticide emissions and higher (warm-blooded) predator ecotoxicity of organic contaminant emissions (Fantke et al., 2018; Rosenbaum et al., 2013), as well as the integration of REACH (Section 2.4) toxicity data (Müller et al., 2017). The emphasis on trace elements (Fantke et al., 2018) and the lack of a terrestrial ecotoxicity model (UNEP, 2019) have been highlighted by the USEtox team. The current (standalone) USEtox model is summarized in Table 3.

2.3 Consideration of contaminants in LCA of organic waste treatments and agricultural recycling

The impact categories/indicators taken into account in LCA studies on OW and OW treatment usually include the global warming potential (occasionally encompassing carbon storage), acidification potential, eutrophication potential, toxicity, and resource depletion (e.g., energy use), as well as other novel indicators such as water and land use footprints. LCA studies focused on OW treatments only consider the toxicity impacts of contaminants (trace elements, organic contaminants) in terms of their absolute quantities emitted over the study/simulation period, as well as their distribution among environmental compartments. OW commonly studied include solid residues from municipal solid waste, food waste and various types of source-separated waste management systems (Bernstad and la Cour Jansen, 2012; Cleary, 2009; Morris et al., 2013), as well as wastewater treatment sludge (Corominas et al., 2013; Lundin et al., 2004; Risch et al., 2015; Suh and Rousseaux, 2002; Teodosiu et al., 2016; Yoshida et al., 2013). For instance, a recent study (Avadí, 2020) compared the main OW treatments used in France for producing organic fertilizers and amendments, and identified the main impact contributors per treatment pathway. Contaminants were not explicitly assessed, as the agricultural recycling of OW treatment products was not a focus.

A few LCA studies on OW have addressed their potential "recycling" pathways. These studies almost exclusively addressed the benefits of substituting chemical fertilizers by treated OW, or were focused on the contributions of their relative absolute emissions to various impact categories, or on trace element concentrations in treated OW (Bernstad and la Cour Jansen, 2011, 2012; Righi et al., 2013).

Various initiatives and tools have been developed specifically to facilitate LCA studies on solid waste management systems and wastewater treatment plants. Among them, EASEWASTE and its successor the EASETECH LCA model (http://www.easetech.dk/) is an assessment tool that is used to an increasing extent in solid waste management LCA studies (Jensen et al., 2016; Yoshida, 2014). For instance, in Boldrin et al. (2011), field application of treated OW is modeled as a function of the compost/digestate composition, crop rotation and soil properties, while taking advantage of the EASEWASTE use-on-land module. The latter is based on an agroecosystem model (Hansen et al., 1991) and field experiments. It includes nutrient uptake and degradation of organic persistent pollutants, various airborne emissions, leaching and runoff of pollutants (trace elements and four organic contaminants: bis(2-ethylhexyl) phthalate, nonylphenol ethoxylates, linear alkylbenzene sulfonate and PAH), as well as carbon sequestration (Hansen et al., 2006a,b). EASEWASTE and EASETECH have been widely used in Danish and German environmental assessments of waste technologies. These include comparisons of different solid-waste treatment technologies (Kirkeby et al., 2006), specific technologies such as composting (Martínez-Blanco et al., 2009, 2013), agricultural recycling of treated OW (Hansen et al., 2006a), uncertainty quantification in LCA of waste management systems (Bisinella et al., 2015; Clavreul et al., 2012), LCA of treatment and recycling of specific feedstock such as biosolids and food waste (Righi et al., 2013; Yoshida, 2014), and LCA of source-separated organics (Morris et al., 2013). EASEWASTE/EASETECH includes the simplified toxicity model described in Hauschild and Wenzel (1998).

2.3.1 Organic waste treatment and soil application

LCA has often been used for environmental assessment of **anaerobic digestion**, focusing on biogas production, substrate transformation (e.g., OW treatment), or both. LCA studies usually focus on the environmental impacts of the process (e.g., Rehl and Müller 2011), while often overlooking contaminants. Hospido et al. (2010) conducted one of the few LCA studies focused on the impact of contaminants associated with OW recycling in soils. The authors assessed the potential impacts of contaminants (trace elements and organic contaminants) on terrestrial ecosystems and their toxicity to humans following agricultural application of undigested sewage sludge and **digestate**. While the fate of pollutants following anaerobic digestion has been experimentally determined (Hospido et al., 2010), their subsequent fate upon soil application was assessed through highly hypothetical, unvalidated concentration estimates in abstract environmental compartments that mobilize little knowledge of related biophysical processes (a constant feature in all LCA toxicity models. Pivato et al. (2015) empirically assessed the ecotoxicological risk associated with using digestate as a fertilizer using a matrix-based approach that integrated the behavior of (and interaction among) pollutants in mixtures and within their real (soil) matrix. The authors derived USEtox-based ecotoxicity characterization factors for digestate as a whole. This was a worthwhile attempt to underscore the limits of conventionally independent assessment of individual contaminants, but the validity of such factors is of course limited to situations similar to the empirical reference.

LCA studies on **compost**ing are less common than on anaerobic digestion, and they often focus on comparisons of alternative composting system scales. A great deal of environmental assessment research has been devoted to investigating the benefits of compost recycling in agriculture (e.g., Martínez-Blanco et al. (2013)), but seldom its impacts due to contaminant transfer to soil. For instance, Saer et al. (2013) assessed nine standard LCA negative impact categories using TRACI, including impacts associated with feedstock collection, compost production and distribution, along with its use as a replacement for peat moss as soil conditioner. Quirós et al. (2014) qualified compost versus mineral fertilizer use based on standard LCA methods. An earlier study by Teglia et al. (2011a,b) also characterized solid digestates for agricultural use after a composting post-treatment. Moreover, LCA has been used to assess different digestate post-treatment technologies, including composting, drying and physicochemical treatments

(Rehl and Müller, 2011; Vázquez-Rowe et al., 2015). These authors identified composting as a suitable digestate treatment geared towards agricultural recycling, while discussing the advantages of nutrient recovery via agricultural recycling compared to alternative disposal pathways. Hermann et al. (2011) calculated the carbon and energy footprints of biodegradable waste material treatment, including home and industrial composting, anaerobic digestion and other treatments. None of these studies took contaminants into consideration, which implies that their conclusions were not fully informed.

Laurent et al. (2014a,b) critically reviewed 222 LCA studies on solid waste management systems, including investigations on the post-treatment use (i.e., recycling) of sewage sludge. At least 10% of the studies in this review addressed the issue of terrestrial use of biological treatment outputs. Another review (Zang et al., 2015) of 44 LCA studies on wastewater treatment plants showed that most authors used LCA to compare the relative environmental effects (negative and positive) of alternative treatment technologies and disposal routes. In these studies, impacts associated with trace elements and organic contaminants were only considered via toxicity LCIA methods (Zang et al., 2015), with their inherent limitations (see Section 2.2.1). Different LCIA methods (ReCiPe, CML, etc.) and toxicity models (USEtox and USES-LCA) were used, thereby leading to marked discrepancies in toxic impact categories. A recent article (Tarpani et al., 2020) compared several sewage sludge recycling alternatives, while taking the ecotoxicity associated with trace elements and PPCP into account, using the ReCiPe life cycle impact assessment method with USES-LCA as toxicity model. The authors partially assessed speciation of trace elements (i.e., the exchangeable/acid soluble bioavailable fraction). They found that composting gave the lowest resource recovery rates, while anaerobic digestion had the highest freshwater ecotoxicity due to the high trace element, as compared to composted sludge spreading, incineration, pyrolysis and wet air oxidation.

No dedicated LCA studies were found regarding agricultural recycling of livestock manure. Manure is included as a fertilizer in agricultural LCAs, but the impacts of its contaminants are seldom investigated, whereas several empirical studies have pointed out that manure is a major source of some trace elements in agricultural soils. Moreover, treated (e.g., stored, composted, digested) manure is more commonly included in LCA studies than raw manure (e.g., Cherubini et al., 2015).

2.3.2 Ecotoxicity of OW-borne trace elements

Considering the major contributions of trace elements to ecotoxicity impact scores in LCA (Pizzol et al., 2011b), substantial improvements in LCA approaches have been achieved over the past two decades concerning trace element impact assessment. Before 2010, all LCA approaches only took the total concentration of trace elements in soil and freshwater into account when assessing their ecotoxicological impact, which meant that there was a high risk of overestimation (Fairbrother et al., 2007). Indeed, there is considerable evidence that total concentrations are poor indicators of fate, bioavailability and toxicity of trace elements. Accordingly, the UNEP-SETAC working groups reached a consensus, i.e., the so-called Clearwater Consensus, to incorporate trace element speciation[e] and bioavailability for freshwater ecotoxicity assessment in the USEtox LCA methodology (Diamond et al., 2010). The proposed approach includes: a fate factor (FF) corresponding to the total trace element concentration in freshwater; a bioavailability factor (BF) representing the trace element fraction exhibiting a toxic interaction with freshwater organisms, estimated as the concentration of trace elements occurring as free ions and inorganic complexes (e.g., $CuCl^+$, $NiCO_3$, and $ZnOH^+$); and an effect factor (EF) corresponding to the PAF of species in freshwater, calculated as the hazardous concentration affecting 50% of species (HC_{50}, see Table 3). HC_{50} is calculated from the effective concentrations of trace elements at which 50% of a population displays a toxic effect (EC_{50}). PAF is estimated by combining environmental concentrations (from interpolated measurements or model simulations) with field bioavailability estimates (Klepper et al., 1998). The Clearwater Consensus further suggested using the Windermere Humic Aqueous Model (WHAM) (Tipping, 1994), with freshwater chemical properties commonly available in databases (notably pH, dissolved organic carbon (DOC) and water hardness) as input parameters, to estimate the concentration of trace elements, in the form of free ion and inorganic complexes, necessary to calculate BF and EF. Gandhi and Huijbregts (2010) and Dong et al. (2014) developed this approach to calculate generic CTP values for 14 trace elements (i.e., Al(III), Ba, Be, Cd, Co, Cr(III), Cs, Cu, Fe(II), Fe(III), Mn(II), Ni, Pb, Sr, and Zn), and to define seven freshwater archetypes ranked according to their chemical properties (i.e., pH, DOC and water hardness). These new CTP values were similar or slightly higher than the default USEtox-derived

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[e] "Speciation takes into account chemical and physical properties such as the element isotopic composition, oxidation state, coordination and molecular structure" (Reeder et al., 2006).

CTPs, and in all cases the differences were within 2 orders of magnitude (Dong et al., 2014). Yet when Gandhi and Diamond (2011) applied the WHAM approach to two case studies for Cd, Co, Cu, Ni, Pb and Zn, they found that the contribution of trace element emissions to the overall freshwater ecotoxicity score was one to four orders of magnitude lower than the overall freshwater ecotoxicity score calculated with default USEtox and USES-LCA. Gandhi et al. (2011) further showed that accounting for the geographic variability in freshwater chemistry was changing both region-specific CTP values for Cu, Ni, and Zn by up to three orders of magnitude and the ranking of CTP values for each trace elements between regions as compared to default USEtox and USES-LCA calculations. More recently, Hedberg et al. (2019) extended the WHAM approach to calculate a CTP value for Cr(VI) and to assess the impact of a temporal change in Cr speciation from Cr(VI) to Cr(III) on the CTP value. While not definitive, the overall results highlighted the need to account for the speciation and bioavailability of trace elements when assessing their freshwater ecotoxicity.

Terrestrial ecotoxicity modeling poses additional challenges with respect to freshwater ecotoxicity, as few toxicity data (especially chronic effects) are available for terrestrial species. Moreover, contrary to freshwater, the solid phase dominates the solution phase and is thereby crucial in the determination of trace element speciation and bioavailability. Recent studies have attempted to include the characterization of terrestrial ecotoxicity of trace elements in USEtox. The model proposed by Owsianiak et al. (2013) includes: a fate factor (FF), calculated as the total concentration of trace elements remaining in soil following their emission; an accessibility factor (ACF), defined as the reactive (i.e., available) fraction of the total trace element concentration in soil that mainly occurs in the solid phase; a bioavailability factor (BF), defined as the free ion fraction in soil solution of the reactive trace element exhibiting an interaction with soil organisms to generate a toxic effect; and a terrestrial ecotoxicity effect factor (EF), as defined for freshwater ecotoxicity. The solid-solution partitioning coefficients used to calculate FF, ACF and BF were estimated from soil physicochemical properties via multilinear regression. EF was estimated using the terrestrial biotic ligand model developed for plants, invertebrates and microorganisms (Thakali et al., 2006a,b). This framework has been applied to estimate the CTP for Cu and Ni in 760 soils worldwide. CTP values for Cu and Ni were found to vary by 3.5 and 3 orders of magnitude over a geographical gradient. CTP values for Cu were mainly affected by the soil organic matter concentration and pH, while those for Ni were mainly impacted by the Mg concentration in soil solution. Owsianiak et al. (2015) further implemented this framework to account for the different types of emission sources (geogenic versus anthropogenic) and aging. While emission sources significantly affected ACF, thereby suggesting the need to account for emission sources in LCIA, the effect of aging was inconclusive.

Plouffe et al., (2015a,b, 2016) proposed an alternative way to calculate CTP for trace elements based on the Clearwater Consensus. Contrary to Owsianiak et al. (2013) who defined an ACF, the soil solid-phase is not specifically accounted for in this approach. BF is calculated from the total soil trace element concentration and WHAM, with soil properties commonly available in databases (i.e., pH, texture, organic matter and carbonate concentration, and cation exchange capacity) as input parameters. BF values are calculated as the total concentration of trace elements in soil solution or as the concentration of trace elements in soil solution in the form of free ions and inorganic complexes. Note that the Clearwater Consensus considers the latter as being the best indicator of trace element species bioavailable for organisms. The ability of the WHAM approach to fit experimental data was assessed for Zn on 80 soil samples and the findings were compared with the multilinear regression-based approach developed by Owsianiak et al. (2013). The results suggest that the WHAM and regression approaches predict BF values similarly based on the total Zn concentration in soil solution, and that the WHAM approach poorly predicts BF values based on the free and inorganic Zn complex concentration. The rankings of BF values calculated with WHAM and measured experimentally were moderately, but significantly, correlated, whereas those calculated with multilinear regressions and measured experimentally were not significantly correlated. Accordingly, the total trace element concentrations in soil solution simulated with WHAM suggested that this is the most reliable approach to calculate BF (Plouffe et al., 2015a). Note, however, that the extent of calculated BF values that were validated encompassed only 25% of the soil types included in the FAO Harmonized World Soil Database (FAO/IIASA, 2009), therefore underlying the need to further validate the WHAM approach.

Plouffe et al. (2016) also calculated CTP values by combining the aforementioned WHAM-based BF with an FF based on a modified USEtox framework using WHAM to estimate the solid-solution partitioning coefficient, as well as with an EF based on the total Zn concentration in soil solution. Grid-specific CTP values were first calculated for 5200 soil samples referenced in the FAO Harmonized World Soil Database, and a global CTP value was finally calculated by summing the product of CTP and population as a proxy of Zn emission in each grid. Interestingly, the resulting global CTP value based on the WHAM approach was 27- and 62-fold lower than the default terrestrial CTP values derived from IMPACT 2002 and USEtox, respectively. Plouffe et al. (2015b) implemented the IMPACT 2002+ method and showed that accounting for trace element speciation with the WHAM-based approach in the LCIA procedure decreased the Zn contribution to the total terrestrial ecotoxicity impact score from 26% in the default approach to less than 2% in the WHAM approach. While the WHAM approach was only validated for Zn, Aziz et al. (2018) and Viveros Santos et al. (2018) further implemented the WHAM approach for Cu and Ni terrestrial ecotoxicity assessment. They showed that the grid-specific and global CTP values, as well as the grid-specific and global impact score based on the WHAM approach, were about 3 orders of magnitude lower than the default IMPACT 2002- and USEtox-derived terrestrial CTP values and impact scores. Moreover, Viveros Santos et al. (2018) showed—with regard to soil Cu contamination in European vineyards—that increasing the spatial resolution of LCIA implementation decreased the CTP value and impact score variability, which suggests the need for a regionalized assessment of terrestrial ecotoxicity. Concomitantly, these overall results suggest that the contribution of trace elements to the terrestrial ecotoxicity impact score derived from current LCIA approaches is overestimated, thus highlighting the need to further account for trace element speciation and bioavailability. This conclusion was, however, recently challenged by the findings of Sydow et al. (2020) based on a comparison of the speciation-based method developed by Owsianiak et al., (2013, 2015), and the toxicity models implemented in the widely used IMPACT 2002+ and ReCiPe 2008 methods for ˜13000 life cycles of unit processes. They observed that CTP values and concomitant impact scores calculated with the speciation-based method were not systematically markedly lower than those calculated with IMPACT 2002+ or ReCiPe 2008 methods. Sydow et al. (2020) further found that, when accounting for their solid and solution speciation in soils, trace elements still contributed to more than 90% of the total terrestrial ecotoxicity impact score (with less than 10% due to organic contaminants). These authors thus concluded that increasing the substance coverage of LCIA methods would be as beneficial as increasing their environmental relevance by considering trace element speciation in soils. This conclusion strongly differs from those of Plouffe et al. (2015b), Aziz et al. (2018), and Viveros Santos et al. (2018). In the light of the high contribution of trace elements on the total ecotoxicity impact score currently calculated by LCIA methods, there is therefore an urgent need to determine whether the time-consuming effort of developing new speciation-based LCA methods would improve LCIA methods by markedly changing the total ecotoxicity impact score calculation.

Leclerc and Laurent (2017) described a framework to inventory worldwide and some national emissions of trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) into agricultural soils due to livestock OW spreading. While some discrepancies were underlined, this framework generally appeared to be consistent with the findings of previous worldwide and national inventories. Leclerc and Laurent (2017) used USEtox 2.02 to further estimate the impacts of trace elements in OW-amended soils on human toxicity (cancer and non-cancer effects) and freshwater ecotoxicity. They showed that Hg had a dominant impact with regard to cancer effects, Zn for non-cancer effects and Cu for freshwater ecotoxicity. More interestingly, the high spatial variability in regional inventories and impact intensity pointed out the need for the development of country- or regional-specific impact assessment. Tarpani et al. (2020) recently suggested a complementary way to account for the ecotoxicological impact of trace elements among other environmental impacts of sewage sludge treatment methods, namely to consider the concentration of the most available trace element fraction (i.e., chemically extracted in the exchangeable/acid soluble pool) as being potentially harmful.

Owsianiak et al. (2015) assessed the influence of the emission source on the terrestrial ecotoxicological impact of some trace elements (Cd, Co, Cu, Ni, Pb, and Zn). Among the emissions sources, an organic-related source associated with anthropogenic activities (i.e., historical soil contamination) was considered. This organic-related source theoretically encompassed a large range of OW, such as biosolids, manure, compost and treated wastewater—it was considered to be characterized by trace elements bound mainly to organic matter in OW in comparison with trace elements occurring as oxides or sulfides respectively originating from combustion processes and mining activities. It was found that the emission source has a significant impact on the reactive pool of Cd, Co, Cu, and Zn, but not Ni and Pb. The organic-related source exhibited a reactive pool that was significantly less reactive than geogenic and airborne sources for Cd, less reactive than any other anthropogenic sources for Cu and, conversely, more reactive than airborne and geogenic sources for Zn. Accordingly, Owsianiak et al. (2015) recommended incorporating the emission source effect, including the OW-related emission source effect, in the CTP calculation to improve assessment of the terrestrial ecotoxicological impact of trace elements in LCA procedures.

Sydow et al. (2018) combined the national inventories performed by Leclerc and Laurent (2017) and the assessment of the terrestrial ecotoxicological impact of OW-related emission sources suggested by Owsianiak et al. (2015) to assess the terrestrial ecotoxicological impact of agricultural OW-bound trace element inputs after spreading on agricultural fields in Europe on a country scale. Trace element and country-specific impact scores were calculated from the product of the total mass of a trace element emitted from OW applied on agricultural land in a given country (m_{total}) and the area-weighted comparative toxicity potential (CTP) for the trace element and the target country. The m_{total} value was calculated directly at the country scale from the product of the total OW applied and the concentration of each trace element in OW. The CTP value per country was first calculated at 1 km^2 grid resolution as the product of the grid-specific agricultural surface area and the grid-specific CTP. The CTP value was then area-weighted at the country scale. Grid-specific CTP values were finally calculated from a grid-specific soil properties database and the framework previously proposed by Owsianiak et al. (2013) for FF, ACF, BF, and EF calculation. To account for the fact that trace elements were added to soil from a specific emission source (i.e., OW), ACF was calculated from the mean ACF determined for the organic-related trace element source, as suggested by Owsianiak et al. (2015). Several major conclusions were drawn from this study. Firstly, the grid-specific CTP values per trace element ranged from 1 to 4 orders of magnitude among the soils in Europe. Despite this marked variability in grid-specific CTP, the country-specific impact scores were closely correlated with m_{total} rather than with the area-weighted CTP. Sydow et al. (2018) attributed the relatively small effect of CTP on the impact scores to the area weighting of grid-specific CTP at the country scale, suggesting that OW, and hence trace elements, are homogeneously applied on agricultural surface areas. Interestingly, this study also pointed out that Cu and Zn dominated among trace elements with regard to the contribution to both m_{total} and area-weighted CTP, and hence to the impact scores.

2.3.3 Ecotoxicity of OW-borne organic contaminants

Despite organic contaminants being included in LCA toxicity models, very few LCA studies on OW management and treatment include organic contaminants in their emission inventory, contrary to trace elements. Although the organic pollutant fate is known to often depend on the sorptive properties, USEtox fate modeling does not take interactions between organic matter and organic contaminants into account, and excludes certain substance groups (see Section 2.2.2).

The fate of trace elements and organic contaminants following OW application on agricultural soils has been assessed by the CML LCIA method, and the findings revealed that trace element leaching from sludge had greater impacts than organic contaminants (e.g., PPCP). In this study, organic contaminant characterization factors not accounted for in the CML method and were estimated by EDIP97 and USES-LCA on the basis of very limited data (Muñoz et al., 2008). The paucity of data available for determining characterization factors for contaminants as hence a major shortcoming of toxicity methods in LCA, yet ongoing research is striving to overcome this issue. For instance, in some other studies, characterization factors (fate and toxicology) for emerging pollutants, their metabolites and transformation products have been approximated through analytical methods such as liquid chromatography combined with mass spectrometry (la Farré et al., 2008). Alfonsín et al. (2014) also used USEtox and USES-LCA to calculate new updated characterization factors for PPCP in a new wastewater treatment implementation context. They enhanced the calculations by including additional physicochemical properties and degradation rates (via the Estimation Program Interface Suite v4.0), as well as human exposure data, human toxicological effect and ecotoxicological effect data (from experimental data and the ECOTOX and IRIS databases).

In reference to a 3-year field experiment where organic contaminants were found to have dissipated in the first months after OW spreading, Hansen et al. (2006b) used the EASEWASTE tool (and its simplified toxicity model) to account for bis(2-ethylhexyl) phthalate, nonylphenol ethoxylates, linear alkylbenzene sulfonate and PAH (sum of 11 compounds) derived from composted or anaerobically digested source-separated municipal solid waste spread on soil. One of the goals in the study of Sablayrolles et al. (2010) was to improve the quantification of human toxicity when dried and composted sludge were spread in fields. The authors calculated human toxicity factors via plants (carrot, tomato) for PAH (sum), PCB (sum), and bis(2-ethylhexyl) phthalate based on postharvest concentrations, dry matter content, plant yield and average consumption using USES-LCA and empirical factors from a previous soil-biosolids-plant study (Sablayrolles, 2004). Hospido et al. (2010) focused on the potential impacts of some emerging pollutants when anaerobically digested sludge (four digestion scenarios according to the temperature and sludge retention time) was applied on soil. Their contribution to human and terrestrial toxicity was found to be small compared to that of trace elements. They used USES-LCA (via CML) and the characterization factors presented in Muñoz et al. (2008) and computed with experimental data and the EDIP97 and USES-LCA toxicity models. All of these studies carried out using USES-LCA to assess terrestrial ecotoxicity inevitably inherit the shortcomings of that model, including the lack of ability to extrapolate aquatic data to estimate terrestrial ecotoxicity. Harder et al. (2017) studied the USEtox-modeled effects on human toxicity and compared the results with regard to sludge spread on soil. In the context studied, 13 organic contaminants were found to be of greatest potential concern, including bis(2-ethylhexyl) phthalate, hexachlorobenzene, 1 PCB, 1 polybrominated diphenyl ether, 17α-ethinyloestradiol, 7 PAH and one biocide (Mirex, CAS No. 2385-85-5). The authors underlined the different sources of uncertainty in the estimation of the aggregate burden of disease: the model adequacy (e.g., overestimation of uptake by plants compared to field measurements), the data gaps regarding contaminants potentially present in sewage sludge but not monitored and the data gaps regarding chemical and biological properties for most of contaminants.

2.4 Toxicity modeling in RA

Risk assessment is another framework commonly used to study waste treatments, their outputs and OW recycling in general, from an environmental/ecological and/or human health perspective (Brooks et al., 2012; Jahne et al., 2015; Magid, 2012). RA relies on models to determine hazards (including toxicity) and exposure to released contaminants in an *ex ante* fashion. The term RA may also refer to *ex post* empirical research studies, but this review focuses exclusively on *ex ante* model-based RA (see Section 2.5.2). OW risk assessments have mainly been conducted to address wastewater treatments and sludge recycling. RA compares measured or estimated concentrations with legal limits (Huber et al., 2016). RA and toxicity studies on sewage sludge for agricultural use have addressed—via empirical research—the load, impacts on human health and occasionally the fate (i.e., the transport and degradation of a substance emitted into the environment) of trace elements, organic contaminants and pathogens (Aparicio et al., 2009; Meng et al., 2014; Moreira et al., 2008; Ning et al., 2015; Singh and Agrawal, 2008; Tobajas et al., 2015; Vaz-Moreira et al., 2008; Walter et al., 2006). Relevant empirical research may involve bioassays, including germination/growth and microorganism isolation tests. RA models focused on hazard, exposure and effect (risk characterization) of European relevance are identified in the European Union Technical Guidance Document on Risk Assessment (EU-TGD[f]) (EC-JRC, 2003) and the European Union Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) legislation (EC 2007; Table 3), such as the quantitative structure-activity relationship (QSAR[g]) for toxicity, as well as the European Centre for Ecotoxicology and TOxicology of Chemicals targeted risk assessment (ECETOC-TRA), Stoffenmanager (Marquart et al., 2008; Tielemans et al., 2008) and the Advanced REACH Tool (ART) for occupational exposure. Exposure models have been compared on a recent review by Riedmann et al. (2015). The findings revealed that each model had different perspectives, as shown in the weighting sets applied to the modeled physical phenomena, and that there is a trade-off between accuracy and precision the model designs, and recommendations on their use ultimately depends on the availability and quality of the available data. The authors identified Stoffenmanager, which consists of system of linear equations for near and far-field exposure, as the most robust exposure model. Another key RA framework is that implemented by the United States Environmental Protection Agency (US EPA), which is also based on the exposure-effect paradigm (see Table 3 for the European REACH), and is highly modeling based (US EPA, 1992; USEPA, 1994). A heterogeneous international list of exposure models, often discussed among scientists at the European Joint Research Centre (JRC), is also presented in the supplementary material associated with Bopp et al. (2019). Contrary to LCA, where toxicity models are focused on a broad range of target contaminants (trace elements and organic contaminants), RA features a separate model per type of contaminant (trace elements, organic contaminants and pathogens). Models used in the OW treatment and agricultural recycling context, as well as those dealing with specific contaminant types, are presented in Section 2.5.

2.5 Consideration of contaminants in organic waste treatment and agricultural recycling RA

2.5.1 Organic waste treatment and soil application

Risk assessment has mainly been used to study digestate recycling rather than anaerobic digestion facilities and their functioning (Brooks et al., 2012;

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[f] EU-TGD has been deprecated and replaced, since 2007, by the REACH legislation (EC, 2007), but many approaches and models were recycled in REACH.

[g] Quantitative structure-activity relationship (QSAR): "computer-based methods able to quickly predict and assess the toxicity of large numbers of chemicals using a mathematical algorithm implemented in a software programme" (REACHnano, 2015).

Pivato et al., 2015; Zhao and Liu, 2019). The contaminants most commonly studied in relation to anaerobic digestion of OW are, in decreasing frequency: trace elements and pathogens, through approaches such as quantitative microbial risk assessment (QMRA) (Section 2.5.4) (e.g., Brooks et al., 2012) and ecotoxicological tests (e.g., Pivato et al., 2015). We did not find any anaerobic digestion RA taking organic contaminants into account, but we did note a few examples of empirical determination and/or measurements of the effects of anaerobic digestion on organic contaminants present in sewage sludge (Bourdat-Deschamps et al., 2017; Carballa et al., 2007; Samaras et al., 2013).

Composting RA studies are also less common than on other waste treatment pathways. These studies address municipal solid waste, agricultural waste and sludge as substrates, and consider the trace elements, pathogens and organic contaminants (Alvarenga et al., 2013; Déportes et al., 1995; Gusiatin and Kulikowska, 2014; Patureau et al., 2012). Gusiatin and Kulikowska (2014), while recognizing that it would be insufficient to only use the total trace element concentration in environmental assessments, proposed trace elements indicators for sludge compost RA (see Section 2.5.2).

A non-peer reviewed meta-review (Magid, 2012), compiled conclusions from more than 150 RA and fertilization studies, where the fate of contaminants, in terms of PEC and PNEC (see Table 3), was determined through long-term field experiments, mathematical modeling compliant with EU-TGD, and worst-case input-based estimation according to REACH. These studies suggested that interactions among trace elements, organic contaminants and pathogens present in sludge are unlikely unless the contaminants share a mode of action, and that there is no conclusive evidence that sludge spreading on agricultural soils (within regulatory boundaries) is harmful for humans or animals. Several issues have been identified that require further investigation, namely the potential impacts of chlorinated paraffin and phthalates on human health, as well as the impacts of PPCP and endocrine-disruptors on soil quality and human health. These studies conclude that the possibility of health impacts from antibiotics and antibiotic-resistant bacteria in sludge is non-negligible, and that this issue requires further research.

For certain organic contaminant categories such as pharmaceuticals and PCPP, despite the growing number of publications, very few data are available on their environmental fate after OW recycling in agricultural fields (Houot et al., 2014).

Recently, Bourdat-Deschamps et al. (2017) studied the fate and exposure of several pharmaceutical residues in agricultural soils after repeated application of several types of OW, applied at usual doses for farmers and in different pedoclimatic settings. Predicted concentrations of pharmaceuticals in soil after several OW applications were higher than the measured concentrations due to degradation, strong sorption to soil constituents and/or leaching. Dissipation half-life times (DT_{50}[h]) were assessed at around 1300–2500, 900 and <300 days for fluoroquinolones, carbamazepine and ibuprofen in temperate soils, and <150 days and 80 days for fluoroquinolones and doxycycline in tropical soils. Based on the few data available on ecotoxicological effects on terrestrial organisms, potential risks were estimated using the risk quotient approach (Section 2.5.3). The authors concluded that the environmental risk was low. However, the study clearly highlighted the lack of available ecotoxicological parameters for such contaminants. More generally, one difficulty encountered was to obtain relevant ecotoxicological endpoints for organic contaminants. This issue is still far from solved, even for compounds such as pesticides undergoing ecotoxicological and toxicological tests for registration purposes. Traoré et al. (2018) noticed that the availability of ecotoxicological parameters was lower for chronic than for acute toxicity endpoints, regardless of the targeted organisms. This distortion is due to the fact that simple cost- and time-effective tests are used for acute toxicity assessment. It is also clear that ecotoxicological parameter measurements are far more available for aquatic organisms (invertebrates) than for terrestrial invertebrates. Moreover, interpretation of results from terrestrial invertebrates requires a far more complex methodology because tests regularly involve non-equilibrium processes.

Brooks et al. (2012) performed QMRA (Section 2.5.4) of scenarios featuring the application of sewage sludge and manure digestates and raw sewage sludge based on previously published experimental data and empirical equations to determine soil and crop contamination levels. They concluded that raw and digestate sewage sludge risks were associated with viruses, whereas manure risks concerned bacteria.

Komnitsas and Zaharaki (2014) reviewed recent ecological RA studies on compost application, performed under the US EPA framework. They presented a broad range of fate and risk factors and indices, while also focusing on human exposure. Thomaidi et al. (2016) performed environmental RA of raw and composted sewage sludge-amended soil, calculated aquatic and soil PEC, and estimated elevated risk quotients for synthetic phenolic compounds and siloxanes. A recent review of the environmental risk literature, including ERA, revealed that the recycling of sewage sludge in soils—raw or stabilized by composting or anaerobic digestion—generates risks from PAH (but not other organic contaminants) and trace element contamination risks (Liu, 2016).

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[h] Dissipation half-life times (DT_{50}): rate of degradation of chemicals, a period after which half of the initial load has degraded. ‘Dissipation’ refers to “a composite of processes describing volatilization, wash-off, leaching, hydrolysis, chemical and biological degradation, and other individual processes” (Fantke and Juraske, 2013)

RA on livestock effluent recycling in agriculture (treated or raw) has been almost exclusively focused on trace elements and organic contaminants. For instance, Río et al. (2011) proposed a dynamic environmental risk assessment multicompartmental model for assessing trace element-induced risks of long-term manure application. Several RA studies have investigated different aspects, including: PEC of selected antibiotics (e.g., tetracyclines, quinolones, sulfonamides) based on EU-TGD and European Medicines Agency (EMEA) guidelines (Carballo et al., 2016; EMEA, 2006; Li et al., 2015) (see Section 2.4); effective internal doses of airborne pathogens (via empirical formulas (Jahne et al., 2015)); aerosol dispersion models (via empirical formulas (Heimersson et al., 2014)); and even qualitative scoring according to pedoclimatic conditions using a qualitative multi-attribute decision model for *ex ante* assessment of agricultural sustainability (Sadok et al., 2009). Prosser and Sibley (2015) assessed the human health risk based on reported empirical research findings on organic contaminant residues in edible tissues of plants grown in sewage sludge- or manure-amended or wastewater irrigated soils. They compared estimated daily intake to acceptable daily intake values (as defined by many different official international agencies). For all three amendment practices, hazard quotients <0.1 (low risk) applied to the majority of the reported residues. Yet the need for further investigation of risks related to antibiotic resistance associated with sludge and manure spreading has recently been pointed out in the light of the rising pharmaceutical contamination levels in the environment (Bondarczuk et al., 2016).

2.5.2 Ecological and human risks due to OW-borne trace elements

Trace element RA has been developed to evaluate the impact of trace elements on ecosystems and human health through two main groups of approaches (Fig. 2). The first involves dedicated experimental procedures and analytical determinations, while the second is based on quantitative and predictive modeling of the fate of trace elements in soils and their

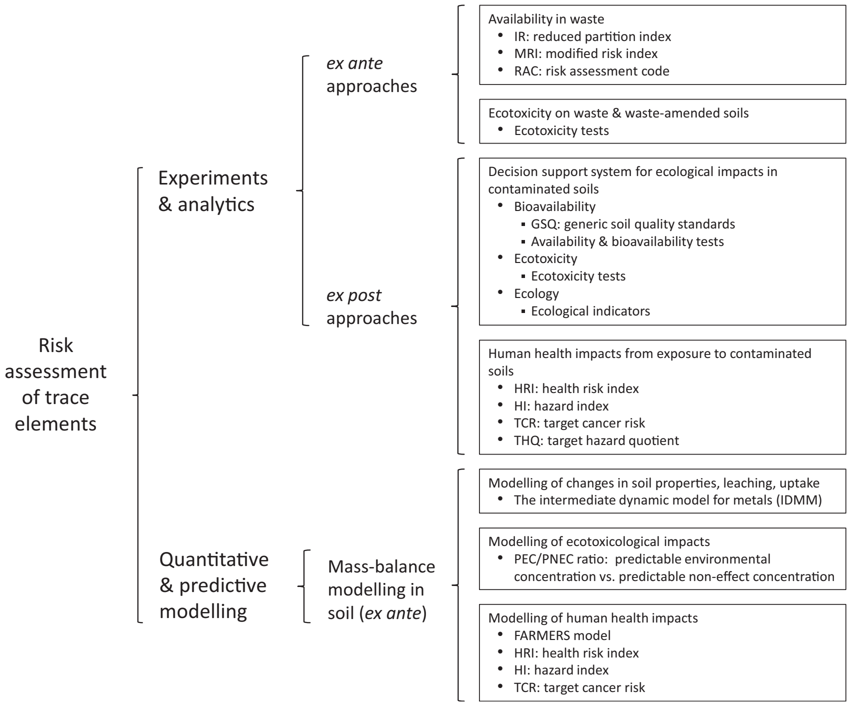
Risk assessment of trace elements
Experiments & analytics
ex ante approaches
ex post approaches
Quantitative & predictive modelling
Mass-balance modelling in soil (ex ante)
Availability in waste
IR: reduced partition index
MRI: modified risk index
RAC: risk assessment code
Ecotoxicity on waste & waste-amended soils
Ecotoxicity tests
Decision support system for ecological impacts in contaminated soils
Bioavailability
GSQ: generic soil quality standards
Availability & bioavailability tests
Ecotoxicity
Ecotoxicity tests
Ecology
Ecological indicators
Human health impacts from exposure to contaminated soils
HRI: health risk index
HI: hazard index
TCR: target cancer risk
THQ: target hazard quotient
Modelling of changes in soil properties, leaching, uptake
The intermediate dynamic model for metals (IDMM)
Modelling of ecotoxicological impacts
PEC/PNEC ratio: predictable environmental concentration vs. predictable non-effect concentration
Modelling of human health impacts
FARMERS model
HRI: health risk index
HI: hazard index
TCR: target cancer risk

Fig. 2 Overall framework of the approaches used for risk assessment of ecotoxicological and human health impacts of trace elements (applicability for organic waste), indicators are detailed in Table 4.

consequent transfer to surrounding environmental compartments, and to the human food chain.

The main equations used to compute the indicators associated with these approaches are summarized in Table 4.

The experimental and analytical approach of RA for trace elements can be further divided in two sub-approaches, based on an *ex ante* RA of trace elements that could accumulate in soil upon OW application or an *ex post* RA of trace elements that were added in fields that have a long history of OW amendment (Fig. 2). The *ex ante* approach is focused on the analytical characterization of trace element availability in OW and/or trace element ecotoxicity in freshly OW-amended soil samples (Komnitsas and Zaharaki, 2014). Trace element availability in OW is usually determined by the application of a sequential trace element extraction procedure to a range of OW types. The trace element concentration in each extracted fraction and their relative proportions enable calculation of three indicators of the potential

Table 4 Computation of risk assessment indicators for trace elements

Indicators	**Main equations**	**Remarks**
Indicators calculated on waste		
Reduced partition index	$IR = \frac{\sum_{i=1}^{k}(i^2 \cdot F_i)}{k^2}$	i is the number of the extraction step from 1 for the first and weakest extractant to k for the last and strongest extractant F_i is the percentage of the total trace element recovered after the extraction step i
Risk assessment code	$RAC = \frac{[TE]_{available}}{[TE]_{total}} \cdot 100$	$[trace\ elements]_{available}$ is the concentration (mg kg^{-1} dry soil) of a given available trace element recovered after the first extraction step(s) $[trace\ elements]_{total}$ is the total concentration (mg kg^{-1} dry soil) of a given trace element
Modified risk index	$MRI = \sum_{i=1}^{n}(T_{r,i}) \cdot \frac{[TE]_{total,i} \cdot (A\beta + B)}{[TE]_{ref,i}}$	$T_{r,i}$ is the toxic-response factor for trace element i (e.g., 1 for Zn, 5 for Cu, Ni, and Pb, and 30 for Cd according to Håkanson (1980)) $[trace\ elements]_{total,i}$ is the total concentration (mg kg^{-1} dry soil) of trace element i A is the percentage of total trace element recovered after the first extraction step β is the toxic index of trace elements recovered after the first extraction step; The β value is defined as a function of the RAC value (see Section 1.2) as follows: 1.0 for $1 < RAC \leq 10$, 1.2 for $11 \leq RAC \leq 30$, 1.4 for $31 \leq RAC \leq 50$, and 1.6 for $RAC > 50$ (Zhu et al., 2012) B is the sum of percentages of total trace element recovered in all extraction steps except the first one $[trace\ elements]_{ref,i}$ is the background or regulatory threshold concentration (mg kg^{-1} dry soil) used a reference for trace element i

Continued

Table 4 Computation of risk assessment indicators for trace elements—cont'd

Indicators	Main equations	Remarks
Indicators calculated on contaminated soils		
Health risk index	$HRI = \frac{[TE]_{food} \cdot D_{food}}{[TE]_{ref} \cdot BW}$	$[\textit{trace elements}]_{food}$ is the concentration (mg kg^{-1} dry food) of a given trace element in food D_{food} is the daily intake of food (kg dry food day^{-1}) $[\textit{trace elements}]_{ref}$ is the reference dose of trace element ingested with food (mg kg^{-1} dry food day^{-1}) BW is the average body weight of an exposed human being (adult or child)
Target hazard quotient	$THQ = HRI \cdot \frac{EF_{nc}}{ME}$	EF_{nc} is the exposure frequency (day) to non-carcinogenic effects of a given trace element for 1 year ME is the maximal exposure (365 days) to carcinogenic or non-carcinogenic effects of a given trace element for 1 year
Hazard index	$HI = \sum_{i=1}^{n} THQ_i$	THQ_i is the target hazard quotient for each trace element i
Target cancer risk	$TCR = \frac{[TE]_{food} \cdot D_{food} \cdot CPS \cdot EF_c}{BW \cdot ME}$	CPS is the carcinogenic potency slope (kg body weight day mg^{-1} trace element) EF_c is the exposure frequency (day) to carcinogenic effects of a given trace element for 1 year

availability level of trace elements that would be added to soil by the application of a given OW (Gusiatin and Kulikowska, 2014). The reduced partition index (I_R) characterizes the binding intensity of each trace element in the OW solid phase, where a low I_R value indicates low binding and consequently a potentially high availability of trace elements in OW and in the amended soil. The risk assessment code (RAC) corresponds to the percentage of the total concentration of each trace element occurring in the most available fraction (e.g., the exchangeable fraction) and characterizes the trace element availability in OW. RAC is usually inversely correlated with the I_R and is typically interpreted according to the following scale: <1% (no risk), 1–10% (low risk), 11–30% (medium risk), 31–50% (high risk) and > 50% (very high risk). Finally, the modified risk index (MRI) corresponds to the sum of the potential ecological risk of each individual trace element and combines a toxic-response factor, the measured availability, and a background or regulatory threshold for each trace element. Although MRI is highly impacted by the number of trace elements analyzed and the background/regulatory thresholds considered, it is typically interpreted according to the following scale: <150 (low risk), 150–300 (moderate risk), 300–600 (considerable risk) and >600 (very high risk). This approach—based on the analytical characterization of trace element availability in waste—has already been applied to OW, including agricultural waste and sewage sludge compost (Gusiatin and Kulikowska, 2014; Komnitsas and Zaharaki, 2014).

When there is not sufficient data to classify an OW based on its chemical composition, Pandard and Römbke (2013) suggested that *ex ante* characterization of its overall ecotoxicity (including the contribution of trace elements and other types of contaminants) could be performed through a battery of aquatic and terrestrial biotests on a dilution series of OW eluate or OW-amended artificial soil samples (Fig. 2). Thresholds based on the level or percentage of OW dilution that induces a given reduction (e.g., 50%) of each ecotoxicological endpoint compared to the control were proposed to classify the OW as hazardous or not. This approach was specifically developed for OW meant for application on agricultural soils and deployed to assess a solid or eluted mixture of artificial soil with nine OW applied at 1- to 100-fold the recommended application rate (Huguier et al., 2015). The authors concluded that the use of terrestrial biotests (particularly plants and earthworms biotests) were the most sensitive and discriminant ecotoxicological endpoints and consequently the suggested minimal procedure to assess the ecotoxicological impacts in OW-amended soils. Similarly, a range of aquatic and terrestrial biotests was also used for the ecotoxicological RA of an agricultural digestate (Pivato et al., 2015). The dose-response curves derived from the measured ecotoxicological endpoints were used to determine a predictable non-effect digestate concentration in soil ($PNEC_{Soil}$, in mass of digestate per mass unit of soil) under which no unacceptable ecotoxicity on soil organisms would be expected. The authors also suggested to further reduce this $PNEC_{Soil}$ by a dimensionless assessment factor, depending on the number of trophic levels assessed, the timespan of the exposure to OW-amended soil (short-term/acute vs. long-term/chronic), and on whether the ecotoxicological RA were performed on laboratory or field data. Renaud et al. (2019) recently proposed to refine the rendition of dose-response curves obtained from OW-amended soils by establishing a species sensitivity distribution for each tested OW. These species sensitivity distributions are based on ecotoxicological endpoints determined for several species (e.g., two endpoints for plants and four endpoints for soil invertebrates were used by Renaud et al. (2019)). The suggested reference ecotoxicological endpoints were the effective concentrations causing 10 or 50% toxic effect (EC_{10} or EC_{50}). A hazardous concentration (HC) was thereafter determined for each OW as a threshold value higher than 5 or 50% (HC_5 or HC_{50}, respectively) of the community of soil organisms accounted for in the corresponding species sensitivity distribution. Interestingly, Renaud et al. (2019) showed that using an HC_5 based on EC_{50} was more protective than an HC_{50} based on EC_{10} and thus seemed more suitable for ecotoxicological risk assessment. The $PNEC_{add}$ value—which corresponds to the so-called hazardous concentration at x% (HC_x)—is hence protective for 1-x% of soil organisms considered in the database. $PNEC_{add}$ is usually calculated for a value of $x = 5$.

The ecotoxicological impacts of OW can be also assessed ***ex post*** on soil sampled in fields that have a long history of OW amendment (Fig. 2). For instance, Roig et al. (2012) sampled soils from a 16-year field experiment where unfertilized control plots and control plots receiving mineral fertilizers were compared to plots amended with anaerobically digested sewage sludge applied at several frequencies and application rates. The resulting physicochemical properties and trace element concentrations were determined in each soil sample. Ecotoxicological parameters (microbial activity in soil via respiration, phytotoxicity via germination and shoot growth tests, etc.) were further determined directly in soil samples or in a soil eluate. The overall ecotoxicological impact was finally assessed by comparing changes in soil physicochemical properties and ecotoxicological parameters between the OW-amended soil samples and control soil samples.

Ex post RA was also developed to assess the impacts of trace elements on human health (cancer and non-cancer effects; Fig. 2) by considering multiple pathways of human (adults and children) exposure to amended soils, such as soil dust inhalation and the ingestion of soil, edible plant organs and livestock products (typically milk, meat and eggs) (Déportes et al., 1995). *Ex post* RA is used to measure trace element concentrations in relevant environmental compartments (i.e., waste, soil, air, water, plant and animal products) and then to calculate a health risk index (HRI) from the ratio between the average daily intake of a given trace element through one or many exposure pathways, along with the corresponding health benchmark value. For each trace element, health benchmark values usually correspond to the reference dose for cancer and non-cancer effects following ingestion (expressed in trace element mass/body weight mass/day) and inhalation (expressed in trace element mass/m^3 of air) (Komnitsas and Zaharaki, 2014). Such health benchmark values have, for instance, been defined for a range of trace elements by US EPA. HRI can integrate the fact that human beings are only occasionally exposed to trace elements by taking the exposure frequency into account when calculating the target hazard quotient (THQ) for non-cancer effects, along with the target cancer risk (TCR). HRI and THQ values below one and TCR values below 10^{-4} are considered to be within the health protection limit. THQ of a range of trace elements can be further summed to calculate the hazard index (HI), which takes the cumulative effect of ingested or inhaled trace elements into consideration. This kind of *ex post* RA of trace elements for human health was recently applied to the findings of a 10-year field experiment with soil amended with mineral fertilizers or OW and revealed that some trace elements (Br and Zn) posed a potential non-cancer risk to human health (Couto et al., 2018).

The approach based on experimental procedures and analytical determinations is sometime tedious, expensive and time-consuming, so a predictive approach (*ex ante* by design) was developed for trace element RA (Fig. 2). This approach is based on quantitative modeling of the fate of trace elements following their emission into soil, and of their ecotoxicological and human health impacts. The primary step in this predictive approach involves mass-balance modeling of trace element inputs and outputs in soil at an annual time step. Trace element inputs in soil usually include atmospheric deposition, pesticide application and fertilization with mineral fertilizer and OW. The intermediate dynamic model for metals (IDMM) also accounts for the impact of OW inputs on soil properties other than the total trace element concentration in soil (Monteiro et al., 2010) (Fig. 2). In IDMM, it is considered that OW is mixed with the top 5 cm soil layer and consequently alters the bulk density and organic matter concentration in this layer. It is further considered that 70% of the organic matter added by OW is mineralized at each time step. Trace element outputs from soil usually considered are uptake in plants and vertical leaching of trace elements in solution. In IDMM, the leaching of trace elements associated with soil particles, as well as the erosion-induced loss of trace elements in soil solution and associated with soil particles, are also considered as outputs (Lofts et al., 2013b; Monteiro et al., 2010). The simplest models directly calculate trace element concentrations in plants (for the plant uptake output) or in soil solution (for the soluble leaching output) from the total trace element concentration in soil and the soil properties (i.e., pH, clay concentration and/or organic matter concentration) using multilinear regression equations (Río et al., 2011). The model of de Vries et al. (2004) estimates trace element leaching in soil solution using empirical multilinear regression equations to first calculate the available pool of trace elements in soil (called the reactive pool) from the total concentration of trace elements in soil and the soil properties (i.e., organic matter and clay concentration) and then the trace element concentration in soil solution from the calculated reactive pool and the soil properties. In IDMM, trace elements are more comprehensively distributed between four different pools: a first mineral pool of trace elements occluded in soil-bound primary and secondary minerals; these can weather over time and give rise to a second pool of available/reactive trace elements bound to the soil solid-phase; the latter is in equilibrium with a third pool of free ionic trace elements in soil solution; and finally this pool is in equilibrium with a fourth pool of trace elements bound to inorganic and organic ligands in soil solution (Lofts et al., 2013b; Lofts and Walker, 2016). The third and fourth pools thus jointly constitute the total pool of trace elements occurring in soil solution. The free ionic concentration of trace elements in soil solution is calculated from the concentration of trace elements bound to the soil solid-phase using multilinear regression based on the soil properties (i.e., pH and the clay and organic matter concentration), while the total concentration of trace elements in soil solution is simulated from the free ionic concentrations and the chemical composition of the soil solution (i.e., pH and the concentration of major cations and anions and DOC) with WHAM. Monteiro et al. (2010) and Lofts and Walker (2016) further implemented IDMM to enable the available pool of trace elements bound to the soil solid-phase to kinetically decrease over time to become strongly fixed to the soil solid-phase following aging. This aged pool was also able to kinetically resupply the mineral pool. The rate of trace element weathering from the occluded pool to the available pool is set at a given value per trace element, while the rate of trace element aging depends on the soil pH. Simulations of trace element accumulation in soil and transport from soil to the surrounding water resources are usually performed over several decades, thereby questioning the relevance of uncertainty in the model parameter estimations. In IDMM, up to three soil layers are considered, corresponding to the top 5 cm layer, the 5–25 cm layer and the layer from 25 cm to the artificial drainage depth (typically 1 m). In the most advanced IDMM version, a surface water model was implemented to manage the supply of drained and eroded trace elements (Lofts and Walker, 2016). The range of trace elements for which each mass-balance model is parameterized usually depends on the model complexity. The simplest models, such as that proposed by Río et al. (2011), are parameterized for five trace elements (i.e., Cd, Cu, Ni, Pb and Zn), while more complex models such as those proposed by de Vries et al. (2004) or IDMM are completely parameterized for one or two trace elements only (i.e., Cu and/or Zn).

Based on mass-balance modeling outputs, ecotoxicological impacts are predicted for a given time horizon by calculating the PEC/PNEC ratio that is considered safe if it is lower to 1 (de Vries et al., 2004; Monteiro et al., 2010) (Fig. 2). The PEC value corresponds to the total trace element concentration in soil predicted by the mass-balance model for a given time horizon. PNEC is usually considered to be the sum of the natural pedogeochemical background concentration of trace elements in an uncontaminated soil layer and the PNEC_{add} specifically calculated for trace elements added to the soil by anthropogenic activities (i.e., contamination). PNEC_{add} is derived from a selected ecotoxic endpoint given for a range of soil organisms (usually plants, invertebrates and microbial processes) in ecotoxicity databases, e.g., preferentially EC_{x} (usually EC_{10} is considered) or, when no reliable EC_{x} is available, the highest no observed effect concentration (NOEC, see Table 3) or lowest observed effect concentration (LOEC) (de Vries et al., 2004; Oorts, 2018). Several corrections are further applied to account for the fact that experimental conditions (e.g., freshly spiked soil samples in laboratory conditions rather than from long-term field experiment) and soil types used to derive EC_{x}, NOEC and LOEC do not comprehensively mimic realistic field conditions, or encompass the whole range of soil properties that may govern trace element ecotoxicity.

The EC_x, NOEC, and LOEC are multiplied by a lab-field (L/F) factor varying between 1 for Cd and 4 for Ni at high soil pH and Pb (de Vries et al., 2004; Oorts, 2018). Jensen et al. (2018) further suggested differentiating two L/F factors to account for the specific case of repetitive long-term OW applications. This proposal was based on the assumption that, if trace elements added to a soil over a period of more than a year are highly aged (and consequently less available) relative to freshly spiked soil under laboratory conditions, OW-bound trace elements applied within the ongoing year would be less aged (and thus more available). A second correction is then applied to EC_x, NOEC, and LOEC to account for the specific physico-chemical properties of studied soils. This soil factor is either empirically set at a given value depending on soil type, e.g., 1.1 for sandy soil to 1.5 river clay soils (de Vries et al., 2004), or semi-mechanistically calculated from the effective cation exchange capacity, organic matter concentration, clay concentration, pH, and/or the background concentration determined for each studied soil (Oorts, 2018). The $PNEC_{add}$ value is finally calculated as the value corresponding the xth (usually $x=5$) percentile of the corrected EC_x, NOEC, or LOEC distribution, and therefore corresponds to the so-called hazardous concentration at x% (HC_x).

Based on the mass-balance modeling outputs, the risk-based decision tool for OW management in agriculture and farming activities (FARMERS) was developed to assess trace element impacts on human health (Río et al., 2011) (Fig. 2). The exposure module considers that human beings will mainly be exposed to trace elements via milk and meat consumption, while dermal contact, ingestion, and soil particle inhalation are considered as negligible exposure routes (Franco et al., 2006). The exposure module therefore first calculates the transfer and consequent concentration of trace elements in cattle meat and milk by accounting for the contribution of the ingestion of forage and soil particles from the area receiving OW and the ingestion of water and feed additives that may contain additional trace elements. The calculated concentrations are then used in the risk characterization module to estimate the cancer and non-cancer risks. The non-cancer risk is estimated by calculating the HRI (as defined above) for each exposure route or for the sum of multiple exposure routes and by summing the HRI for each trace element in a global non-cancer risk, i.e., HI (as defined above), whose maximum permissible limit must be provided to run a RA simulation. The cancer-risk is estimated by calculating the TCR (as defined above). Accordingly, FARMERS basically calculates the cancer and non-cancer risks for an OW recycling scenario in a given agricultural area and may highlight human health risks by integrating a geographical information system (GIS). In addition, FARMERS can optimize conversely parameters based on targeted HI and TCR criteria to calculate the maximum permissible concentration of each trace element in soils, or the maximum OW application rate to remain within an acceptable health risk context (Río et al., 2011).

2.5.3 Ecological and human risks of OW-borne organic contaminants

It is not possible to perform comprehensive experiments to assess waste-bound organic compound exposure and hazards due to the high diversity of organic compounds, OW and agricultural conditions (soils, crops). Several RA strategies have been developed to deal with this, ranging from elementary ranking approaches to complex dynamic models.

Screening/ranking approaches aim at assessing the likelihood of organic contaminants posing risks to surface water, groundwater, human health or of accumulating in the food chain following waste application on agricultural soils, while prioritizing compounds of most concern (Clarke et al., 2016; Duarte-Davidson and Jones, 1996; Wilson et al., 1996). These approaches are mainly based on organic compound physicochemical properties, such as water solubility, vapor pressure, Henry constant, octanol-water partition coefficient, adsorption coefficient and degradation half-life, or on empirical (e.g., multi-parameter exponential/logarithmic) models based on these properties (Duarte-Davidson and Jones, 1996; Wilson et al., 1996). A more complex ranking approach was developed by Clarke et al. (2016) from the probabilistic Environmental Potential Risk Indicator for Pesticide indicator of Trevisan et al. (2009) to estimate human exposure to organic contaminants bound in biosolids destined for grassland application. The approach considers four major compartments: concentration in top soil, surface runoff and groundwater, and the chemical intake level (or human exposure). Human health risk is estimated using the intake toxicity ratio, which corresponds to the ratio of the measure of the effects (concentration lethal to 50% of the population, LC_{50}) to the estimated exposure (i.e., concentration in runoff or groundwater). The environmental fate of each contaminant is assessed using parameters such as those described previously (adsorption coefficient, half-life) to estimate the concentration in soil after application, potential subsequent runoff from the OW-treated field into surface water, leaching into groundwater, water consumption and overall toxicity. Beyond the usefulness regarding individual contaminants, the data are used to rank the human health risk of contaminated water consumption (Clarke et al., 2016). Screening is a useful tool for determining the possible fate of organic compounds introduced in the soil system via OW and for prioritizing compounds for experimental validation (Wilson et al., 1996). Other ranking methods not focused on OW could also be used to prioritize organic contaminants, e.g., methods based on quantitative structure-activity relationships (Sangion and Gramatica, 2016). The screening/ranking approach has major limitations as it does not allow quantitative environmental risk assessment of waste-bound organic contaminants. Moreover, since the processes determining their fate are not considered, interactions between contaminants and waste and subsequent modifications in interactions are also not taken into account. Sludge application increases the soil organic matter content and introduces complex components in soils, which change the soil properties. Organic contaminants may adsorb on (organic matter-rich) sludge particulates, and subsequently strongly bind the soil solid phase, thus decreasing the leaching potential, volatilization and/or plant uptake (Duarte-Davidson and Jones, 1996; Wilson et al., 1996). In other cases, some organic materials can enhance organic contaminant leaching by increasing the contaminant infiltration rate through the formation of soluble complexes and/or sorption on colloidal material (Wilson et al., 1996).

The **risk quotient (or hazard quotient) approach**, as recommended by EU-TGD (Section 2.4) and EMEA (Section 2.5.1), is one of the most highly used approaches to assess the environmental risk related to OW-bound organic contaminants after application on soils (Bourdat-Deschamps et al., 2017; Chen et al., 2011; González et al., 2010; Hernando et al., 2006; Kloepper-Sams et al., 1996; Langdon et al., 2010; Liu et al., 2014; Martín et al., 2012; Martin, 2015; Thomaidi et al., 2016). The risk quotient corresponds to the PEC/PNEC ratio (Table 3). In most case studies, risk quotients are calculated for terrestrial risk assessment using measured or calculated (according to EU-TGD) PEC_{soil} values corresponding to the level 1 year after one OW dose application (EC-JRC, 2003; García-Santiago et al., 2016; Verlicchi and Zambello, 2015). Some authors have also assessed the risk for aquatic organisms from PEC_{water} and $PEC_{sediment}$ (Hernando et al., 2006; Langdon et al., 2010). According to EU-TGD, risk assessment in soil is based on short-term toxicity impact data on terrestrial organisms, such as plants, earthworms and/or soil microorganisms. If no terrestrial toxicity data are available, $PNEC_{soil}$ are sometimes determined from $PNEC_{water}$ (González et al., 2010; Martín et al., 2012; Thomaidi et al., 2016). PNEC for the aquatic compartment can be estimated from the half maximal effective concentration (EC_{50}), from LC_{50} values obtained via acute toxicity tests or from NOEC values obtained in the long term (on algae, daphnia and fish), as well as by application of assessment factors to account for extrapolation from intra- and inter-species variability in sensitivity (EC-JRC, 2003; EMEA, 2006). For final risk assessment, a common criterion, as proposed by Sánchez-Bayo et al. (2002) and Hernando et al. (2006), is generally applied: low risk if $0.01 < \text{risk quotient} < 0.1$, medium risk if $0.1 \leq \text{risk quotient} \leq 1$, high risk if risk quotient ≥ 1. To calculate the mixture toxicity risk quotient of several compounds, Thomaidi et al. (2016) chose to sum up their risk quotient according to Escher et al. (2011). This approach is also consistent with the findings of Backhaus and Faust (2012) who obtained evidence that concentration addition is a precautious first tier mixture risk assessment model, and that summing up PEC/PNEC ratios might serve as a justifiable concentration addition approximation. The risk quotient approach should only be seen as a preliminary way to estimate the ecological threat for terrestrial and/or aquatic organisms. A number of uncertainty sources is often included, such as the use of aquatic toxicity due to the lack of terrestrial experimental toxicity data for most organic compounds. In addition, most risk quotients are calculated from PNEC determined from acute data rather than from long-term exposure data (e.g., chronic toxicity tests or bioaccumulation studies) (Bourdat-Deschamps et al., 2017; Hernando et al., 2006; Martín et al., 2015). Finally, as degradation patterns observed for OW-borne organic compounds may differ from those that are spiked in soils, it may be misleading to use these degradation rates at this hazard assessment level (Langdon et al., 2010). Note, however, that risk quotient values are likely to be overestimates of the actual risk due to conservative assumptions used throughout the assessment process (i.e., PEC calculation is based on the maximum organic compound concentration in OW without taking sorption, degradation, etc., into account).

Various **other basic approaches** have been proposed. For instance, to assess whether PAH in textile dyeing sludge would have adverse biological effects, Ning et al. (2014) compared measured PAH concentrations in sludge to the effects range-low (ERL) and effects range-median (ERM) values, as developed by Long et al. (1995). ERL and ERM define the chemical concentration ranges that will rarely (<ERL), occasionally (>ERL and <ERM) and frequently (>ERM) have adverse biological effects. ERL is defined as the lower 10th percentile of the effects data range per chemical, while ERM is the 50th percentile of the effects data range (Long et al., 1995). Since ERL and ERM values based on sediment quality assessments may overestimate or underestimate the risk, Ning et al. (2014) also compared PAH concentrations to ecological soil screening levels (USEPA, 2007). These are contaminant concentrations in soil that are protective of ecological receptors that commonly come in contact with and/or consume biota that live in or on soil. Ecological soil screening levels are derived separately for four groups of ecological receptors: plants, soil invertebrates, birds and mammals. Chaney et al. (1996) used the pathway risk assessment approach to assess risks related to PCB in municipal sewage sludge applied on soil. Risk assessment was conducted to protect highly exposed individuals who use biosolid products on their lawns, gardens or farms, and who ingest foods produced on biosolid-amended soils as a high portion of their diet over a 70-year period of their lives. Several scenarios of exposure to PCB through biosolids, such as "biosolids to human," "biosolids to soil to animal to human," and "biosolids to soil to plant to animal to human" were defined and studied. Several parameters were calculated for each scenario, such as the allowed daily ingestion or the reference soil concentration that cannot be exceeded at the selected risk level. It should be underlined that the highly exposed individuals approach is very conservative because it considers that humans (adults or children) are continuously exposed to the same amount of biosolid-bound PCB (Chaney et al., 1996). Chari and Halden (2012) developed an empirical equation to estimate the aqueous-phase concentration of hydrophobic organic contaminants that could leach from biosolids and potentially reach groundwater and/or surface water. The equation estimates the pore-water concentration of a compound at equilibrium in the solid and liquid phases (Langdon et al., 2010). Pore-water concentrations indicate the migration potential of compounds applied on soils through biosolids (Chari and Halden, 2012). The pore-water concentrations are then compared to aquatic toxicity values for risk assessment. Note that the mass fraction of compounds present in pore water is very small compared to the amount of chemical sorbed onto particles, and that equilibrium concentrations in pore water will be substantially diluted during rainfall events thereby lowering the risk of harmful exposure (Chari and Halden, 2012; ECHA, 2016). Hazard assessment based on equilibrium pore-water concentrations should therefore be interpreted as a worst-case scenario. Brambilla et al. (2016) evaluated the potential carryover of persistent organic contaminants from amended soil-to-milk of extensive farmed sheep. The prediction model was based on farming practices, soil intake, organic pollutant toxicokinetics and dairy product intake in children. The PEC in topsoil relevant for intake assessment in exposed animals was based on the "agronomic evaluation" of fate and behavior of the considered persistent organic contaminants in soil in the treated area. Inputs of the considered contaminants from OW in topsoil were thus estimated by accounting for the median organic carbon content of agricultural topsoils and the annual maximum inputs of organic carbon from waste application. The annual progressive input of persistent organic contaminants from waste was then computed by dividing the level of waste contamination descriptors with various computed timeframes for the different fertilizer typologies. This was based on the following assumption: levels of considered hydrophobic contaminants in soil were correlated with the organic carbon content, while taking into account inputs from sources other than biosolids and losses due to degradation. The impact of predicted environmental concentration in topsoil on food safety/security was computed using a consolidated physiological toxicokinetics model based on the soil uptake of the considered contaminants, their oral bioavailability, distribution, metabolism and excretion rate in sheep milk. In line with the screening/ranking and risk quotient approaches, the simple approaches described above do not account for the various processes involved in the fate and impacts of organic compounds in OW applied on soils such as interactions between compounds and waste.

In the REACH context, risk assessment distinguishes between releases before and after a biological sewage treatment plant. Releases "before" are those from the use-process as such, with or without specific measures to prevent losses and/or to treat emissions onsite. Biological treatment—i.e., biodegradation and associated mechanisms that remove substances from the waterway (adsorption and sedimentation, volatilization, etc.)—is modeled by static and dynamic models such as SimpleTreat (Kah and Brown, 2011; Struijs, 2014; Struijs et al., 2016), WWTREAT (Cowan et al., 1993), Water9 (USEPA, 1994), TOXCHEM (Melcer et al., 1994), or activated sludge models such as WEST (Plósz et al., 2012). Various reviews have been published on contaminant fate models in wastewater treatment plants, describing their dynamicity and listing the pollutant families modeled (Clouzot et al., 2013; Plósz et al., 2013; Pomiès et al., 2013). The outputs of these models are concentrations/fluxes discharged into water which are then used by EUSES for impact assessment at local and regional scales based on mechanistic models (ECHA, 2016). At both scales, the exposure calculation covers soil, air, groundwater, fresh and marine water and sediment, secondary poisoning (fish-eating and worm-eating predators) and humans via the environment (through food consumption, e.g., fish, crops, meat and milk, and drinking water [oral route], and via the inhalation of air [inhalation route]). Once the expected exposure is estimated, exposure levels are used to characterize the risks by comparing them with the hazard assessment outcome. Quantitative risk characterization can involve comparing the exposure concentration in each compartment with the relevant PNEC (so-called risk characterization ratios) (ECHA, 2016). This approach is similar to the risk quotient approach, but the PEC calculation is based on a more complex method. To assess exposure following the release of pesticide co-formulants into agricultural soil and into edge of field water bodies via spray drift and runoff/drainage, the European Crop Protection Association Local Environment Tool (ECPA LET[i]) can be used instead of EUSES, since the latter is not able to take direct and indirect releases into edge of field water bodies into account. While widely used, EUSES has the following limits: it does not cover substances such as ionizing chemicals, trace elements, nanomaterials or substances which undergo transformation within the environment, and it only takes direct releases into soil at the local scale into account. New release mechanisms should therefore be included into the model, while the fate and transport mechanisms such as bioaccumulation in fish and secondary poisoning, human exposure via the environment need to be updated (ECHA, 2016). Exposure dynamic models such as SimpleTreat 3.1 (Legind et al., 2011) do not take any organic compound transformation in plants into account (Polesel et al., 2015). These models, while very useful for preliminary risk assessment, do not consider OW and organic compound interactions or compound degradation products.

2.5.4 *Ecological and human risks of OW-borne pathogens and antibiotic resistance*

Risk assessments include the following four basic steps: hazard identification, exposure assessment, dose-response assessment, and risk characterization (National Research Council, 1983). The **quantitative microbial risk assessment** (QMRA) approach has been added to the risk analysis process (Havelaar et al., 2008): it contains the last four basic steps (illustrated in Fig. 3), as well as risk management and risk communication (National Research Council, 2009). QMRA combines information, data and mathematical models to describe the exposure to and spread of pathogens and to illustrate the nature of the adverse outcomes. A description of the different types of models used in QMRA that are applied to water safety management is available in (WHO, 2016). Large datasets and information are thus needed

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[i] ECPA LET (http://www.ecpa.eu/industry-resources/reach-registration-evaluation-authorisation-and-restriction-chemicals)

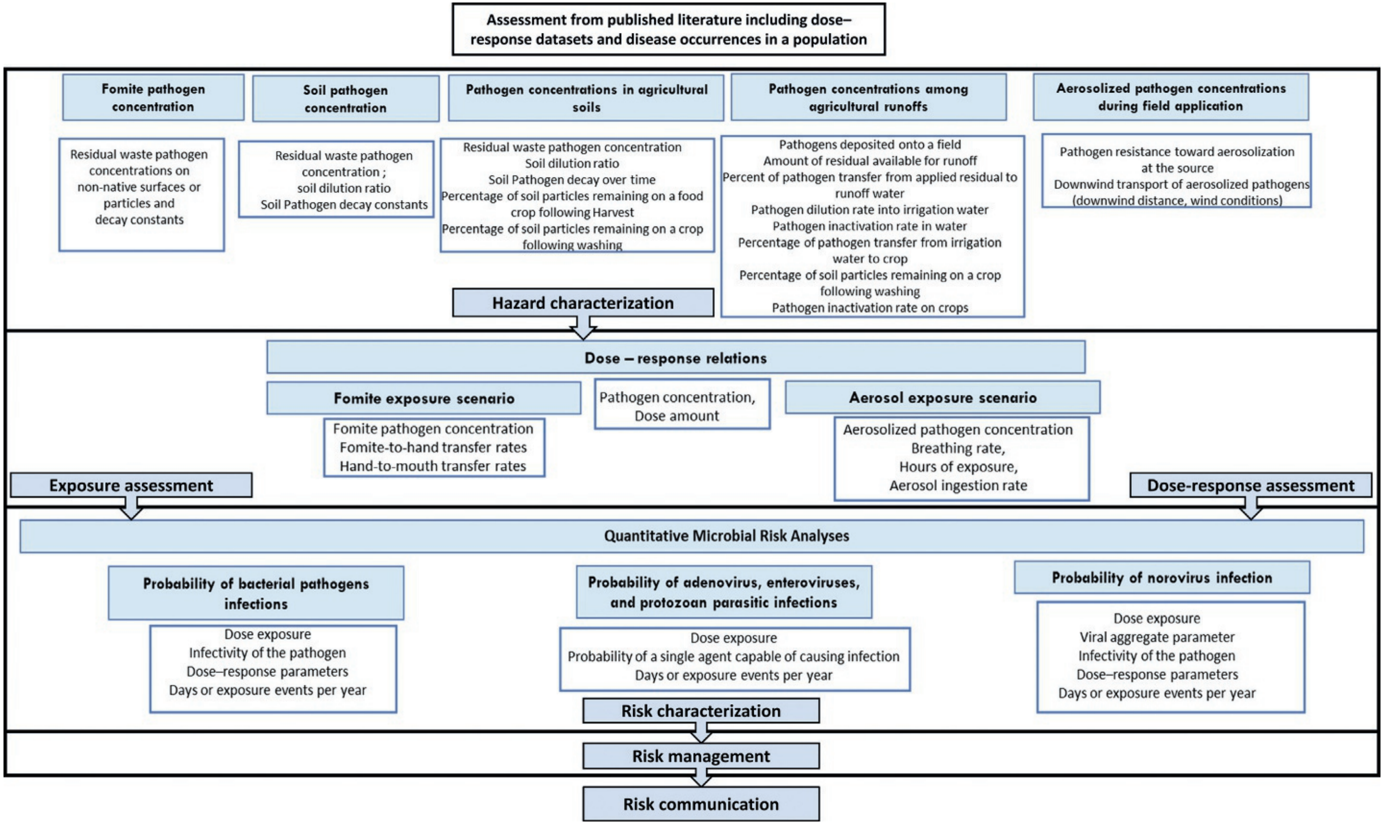
Assessment from published literature including dose–response datasets and disease occurrences in a population
Fomite pathogen concentration
Soil pathogen concentration
Pathogen concentrations in agricultural soils
Pathogen concentrations among agricultural runoffs
Aerosolized pathogen concentrations during field application
Residual waste pathogen concentrations on non-native surfaces or particles and decay constants
Residual waste pathogen concentration ; soil dilution ratio Soil Pathogen decay constants
Residual waste pathogen concentration
Soil dilution ratio
Soil Pathogen decay over time
Percentage of soil particles remaining on a food crop following Harvest
Percentage of soil particles remaining on a crop following washing
Pathogens deposited onto a field
Amount of residual available for runoff
Percent of pathogen transfer from applied residual to runoff water
Pathogen dilution rate into irrigation water
Pathogen inactivation rate in water
Percentage of pathogen transfer from irrigation water to crop
Percentage of soil particles remaining on a crop following washing
Pathogen inactivation rate on crops
Pathogen resistance toward aerosolization at the source
Downwind transport of aerosolized pathogens (downwind distance, wind conditions)
Hazard characterization
Dose – response relations
Fomite exposure scenario
Pathogen concentration, Dose amount
Aerosol exposure scenario
Fomite pathogen concentration
Fomite-to-hand transfer rates
Hand-to-mouth transfer rates
Aerosolized pathogen concentration
Breathing rate,
Hours of exposure,
Aerosol ingestion rate
Exposure assessment
Dose-response assessment
Quantitative Microbial Risk Analyses
Probability of bacterial pathogens infections
Probability of adenovirus, enteroviruses, and protozoan parasitic infections
Probability of norovirus infection
Dose exposure
Infectivity of the pathogen
Dose–response parameters
Days or exposure events per year
Dose exposure
Probability of a single agent capable of causing infection
Days or exposure events per year
Dose exposure
Viral aggregate parameter
Infectivity of the pathogen
Dose–response parameters
Days or exposure events per year
Risk characterization
Risk management
Risk communication

Fig. 3 Schematic depiction of quantitative microbial risk assessment (QMRA) processes associated with each parameter or step in the land application of residual waste (manure and Class B biosolids). Exposure process during scenarios involving fomite, soil, crop, and aerosol exposure are included.

to calculate the microbiological risk, by defining the pathogen-specific dose-response assessment, which requires fitting of a dose-response model (e.g., exponential, Beta-Poisson) (Rose et al., 2008). The infective dose, taking all potential exposure routes into account, must also be calculated based on the quantity of medium involved in the exposure and the associated pathogen concentration (Soller and Olivieri, 2003). QMRA relies on important inputs such as pathogen loads, decay rates, transport, inactivation, as well as on dose response parameters (Brooks et al., 2012; Haas et al., 2014). A typical example of the QMRA model output is the probability of infection or illness associated with the application of OW treatment end-products on agricultural soils. Pathogen fates following raw sludge, digested sewage sludge and manure applications on agricultural soils have been assessed by QMRA (Brooks et al., 2012). Infectious risks by pathogen groups confirmed the greater bacterial risk from manure, whereas viral risks were exclusive to biosolids. The greatest single risk in various pathogen exposure scenarios involving fomite (e.g., truck or tractor handles), soil, crop or aerosol exposure was found to be associated with *C. jejuni* and enteric viruses. Fig. 3 depicts the QMRA processes associated with each parameter or step regarding land application of residual waste.

Current microbial RA models need to be fitted with high quality datasets. Furthermore, their use should be associated with uncertainty values reflecting the dataset quality per simulation or investigation according to the *Codex Alimentarius* (FAO-WHO, 2014) or other guidelines (e.g., FAO-WHO, 2003; Vose, 2008). QMRA is limited by the pathogen-specific dose-response data quality, thereby calling for appropriate treatment of QMRA output uncertainty (Beaudequin et al., 2015). Westrell et al. (2004) proposed the first published hazard analysis and critical control points (HACCP,[j] see Section 3.4.1) approach for the anaerobic digestion process (no HACCP/QMRA composting frameworks were found in the literature). As a first step, exposure scenarios were defined by Westrell et al. (2004), and ranked in order of severity. These scenarios were based on standard operating conditions. As pathogen die-off is hard to assess during the process, pathogen concentrations were considered to not have changed from those measured in the initial waste. Inhalation exposure was considered to be the most hazardous. The ingestion exposure frequency was also estimated.

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[j] According with the FAO/WHO Codex Alimentarius (http://www.fao.org/3/y1579e/y1579e03.htm), HACCP is “a system which identifies, evaluates, and controls hazards which are significant for food safety”.

Workers at the digestion plant were considered the most likely to ingest particles (1–5 g/year), followed by those involved with the spreading of the digestates as fertilizer. The consumption of raw vegetables grown on digestate-amended soils was shown to have a low pathogen exposure risk, but could lead to some infections. A major difficulty with this first HACCP proposal was the great diversity (parasites, bacteria and viruses) and variations in numbers of pathogens in the OW. Specifying the microbial pathogens that could occur in such OW is thus a key yet hard to determine factor. However, their presence appears to be highly stochastic. This is likely because of the overall lack of knowledge on the origin and nature of OW involved in such processes. Nevertheless, this first scheme suggested that gastrointestinal viruses represented the highest risk. According to this study, all workers taking part in OW handling would be exposed to these viruses, and could thereby regularly suffer from a related infection. However, these workers did not seem to have used suitable recommended protection materials to reduce exposure risks. This specific situation is not representative of actual practices. Entero-hemorragic *E. coli* was found to be the second most likely pathogen that could infect these "unprotected" workers. This first HACCP framework for OW treatment identified major critical points that would need to be considered in any HACCP framework. In anaerobic digestion, pathogen inactivation is directly dependent on the four main transformation steps, which drastically modify the physicochemical conditions in the digester. A major critical HACCP to be assessed would thus be the proper functioning of each microbial functional group. Any deviation in these groups and in their synergistic functioning could result in failure of the digestion process, and would constitute a strong warning of the risk of production of hygienically inadequate treatment products. Another key critical point is the duration of the digestion processes. A mesophilic anaerobic digestion process must run at a temperature of 34–42 °C for at least 50 days, while a thermophilic process has to run at 50–65 °C for at least 30 days (JORF, 2017). pH is also a major critical point and must be between 7 and 8.5 to ensure proper functioning of the digestion process. Regarding the composting process, critical HACPP is the number of days (which should be >6 according the requirements in most countries [e.g., Hogg, 2002]) at a minimum temperature of 65 °C. Furthermore, as the level of pathogenic bacteria remaining at the end of the composting process is dependent on the pH value (should be >8), this critical parameter should be monitored.

No models for biological contaminants have been developed so far to assess the impact of OW recycling on human health. However, as mentioned by Ashbolt et al. (2013), "environmentally derived antibiotic-resistant bacteria may adversely affect human health (e.g., reduced efficacy in clinical antibiotic use, more serious or prolonged infection) either by direct exposure of patients to antibiotic-resistant pathogen(s) or by exposure of patients to resistance determinants and subsequent horizontal gene transfer [...] to bacterial pathogen(s) on or within a human host." A quantitative model would need to be developed to assess the risk of transmission of resistance to humans (i.e., infection by antibiotic-resistant bacteria/pathogens). The overall risk for ARB and ARG can be estimated through outputs resulting from the combination and integration of all **microbiological risk analysis** (MRA) steps, namely hazard identification, hazard characterization and exposure assessment, based on the WHO framework used for food safety purposes (WHO, 2010), which is not commonly used in RA. This MRA approach for assessing the risk of antibiotic resistance transmission from the environment to humans has been well described by Manaia (2017). MRA applications performed to estimate the adverse health effects of resistant fecal bacteria on human populations exposed to recreational waters (Limayem and Martin, 2014) or of resistant *E. coli* in lettuce attributable to irrigation water and gene transfer (Njage and Buys, 2017) are exemplary examples.

Quantitative risk assessment (QRA) of antibiotic resistance associated with the application of OW treatment end-products on agricultural soils could require: (i) determination of the level and dynamics of prioritized ARG in the raw OW, in treated OW and then in soil after treated OW spreading, (ii) assessment of flows of these ARG between ARG-bearing non-pathogenic species to pathogens and the extent of occurrence in the various environmental compartments, and iii) determination of the extent to which abiotic and biotic parameters control horizontal gene transfer of these ARG and/or the selection and growth of ARG-bearing pathogens. Antibiotic resistance may be measured within an environmental matrix by detecting and quantifying ARB and/or ARG using culture-dependent and -independent methods. The former rely on bacterial extraction on selective (i.e., single or multiple antibiotic addition) or non-selective media, with or without further species and ARG identification. The latter involve total DNA extraction from the environmental sample and quantitative polymerase chain reaction (PCR) targeting ARG, or metagenomic analysis. The culture-independent approach is being used to an increasing extent as it is less time consuming and provides a broader view of ARG diversity. Single-genome and metagenome analysis have revealed the tremendous amount and diversity of ARG and their widespread distribution across bacterial phyla and environments, including OW, treated products and soil. Changes in ARG abundance over time have been studied using quantitative PCR targeting a small fraction of ARG related to specific antibiotic families (i.e., frequently *sul*, *tet*, *bla* and *erm* associated with resistance to sulfamide, tetracycline, beta-lactam and macrolide, respectively), or hundreds of antibiotic families using high-throughput qPCR. These approaches might, however, overestimate antibiotic resistance as bacterial hosts might carry an ARG without having a resistant phenotype as expression is a matter of host and gene location on the genome. Furthermore, it is likely that not all ARG are equivalent regarding risks to human health. A classification could be based: (i) on those conferring resistance to last resort antibiotics and/or highly virulent pathogens, and (ii) those easily transferable and/or associated and frequently co-transferred with high ARG counts (Martínez et al., 2015; Oh et al., 2018). Zhang et al. (2019) recently used an empirical approach to categorize the risk of ARG to human health based on three factors, namely anthropogenic enrichment, mobility and host pathogenicity. They ranked 4050 known ARG in four categories and prioritized 3% (i.e., 132) of them in Rank I (the most at risk of dissemination among pathogens) and 0.3% in Rank II (high potential emergence of new resistance in pathogens). The authors observed that "Rank I was strongly correlated with the potential exposure of clinical antibiotics, while Rank II was associated with industrialized lifestyles."

3. Gaps in environmental assessment methods and empirical knowledge regarding contaminants in organic waste treatment and agricultural recycling

3.1 Empirical knowledge on contaminants in organic waste

A major limitation in the environmental assessment of contaminants is that the development of assessment methods lags behind advances in knowledge in analytical research fields. The effects of contaminant **speciation** have not yet been accounted for in assessment methods. For instance, Schaubroeck et al. (2015) investigated the impacts of sludge-borne trace elements during agricultural recycling via USEtox and USES-LCA. By assuming that trace elements are exclusively present in ionic form, the authors estimated a highly theoretical human toxicity effect. Recent empirical research reported findings on a wide range of effects of agricultural reuse of digestate and compost.

As typical examples, Hargreaves et al. (2008) performed an analysis on the findings of 30 case studies on municipal solid waste composting, while Brändli et al. (2007) characterized a high variety of organic contaminants in compost and digestate. Both studies overlooked the dynamics of these pollutants after soil applications. Du and Liu (2012) highlighted the potential ecological risks and public health threats of antibiotic pollution in soil–vegetable systems, and reviewed research on the fate and ecological risks of antibiotics. Empirical research has been focused especially on the following issues: changes in soil physical and biological properties, and trace element and persistent organic contaminant loading (Hargreaves et al., 2008); contaminant biodegradation and bioavailability (Smith, 2009a,b); pathogen risks of manure and biosolids (Brooks et al., 2012); characteristics and risks of biosolid use (Uggetti et al., 2012); accumulation and risk of pharmaceuticals and PPCP (Chen et al., 2014); and ecotoxicological impacts (Pivato et al., 2015). A substantial corpus of knowledge has thereby been collected to date, even concerning pollutants that are emerging like pharmaceuticals, notably present in urban sewage sludge (Mailler et al., 2014). A recent review of experimental results (Insam et al., 2015) discusses the effects of the digestion process on digestate properties. It provides an exhaustive overview of existing findings concerning all digestate-borne substances and the pathways through which soil fertility might be affected following digested OW spreading as compared to raw OW. The authors do not provide clear evidence on the fate and risk of contaminants, although they suggest that a reduction in trace element solubility and availability upon digestion would affect the subsequent fate of these compounds. The review also demonstrates the disparity of knowledge available on various compounds, as well as the difficulty of drawing general conclusions in the absence, in many cases, of a sound understanding of the mechanisms involved. The review concluded that, in comparison to raw OW, the pros of recycling digestate outweigh the cons. Nkoa (2014) stresses the importance of the application conditions and timing, non-respect of which could induce various types of hazard. Surprisingly, this review overlooks organic contaminants. Bonetta et al. (2014) performed an exhaustive experimental study, but again surprisingly overlooked organic contaminants and, moreover, their experimental setup did not account for contaminant mobility in soil beyond plant uptake. Teglia et al. (2011a,b) found that post-treatment of digestate with composting would reduce risks and largely enhance the agronomic value of feedstock compared to conventional composting. Table 5 lists some of the most representative reviews of empirical

Table 5 Recent reviews of empirical research-based knowledge on the fate of contaminants contained in organic waste following soil application

Publication (reviewed studies)	Waste streams and treatments	Nutrients, contaminants and impacts considered	Main findings and recommendations
Bondarczuk et al. (2016): dozens	Sewage sludge	Antibiotics, antibiotic-resistant bacteria and antibiotic resistance genes Links: trace elements–pathogens, via maintenance of antibiotic resistance, organic contaminants—pathogens, via antibiotics	• There is increased pharmaceutical pollution in the environment • Significant correlations have been observed between the presence of trace elements and antibiotics in sludge • Spreading contributes to the dissemination and further development of antibiotic resistance • Need for further investigations on human and ecological risk assessment and the fate of antibiotic resistant bacteria and genes
Hargreaves et al. (2008): 30	Biowaste compost	Nutrients, trace elements, persistent organic contaminants	• Safe use in agriculture of municipal solid waste compost depends on the production of good quality compost, specifically, mature and sufficiently low in trace elements and salt content • The best method of reducing the trace element content and improving the quality of this type of compost is early source separation • Further bioavailability research would be warranted
Insam et al. (2015): dozens	Manure, anaerobic digestion	N, P, K, trace elements, organic contaminants, antibiotics, pathogens	• Despite concerns of environmental impacts, odor emissions, and pathogen spreading associated with the production and agricultural recycling of digestate, its use is preferable to that of raw manure, from agricultural and environmental standpoints
Nkoa (2014): dozens	Anaerobic digestates (unspecified)	Environmental impacts (atmospheric, water and soil pollution; chemical and biological)	• Efficacy of digestates as fertilizer lies between that of livestock manure and mineral fertilizers • Digestate has a higher potential than livestock manure regarding ammonia and nitrous oxide emissions, and may contribute to soil contamination by trace elements

research-based knowledge on the fate of contaminants in OW following soil application. These reviews showcase the frontiers in empirical research, including the importance of the condition of contaminants (trace element speciation and organic contaminant metabolites) on their fate. A critical view of the comprehensiveness of contaminant consideration in environmental assessment is presented in the following subsections.s

3.2 Trace elements in LCA and RA: Limits and solutions

Fantke et al. (2018) proposed a harmonized framework for the improvement of ecotoxicity assessment in LCIA. They recognized that trace elements deserved special attention in the light of both the enhanced knowledge on the environmental fate of trace elements and the major impact of trace elements on ecotoxicity results in LCIA. Moreover, the need for a terrestrial ecotoxicity model has been pointed out (Aziz et al., 2018; Fantke et al., 2018). The following aspects of biophysical processes deserve more specific attention: (i) chemical properties of OW, (ii) physicochemical processes that drive trace element availability in soil, and (iii) the ways soil organisms influence trace element bioavailability in soil. The following subsections discuss the relevance of these aspects and propose modeling approaches that could be suitable for their inclusion in LCA and RA.

3.2.1 Chemical properties of organic waste altering trace element availability in soil: trace element speciation in organic waste

As underlined in Section 2.3.2, one approach has already been shown to improve ecotoxicity assessment by accounting for the trace element origin (Owsianiak et al. 2015). For instance, the ACF of trace elements from atmospheric emissions was differentiated from that from organic sources, encompassing a broad range of OW such as biosolids, manure, compost and treated wastewaters. Trace element speciation and availability in all of these OW have so far been viewed as homogeneous in this approach, with trace elements mainly considered to be bound to organic matter. Yet recent research has shown that trace element speciation and availability in OW (which may be related to the ACF) can vary substantially according to the trace elements, OW solid or liquid state and OW treatment.

Two methods are mainly used to study trace elements in OW, namely chemical extraction and X-ray absorption spectroscopy (XAS). Chemical extraction is widely used, as it is inexpensive, easy to apply and highly reproducible (Bacon et al., 2005). Concerns regarding the non-selectivity of reagents (Doelsch et al., 2006, 2008) or readsorption of elements following release are frequently reported (Martin et al., 1987). However, this method is well suited for assessing available and exchangeable fractions of a substantial number of trace elements in various OW (Doelsch et al., 2010). For example, Flyhammar (1998) studied Zn, Cu, Pb, Cr, Ni and Cd in municipal solid waste and sewage sludge and highlighted that the exchangeable fraction (ammonium acetate extraction) accounted for 1–20% of the total trace element concentration. XAS is used to a much lesser extent than chemical extraction as synchrotron beamtime is limited. XAS is nevertheless a powerful tool that enables determination of trace element speciation in complex samples. XAS is notably able to distinguish trace element species such as metal sulfides that otherwise would be overlooked by chemical extraction (Legros et al., 2017). Recent studies highlighted that trace element speciation in OW is trace elements-dependent. For instance, Zn is mainly related to OW inorganic phases (Zn sulfide, amorphous Zn phosphate and Zn sorbed to iron hydroxide), whereas Cu is mainly associated with organic matter (Donner et al., 2011; Legros et al., 2010). But this general pattern is affected by the physicochemical storage conditions (i.e., dry matter and oxidation-reduction potential) and by the OW treatment (i.e., composting, anaerobic digestion). Liquid OW in suboxic to anoxic redox conditions tend to have a majority of reduced trace element species. For example, Zn and Cu occur mainly or entirely as sulfides, with Cu in the form of reduced Cu(I) in swine slurry (Formentini et al., 2017; Legros et al., 2010). Only oxidized trace element species are present in solid OW under oxic redox conditions —Zn phosphate, Zn sorbed to iron hydroxide and Cu(II) complexed to organic matter are the major species in biosolids (Donner et al., 2011). Anaerobic digestion has been found to always favor nanosized Zn sulfide (nano-ZnS) formation (>70% of zinc in digestate) (Le Bars et al., 2018; Legros et al., 2017; Lombi et al., 2012). However, nano-ZnS becomes a minor species (<10% of zinc) after 1–3 months of OW composting. In compost, Zn is consequently mostly present as amorphous Zn phosphate, with Zn sorbed to ferrihydrite (Le Bars et al., 2018; Lombi et al., 2012).

The relationship between trace element speciation in OW and trace element availability in OW-amended soils was further investigated in short- and long-term studies. Tella et al. (2016) studied single ex situ soil application of six OW mainly stabilized under oxic conditions. They put forward the hypothesis that the increased Zn availability measured with the diffusive gradient in thin films (DGT) technique in OW-amended soil could be explained by the desorption of Zn sorbed to iron hydroxide in OW. In a long-term field experiment (22 pig slurry applications), Formentini et al. (2017) observed that ZnS, which had accounted for 100% of Zn speciation in swine slurry, was not detected in the amended soil despite a nearly 2-fold increase in the soil Zn concentration due to swine slurry spreading. Instead, the initial Zn speciation (i.e., Zn bound to kaolinite and Fe oxyhydroxide) in the un-amended soil remained predominant in the amended soil along with organic matter-bound Zn accumulation. The authors hypothesized that the ZnS initially present in the swine slurry was weakly stable under the soil oxic conditions, thereby explaining the radical change in Zn speciation after soil application. This hypothesis was reinforced by a the findings of Le Bars et al. (2018) who demonstrated that OW-borne ZnS was present as nanosized ZnS, which is much less chemically stable than the macroscopic counterparts. Contrary to Zn, Cu speciation in OW was mainly dominated by organic matter-bound Cu (Donner et al. 2011; Tella et al. 2016; Legros et al. 2017). In a study of single ex situ soil application of six OW, Tella et al. (2016) found that the increase in Cu availability measured by DGT in the OW-amended soil was linearly correlated with the mineralization potential of the OW-bound organic carbon. Accordingly, the authors suggested that the release of available Cu in OW-amended soils could be driven by the mineralization of organic matter from OW. Trace element speciation in OW is the main driver controlling the fate of this element in amended soil (Hodomihou et al., 2020). Clearly, trace element speciation must be taken into account to gain an overall understanding of the environmental fate of trace elements. Chemical extraction has already been used in RA and LCA (e.g., Tarpani et al., 2020) but this approach is not well suited for determining trace element speciation in OW, as we discussed above. It would, however, not be feasible to routinely determine trace element speciation in OW via XAS. An alternative option could be to develop a qualitative typology of OW based on basic OW characteristics (e.g., OW nature and treatment) related to physicochemical parameters such as the pH and redox potential which drive trace element speciation in OW. It would also be essential to consider an indicator based on the mineralization potential of OW organic matter in this typology. Considering the broad diversity of OW treatments, the mineralization potential of organic matter over time is very heterogeneous between OW (Thuriès et al. 2002). An indicator of residual organic carbon remaining in amended soils (I_{ROC}) based on some OW biochemical properties and the short-term mineralization of organic carbon has been developed for the main types of OW applied to soils (Bouthier et al., 2009; Lashermes et al., 2009, 2010). This typology could be further used to develop a correcting factor to the availability of trace elements estimated with the generic methodology used for assessing environmental risk.

3.2.2 Soil physicochemical processes driving the trace element fate in soil

OW application on soil induces a net increase in the soil trace element concentration and can lead to trace element export, in soluble form, via water drainage depending of the type of trace elements. Yet this trace element export has a relatively low net impact. Total trace element export by drainage always represents a few percentage of the OW trace element inputs (Cornu et al., 2001; Formentini et al., 2015; Hodomihou et al., 2020; Legros et al., 2013; Lekfeldt et al., 2017; Richards et al., 1998).

3.2.2.1 Colloidal transfer for trace element leaching prediction

Colloidal transfer is suspected to facilitate trace element transport through the soil to groundwater. Colloids are generally characterized by dispersed particles with average diameters of 1 nm to 10 μm. According to Kretzschmar et al. (1999), four key conditions are required for colloid-facilitated contaminant transport to become environmentally significant: (i) mobile colloidal particles must be present in sufficiently high concentrations, (ii) the particles must be transported over long distances through uncontaminated zones of the porous medium, (iii) the contaminants must sorb strongly to the mobile particles and desorb slowly, and (iv) the contaminant must be toxic at low concentration so that even trace concentrations in groundwater cannot be tolerated.

Contaminants that meet the latter two criteria notably include trace elements. For example, nanosized metal oxide (including ferric, manganese, aluminium, titanium, magnesium and cerium oxides) provide high surface area and specific affinity for trace element adsorption (Hua et al., 2012).

Regarding the first criterion, many studies have shown the presence of colloids in soils. For example, clays minerals that make up the colloid fraction of soils, sediments, and water. There is also evidence that colloids are present in OW. For example, nano-ZnS is a major Zn species in raw liquid OW (Kim et al., 2014; Le Bars et al., 2018), and organic colloids have been observed in biosolids (Ghezzi et al., 2014).

Regarding the second criterion, soil colloids can transfer trace elements to groundwater. According to Kretzschmar and Schäfer (2005), under certain conditions, colloid facilitated transport can become the major transport mechanism of strongly sorbing trace elements in soils and aquifers. This was demonstrated for Pb transport in water-saturated soil columns (Grolimund et al., 1996), for Cu, Zn and Pb in biosolid amended soils (Karathanasis et al., 2005), and more recently for Cu, Cr and Pb in a cattle slurry amended soil (Lekfeldt et al., 2017).

In almost all fate modeling approaches for environmental risk assessment, trace element leaching is conceptualized with two compartments—the immobile solid matrix phase and the mobile aqueous solution phase. A third compartment is considered in the conceptual model when colloidal transport is considered (Mccarthy and Zachara, 1989). Mallmann et al. (2017) suggested accounting for colloid-facilitated transport of trace elements, increasing the range of transport processes considered in HYDRUS 1D simulation of Cu and Zn transport in amended soil. However, models that consider such processes, such as the HYDRUS-1D C-Ride module, require many additional parameters, such as those characterizing trace element sorption on colloids, which have to be measured experimentally. Whether colloid facilitated transport of trace elements should be considered in fate modeling and in environmental risk assessment depends on the added value vs additional uncertainty and complexity trade-off.

3.2.2.2 Variability in dissolved organic matter binding properties

The most advanced approaches used to calculate BF in LCA (Sections 2.2.2 and 2.3) and several RA approaches (Section 2.4) estimate soil organism exposure to trace elements through the determination of trace element speciation in soil solution. These approaches all directly or indirectly consider that the binding properties of dissolved organic matter (DOM) to trace elements are a major driver of trace element speciation in solution, in line with the findings of specialists in this field (e.g., Weng et al., 2002). Moreover, between-soil variations in trace element binding to DOM are considered to be solely dependent on the DOM concentration, not the DOM binding properties (i.e., the density of binding sites and their binding affinity towards trace elements). This has led scientists conducting ERA to use geochemical models, e.g., WHAM, with the benchmark fulvic acid binding properties representing those of DOM (e.g., Lofts et al., 2013b; Tipping et al., 2003). Yet research focused on DOM binding properties in the past decade have shown that the binding properties of DOM to trace elements can vary considerably in soil and freshwater (Chen et al., 2018; Li et al., 2017; Weng et al., 2002). This has firstly been attributed to the substantial proportion of DOM corresponding to non-humic substances with binding properties that differ from that of benchmark fulvic acid (Baken et al., 2011; Groenenberg et al., 2010; Ren et al., 2015), and secondly to the variability in DOM properties such as its aromaticity, which seems to partly account for DOM binding properties (Amery et al., 2008; De Schamphelaere and Janssen, 2004). Djae et al. (2017) studied more than 50 soil samples exhibiting very contrasted physicochemical properties and confirmed that WHAM parameterized without accounting for DOM binding property variability skewed the prediction of Cu^{2+} activity in soil solution by up to three orders of magnitude, while also showing that the prediction of Cu toxicity to microbial functions, invertebrates and plants in soils was substantially skewed as well. Laurent et al. (2020) recently studied dozens of field samples of soils that had been amended or not with OW over a decade and showed that adequate WHAM prediction of Cu (but not Zn) speciation in soil solution required DOM binding property optimization. When considering the chemical properties of trace elements, it is thus crucial to account for the variability in the binding properties DOM to trace elements exhibiting a high affinity for organic matter (e.g., Cu and Pb), except with regard to trace elements exhibiting a much lower affinity for organic matter (e.g., Cd, Ni and Zn).

The point is to know how, in practice, to account for DOM binding property variability in RA and LCA approaches. The only recommendation the specialized literature to date is to perform additional analytical determinations. Among these, specific UV-absorbance and fluorescence analysis of soil solution samples seem to be the only analytical determinations strategy that could be routinely applied to a high number of samples while, in addition, revealing some correlations with DOM binding properties that could be optimized in geochemical models (Amery et al., 2008; Baken et al., 2011; Zhang et al., 2020). Although specific UV-absorbance was found to be a better candidate from a practical standpoint and Amery et al. (2008) showed that specific UV-absorbance was a good proxy when assessing a soil receiving a single low OW application, Baken et al. (2011) and Laurent et al. (2020) suggested that specific UV-absorbance would be a much less relevant proxy for DOM binding properties in freshwater and soil receiving high repetitive OW inputs. When developing a method for RA of Pb bioavailability in a lake, Zhang et al. (2020) also underlined the importance of accounting for the variability in the binding properties of DOM to Pb and that fluoresence analysis could be helpful in this respect. These authors thus developed a multilinear regression model based on fluoresence and usual water chemical parameters to predict Pb binding to DOM in the target lake at a regional scale. In the light of this example, we therefore stress the need to develop such regression models to estimate trace element binding to

DOM in soil. These regression models could then be applied in site-specific RA, providing that fluorescence analyses could be done on each specific investigated site. Such analytical determinations would, however, not be feasible in LCA context. A second step would thus be necessary and could, for instance, consist of developing an empirical regression model to predict the fluorescence properties of DOM with conventionally determined soil physicochemical parameters, as previously carried out in LCA to predict DOC concentrations (Owsianiak et al. 2013). Such regression models have yet to be developed and would therefore deserve further attention.

3.2.2.3 Kinetics of soil physicochemical processes

In all RA and LCA approaches, physicochemical processes that drive trace element availability in soil are assumed to occur under equilibrium conditions, and thermodynamic constants are used to determine the solid-solution partitioning and the proportion of each trace element chemical species (Degryse et al., 2009a; Weng et al., 2001). There is, however, a growing body of evidence that when trace elements interact with a soil organism the physicochemical process kinetics can become a major driver of trace element availability in soil (Almås et al., 2004; Bade et al., 2012; Bravin et al., 2010a; Nolan et al., 2005). Although the free trace element species is still considered to be the main (if not sole) trace element species taken up by soil organisms under kinetically-driven conditions, the expected depletion of free trace element activity in solution at the soil-organism interface means that trace element uptake would no longer be driven by the trace element activity. It is instead driven by the ability of soil (i.e., trace elements bound to the solid phase and to ligands in solution) to resupply free trace element species in solution, which depends on the diffusion limitations and dissociation kinetics (Degryse et al., 2012). Accordingly, new soil tests were developed to determine the extent to which soil could resupply trace elements in solution under kinetic limitations. Among these, DGT seems particularly promising (Davison and Zhang, 2012; Degryse et al., 2009b; Zhang and Davison, 2015). Kinetic considerations could therefore be integrated in RA and LCA approaches by developing an empirical regression model to predict DGT measurements with conventionally determined soil physicochemical parameters (Owsianiak et al., 2013). Such empirical regression models have already been designed in specific case studies (Bravin et al., 2010b; Guan et al., 2018), but would now be developed on a broader range of soils. Note that estimation of trace element availability in soil via a tool like

DGT would require modification of the mathematical expression of exposure in RA and LCA approaches. In LCA, for instance, the exposure factor—the ACF × BF product—is currently expressed as the mass ratio of free to total trace elements in soil. Estimating the exposure factor with DGT would lead to expression of the ACF × BF product as the mass ratio of all DGT-available soil-borne trace elements. Consequently, EF should also be expressed as a function of DGT-available trace elements. Ecotoxicological endpoints based on DGT-available trace elements have already been determined, but only for one trace element (i.e., Cu) and one toxic endpoint (i.e., tomato shoot growth) (Zhao et al., 2006). Empirically deriving new ecotoxicological endpoints for a meaningful range of trace elements, soil organisms, soil types and toxic endpoints is a huge tedious task that has already been consistently carried out for numerous ecotoxicological endpoints based on total and free trace element concentrations in soil (Hamels et al., 2014; Lofts et al., 2013a; Thakali et al., 2006b). Toxic endpoints based on DGT-available trace elements could thus be derived from toxic endpoints based on total or free trace element concentrations by using the empirical regression models suggested above to predict DGT measurements from conventionally determined soil physicochemical parameters.

3.2.2.4 Effects of repetitive long-term organic waste applications

Organic waste is usually applied on soils annually over the long-term and seldom only once. Repetitive long-term OW application has three major consequences on trace element availability in soil that have yet to be accounted for in RA and LCA approaches. The first is related to the aging process, which usually tends to decrease trace element availability in soils over time. This aging process is, however, likely counteracted by fresh trace element inputs following each new OW application. Accordingly, Jensen et al. (2018) suggested an RA approach in which the availability of newly added trace elements would be higher in comparison to the availability of trace elements added over a year earlier. This factor should also be incorporated in the LCA approach by deriving an ACF through the integration of individual ACF values calculated at each time step (i.e., each OW application) over the whole LCA time scale (typically infinite). The second consequence is related to the specific pattern of trace element availability in soils contaminated by long-term OW application in comparison to trace element availability in soils contaminated by other trace element sources. Smolders et al. (2012) showed that trace element availability in soils at 22 sites where

OW had been applied on soils for 1–112 years was on average 5.9-fold lower than in the corresponding unamended soils spiked with Cu salt and pH adjusted in the laboratory so as to have a total Cu concentration and pH similar to the levels found in OW-amended soils. Such a protective factor could thus be applied to the Cu availability value calculated in RA and LCA approaches. Although this kind of protective factor has not been derived for any other trace elements, a similar protective effect was observed for Cd by Kukier et al. (2010), who showed that the increase in plant Cd uptake due to Cd spiking under laboratory conditions was lower in soils amended with OW for 20 years than in the corresponding unamended soils with adjusted pH. The derivation of protective factors for a range of trace elements would thus deserve further investigation for potential incorporation in RA and LCA approaches. The third consequence of the repetitive and long-term OW application on soil is the fact that, in addition to trace elements, OW also supplies many other types of organic and inorganic matter. This regular supply of additional materials usually ultimately leads to the modification of some important physicochemical properties in soils, such as pH and the organic matter concentration and binding properties (Nobile et al., 2018; Senesi et al., 2007; Smolders et al., 2012). These soil properties are known to highly influence trace element availability in soils (Degryse et al., 2009a; Sauvé et al., 2000; Weng et al., 2001), so their modification is expected to gradually alter the trace element availability in OW-amended soils over time. Laurent et al. (2020) recently obtained clear evidence of this effect. In three field trials, they showed that the increase in pH and in the DOM concentration, aromaticity, and binding properties induced by OW application over a decade mitigated Cu and Zn availability in amended soils despite a concomitant increase in the soil contamination level. This is consistent with the findings of Alvarenga et al. (2017), who showed that sewage sludge application promoted a significant increase in the plant concentration of Cu, Ni and Zn, which otherwise did not occur in association with compost application. This could be explained by the fact that sewage sludge application induced a decrease in soil pH, which was not observed following compost application. To be able to account for temporal changes in pH and organic matter properties in OW-amended soils in RA and LCA approaches, it would be necessary to be able to predict pH and organic matter patterns over time with routine models. Apart from predicting temporal changes in soil organic matter concentrations, such models have yet to be developed and future research should consequently be focused on overcoming this issue.

3.2.3 *Influence of soil organisms on trace element availability and bioavailability*

Living organisms at risk of soil contamination are not passive trace element samplers, but instead may have a biological effect by substantially altering the soil physicochemical parameters and actively regulating trace element interactions with biological surfaces and by consequence trace element uptake. We identified four aspects for which RA and LCA approaches could better account for this influence of soil organisms on trace element availability in soils and consequently on trace element bioavailability and toxicity to soil organisms.

The most advanced RA and LCA approaches use the biotic ligand model to link trace element speciation in solution to trace element toxic effects on aquatic and soil organisms (Niyogi and Wood, 2004; Thakali et al., 2006a,b). Despite the obvious assets of the biotic ligand model, there is high variability in the binding constant numbers and values thus defined in comparable experiments (Ardestani et al., 2014), thereby questioning whether the biotic ligand model parameterized in this way would be sufficiently generic for operational application in RA and LCA approaches. The recent development of a more complex biotic ligand model formalism for predicting the toxic effects of trace element mixtures has further fuelled the debate on this issue. To deal with this complexity, Tipping and Lofts (2013, 2015) suggested using WHAM to predict not only trace element speciation in solution but also trace element binding and toxicity to aquatic and soil organisms using the humic acid profile defined in the WHAM database as a surrogate of biological surfaces. Coupling the WHAM default parameterization with a toxicity function (F_{TOX}), the WHAM-F_{TOX} approach was found to successfully predict the toxic effect of trace element mixtures for a range of aquatic and soil organisms (Balistrieri and Mebane, 2014; Guigues et al., 2016; He and Van Gestel, 2015; Qiu et al., 2016; Yen Le et al., 2015). This WHAM-F_{TOX} approach therefore seems promising for ecotoxicological assessment in RA and LCA approaches.

Soil organisms are known to interact with the surrounding soil, e.g., the so-called rhizosphere for plants and the drilosphere (bioturbated soil) for earthworms. Plants excrete protons or hydroxyls, thereby changing the rhizosphere pH by up to several orders of magnitude compared to the bulk-soil pH (Hinsinger et al., 2003). Plants also exude a broad range of small molecular weight organic molecules, some of which are able to bind trace elements while the rest are known to increase microbial activity in the rhizosphere (Jones et al., 2009). Such plant-induced changes in the physicochemical and biological properties of the soil are known to alter the trace element availability in the rhizosphere compared to the bulk soil, and consequently the trace element bioavailability and toxicity to plants (Bravin et al., 2012; Michaud et al., 2007; Wenzel et al., 2011). Earthworms have also been found to be able to alter the pH, DOM concentration, microbial populations and consequently the trace element availability in their drilosphere (Sizmur and Hodson, 2009). Ecotoxicological tests are able to account for the effects of the biological response of soil organisms on the soil physicochemical and biological properties, but estimates of soil organism trace element exposure do not. This is because the latter estimates are based on measurements of trace element availability and speciation in bulk soil rather than in the volume of soil impacted by the presence of soil organisms. To the best of our knowledge, no models are available that could be operational in current RA and LCA approaches. Some biotests, such as the RHIZOtest for plants (Bravin et al., 2010b), have nevertheless been developed to specifically account for this influence of soil organisms in the assessment of trace element bioavailability to soil organisms. Such biotests could first be used to assess the extent to which this influence of soil organisms could skew current soil ecotoxicological assessments, before designing a way to use these biotests in RA and LCA approaches.

Conventional ecotoxicology methods to derive ecotoxicological endpoints used in RA and LCA approaches are based on dose-response curves regarding soil organism exposure to single trace elements or mixtures. In these experimental procedures, only the trace element exposure level is expected to change. This context differs markedly from that of soil organism exposure to OW-amended soils, as OW brings a mixture of organic and inorganic contaminants but also alters the soil physicochemical environment overall (see above). Some statistically significant relationships may be noted between some soil parameters and the measured toxic effect when soil organisms are exposed to increasing OW application rates, but it is very difficult to identify the soil parameters to which the measured toxic effect could be mechanistically related. It would therefore be highly challenging to design mechanistic models able to predict the toxicity of given trace elements to organisms in OW-amended soils. This issue could first be addressed by no longer relating the measured toxic effect to the trace element availability (or that of any other soil contaminant), but rather more empirically relating it to the soil OW application rate. Application of this strategy in RA and LCIA has been supported by the findings of Pandard and Römbke (2013), Huguier et al. (2015), Pivato et al. (2015) and Renaud et al. (2019).

This issue could alternatively be addressed by relating trace element exposure to trace element bioaccumulation in soil organisms, since this bioaccumulation is considered as a prerequisite for any toxic effect. Such biotests are already being used to assess trace element bioaccumulation in plants and soil macroorganisms such as earthworms (Beaumelle et al., 2016; Bravin et al., 2010b). For microorganisms, quantitative measurement of trace element-resistant genes is currently a promising approach for relating biological responses to the exposure to specific soilborne trace elements (Miranda et al., 2018; Roosa et al., 2014). The potential benefits of such biotests should be first assessed in the specific context of OW-amended soils before being proposed as new ecotoxicological endpoints in RA and LCA approaches.

Among the range of trace elements added to soil by OW application, some trace elements (i.e., B, Cu, Mo, Ni, and Zn) can have a beneficial effect on soil organisms by serving as micronutrients at a low concentration before generating eventually a toxic effect at a higher concentration. This beneficial effect of trace elements has yet to be accounted for in RA and LCA approaches. The UNEP-SETAC Ecotoxicity Task Force addressed this issue and decided for the moment not to consider such beneficial effects in ecotoxicity characterization in the USEtox framework (Fantke et al., 2018), but suggested that future research should focus on this issue.

3.3 Organic contaminants in LCA and RA: Limits and solutions

As for trace elements, the fate of OW-borne organic contaminants highly depends on the OW composition and speciation, as well as on the nature of contaminant binding in soils upon which OW is applied. The nature of this binding will affect: the persistence of soilborne contaminants, their mobility from amended soil into water and their bioavailability to plants and animals. In contrast to trace elements, organic contaminants are degradable but the possibility of degradation is very variable. Their biotic or abiotic breakdown entails the transformation of known parent molecules into sometimes unknown, and often scarcely studied, transformation products. Certain categories of organic contaminants, moreover, form strong bonds with organic particles in OW or in the soil, giving rise to "bound residues" (non-extractable residues) which cannot be quantified by the chemical extraction methods used to measure contaminant levels. Total organic contaminant levels in OW are consequently not always known. Organic pollutants are often divided into two major groups according to their apparent half-life in soil: (1) persistent contaminants (apparent half-lives ranging from one to several years: PCB, PAH, dioxins, flame-retardants, etc.) and (2) non-persistent contaminants, whose dissipation is more rapid (half-lives ranging from a few days to a few months: phthalates, bisphenol A, detergents, etc.). This distinction is usually accounted for in a first approach through dissipation half-life time parameters but also involves the consideration of non-extractable residue formation in process-based models describing the fate of organic contaminants.

Improvements to existing RA approaches, although being limited by empirical data collection costs, is possible through a combination of different modeling approaches. In silico approaches based on QSAR knowledge can be used to classify organic contaminants according to their potential behavior and effects. For instance, TyPol (typology of pollutants) is a suitable classification method (Servien et al., 2014). It is based on statistical analyses combining several environmental (i.e., sorption coefficient, degradation half-life, Henry constant) and ecotoxicological (i.e., bioconcentration factor, EC_{50}, NOEC) parameters, as well as structural molecular descriptors (i.e., number of atoms in the molecule, molecular surface, dipole moment, energy of orbitals). Molecular descriptors are calculated using an in silico approach. Environmental and ecotoxicological parameters are extracted from available databases and the literature (Servien et al., 2014). TyPol has so far mainly focused on pesticides and few transformation products. Recent improvements in TyPol have addressed the implementation of pesticide ecotoxicological endpoints (Traoré et al., 2018), prediction of the environmental fate of putative or recently detected transformation products (Benoit et al., 2017; Storck et al., 2016), and the expansion of the database to encompass pharmaceuticals and personal care products and some of their transformation products. This approach is generic but not sufficient for RA since it cannot account for the environmental specificity (pedoclimatic conditions, OW characteristics and agricultural practices), or for the organic contaminant concentrations, forms and bioavailability. However, the method may initially help rank organic contaminants in different clusters, each with relatively similar behavior or impact. Therefore, it could help select representative molecules from each cluster so as to be able to conduct more comprehensive studies based on analytical studies or biophysical modeling, as described below.

3.3.1 Interactions between organic matter and contaminants

To the best of our knowledge, few models have been developed to assess the fate of organic contaminants during applied OW decomposition in soil, despite the recently demonstrated importance of soil organic matter for soil microbiota that degrade organic contaminants (Neumann et al., 2014). The COP-Soil model describes the fate of organic contaminants during compost decomposition in soil (i.e., mineralization, adsorption/desorption, and formation/remobilization of non-extractable residues) combined with the organic carbon dynamics (Geng et al., 2015). The model uses one module for organic matter and one for organic contaminants, both of which are linked by several common assumptions. The organic C module is based on that proposed by Zhang et al. (2012) which describes organic matter transformation during composting and is adapted to the soil environment. Organic C in compost is divided into several pools: available organic carbon, soluble in neutral detergent, hemicellulose-like, cellulose-like and lignin-like. The organic contaminant module is inspired by the COP-Compost model that was developed to simulate the coevolution of organic contaminants and organic matter during composting (Lashermes et al., 2013), and is based on the same four pools and the same equations. Organic contaminants are distributed among mineralized, water-soluble, adsorbed and non-extractable residue fractions. The model was tested against experimental data and its performance was found to be acceptable (Geng et al., 2015). The model does not consider organic contaminant volatilization because it is assumed that this mainly occurs earlier in the process. Finally, the model does not consider the formation of degradation products nor include leaching or runoff processes. Brimo et al. (2018b) modified the approach of Geng et al. (2015) to model the fate of compost-bound PAH in amended soil. Goulas (2006) used the same model to simulate the fate of sulfonamide antibiotics in soil amended by manure and by sewage sludge compost. The model consists of three modules: (1) a biodegradation/adsorption module, where adsorption is based on a bi-phasic first-order kinetic model and where PAH biodegradation can produce CO_2, metabolites and non-extractible residues (the influence of the temperature and water content on biological processes are also taken into account (Brimo et al., 2016)), (2) an organic carbon module which describes organic matter transformation during composting and compost decomposition in soil (Geng et al., 2015; Lashermes et al., 2013), and (3) a PAH release module which describes the release of compost-bound PAH during the decomposition of compost applied to the soil. The model assumes that PAH is distributed among the organic carbon fractions proportionally to the relative mass of each fraction. One fraction of PAH is taken up in the soil solution, the other is strongly sorbed on the surface of the soil-compost mixture. Following calibration of some parameters, the model gave acceptable predictions of PAH transformation in soils. The most significant features of this model are that it considers the organic matter characteristics of the applied compost, the production of non-extractable residues and the biodegradation route (Brimo et al., 2018b). The model was then mainstreamed in the Virtual Soil Platform (Lafolie et al., 2014) to predict the long-term fate of phenanthren. The performance of the model was tested against field data and found to be acceptable. The model was further used to test different long-term climate change or increased PAH bioavailability scenarios (Brimo et al., 2018a). This model could hence be a useful tool to test various organic contaminants/OW soil application scenarios. In the future, a module incorporating plant functions and compost fertilization will be mainstreamed in the Virtual Soil Platform (Brimo et al., 2018a).

Using the same Virtual Soil Platform, biogeochemical processes occurring during organic contaminant and dissolved organic matter transport in deep soil horizons were included in another model (PolDOC) for the purpose of assessing agricultural soils receiving urban waste compost as organic amendments (Chabauty, 2015). In the PolDOC model, two types of dissolved organic matter have been considered: native dissolved organic matter present in the illuviated[k] horizon and dissolved organic matter percolating from the surface horizon. The model considers associations between percolating dissolved organic matter and organic contaminants such as pesticides and pharmaceuticals (ibuprofen and sulfamethoxazole) and can simulate reductions in pollutant transport through cosorption processes (Totsche et al., 1997) or accelerations in pollutant transport through cotransport processes (Keren and Communar, 2009).

3.3.2 Extending and complementing hazard and exposure models used in LCA and RA

3.3.2.1 Plant and animal uptake models

A major public concern regarding agricultural application of treated wastewater and biosolids is the plant uptake of OW-bound contaminants because it may pose potential human health risks (Christou et al., 2017; Prosser and Sibley, 2015; Wu et al., 2015).

The Biosolids-Amended Soil: Level 4 (BASL4) model calculates the fate of chemicals entering soil in association with contaminated biosolid amendment (Hughes et al., 2005; Hughes and Mackay, 2011). The model simulates the fate of organic chemicals present in biosolids applied to a two-layer soil and addresses the processes of chemical degradation, volatilization, leaching, diffusion and sorption to decaying organic matter (fast- and slow-degrading organic matter). Uptake in invertebrates (worms), small mammals (shrews) and vegetation is simulated according to three complexity levels, namely simple equilibrium partitioning, steady state bioaccumulation and dynamic bioaccumulation. For simple equilibrium partitioning, biota are assumed to achieve the same fugacity as the soil (the assumption is that the plant roots and foliage achieve equilibrium with the soil pore water at all times). For steady state bioaccumulation, the mechanistic bioaccumulation model includes the possible effects of concentration increases by biomagnification and concentration decreases by metabolic conversion, reproductive loss and growth dilution. For dynamic bioaccumulation, a dynamic mechanistic model simulates the time course of uptake and clearance. Amendment is considered as 100% (dry) organic matter, and the chemical and organic matter masses are directly increased upon the addition of chemical or biosolid amendments. The soil properties and chemical distributions between phases are then adjusted accordingly. The increase in the soil water retention capacity with increased organic matter is ignored. Layer depths change because of changes in the quantity of organic matter present, but these changes are considered sufficiently small that diffusion distances remain constant. Leaching and diffusion rates thus remain unchanged throughout the simulation. The model does not simulate runoff. Concentrations in edible tissue predicted by the model can then be used to calculate estimated daily human consumer intake values. Finally, the ratio of the estimated daily intake value to the acceptable daily intake value allows calculation of a risk coefficient and a risk coefficient ≥ 0.1 is considered as an indicator of a potential hazard to human health (Prosser et al., 2014). The model is designed to run for a simulation period of a single growing season because, in its present version, there is no option for entering changing temperatures and other seasonal effects. Multiple runs of the model in which the user manually determines any losses that may occur during the winter months, however, may determine year-to-year accumulation. Alternatively, users may choose to run the model for many months to obtain an estimate of long-term accumulation (Hughes et al., 2005; Hughes and Mackay, 2011). The model assumes that chemicals in the soil are mobile and therefore constantly available to plants, but this assumption is problematic for chemicals that strongly sorb to soil solids. In addition, the model does not take growth dilution or biotransformation into account, and as such are likely to give higher than realistic plant concentrations (Wu et al., 2015). It does not account for sorption of chemicals to root surfaces where equilibrium with the surrounding soil may be achieved, it cannot account for the non-linearity of degradation, and there is considerable uncertainty about parameter values that control partitioning, degradation and transport.

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[k] Illuviation: "accumulation of dissolved or suspended soil materials in one area or horizon as a result of eluviation from another"(https://www.merriam-webster.com/dictionary/illuviation)

Legind et al. (2012) coupled SimpleTreat 3.1 (Legind et al., 2011) with a model for water and solute transport in soil, which includes a discrete cascade approach for the water balance (tipping buckets model) (Trapp and Matthies, 1998), to simulate the uptake and fate of organic contaminants from biosolid amended soils. The model consists in five soil layers and four plant compartments (root, stem, leaf, and fruit/seed). In each period, the water and substance balance in the five soil layers is solved iteratively while considering precipitation, soil surface evaporation, infiltration, leaching and transpiration (i.e., water uptake from soil by growing plants). Chemical contaminant input via organic amendment is calculated from measured contaminant concentrations in OW and simulated as pulse inputs by the model (Prosser et al., 2014; Trapp and Eggen, 2013). The dissolved concentration is calculated from the chemical distribution coefficient in soil. Chemical uptake in plants occurs via the water taken up by the roots at various depths. It is assumed that the roots grow to where water can be accessed. A similar approach was used to simulate the fate of three ionisable trace chemicals from human consumption/excretion to the accumulation in soil and uptake in plants following field amendment with sewage sludge or irrigation with river water receiving treated wastewater (Legind et al., 2012; Polesel et al., 2015; Trapp and Eggen, 2013). A comparison with previously published results showed that the model predictions were close to experimental data regarding elimination in sewage treatment plants, concentrations in sewage sludge and bioconcentration factors in plant tissues, for which high variability was nevertheless noted (uncertainty of the combined models). One shortcoming of the plant uptake model is that organic contaminant transformation in plants is not taken into account (Polesel et al., 2015).

3.3.2.2 Multi-compartment transport models

A wide range of exposure estimation models can be used to simulate the fate and distribution of substances among the different environmental compartments. These models vary in their complexity and purposes (ECHA, 2016; Kester et al., 2005). However, the models tend to be based on simplified assumptions, and field application of the models must consider heterogeneity issues. Land application of organic contaminants is also often assumed to be random rather than uniform in the models. Several methods can be used to account for this heterogeneity. One way is to run the model under the range of conditions found in the field, with the most conservative (i.e., the lowest thresholds from an RA standpoint) results selected for the target organic contaminant. This generates a conservative model result that may be taken into account when making risk management decisions (Kester et al., 2005). The models most commonly used to assess the environmental fate of pesticides, especially their transfer to groundwater, surface water and sediment, are those used in the European pesticides registration framework: MACRO (Larsbo et al., 2005), PEARL (van den Berg et al., 2016), PELMO (Klein et al., 1997), PRZM (Carousel et al., 2005) for groundwater (FOCUS, 2014, FOCUS, 2000), and STEP1–2 and SWASH—which includes a substance characteristics database (SPIN), spray drift calculations, soil drainage (MACRO), run-off (PRZM) and surface water (including sediment) fate (TOXSWA) models—for surface water and sediment (ECHA, 2016; FOCUS, 2001). These models can be used for any organic contaminants, but they are not able to represent OW and its interaction with contaminants, and agricultural practices (tillage, organic matter management, etc.) are not fully represented (Mottes et al., 2014). RZWQM is a process-based agricultural management model that includes water, chemical, and heat transport modules; a plant growth module; an evapotranspiration module; an equilibrium chemistry process module; an organic matter-N cycling module; a pesticide fate module; and a management practices module with crop rotation, tillage, irrigation, fertilizer, pesticide and manure applications (Ma et al., 1998; Malone et al., 2004). RZWQM was successfully used to simulate the fate of N in manure and poultry litter amended soil (Feng et al., 2015; Ma et al., 1998), so it might be suitable for simulating the environmental fate of organic contaminants present in manure/OW applied on soil. Lammoglia et al. (2017) combined the STICS (Brisson et al., 2003) crop model and the MACRO (Larsbo et al., 2005) pesticide fate model to simulate the fate of pesticides in complex cropping systems. STICS simulates the decomposition of OW, including farmyard manure, compost and sewage sludge. Enhanced coupling of STICS-MACRO could allow simulation of the fate of organic contaminants present in various OW applied on soil. Finally, inverse modeling showed that the HYDRUS-1D model (Šimůnek et al., 2012) and a two-site sorption model were able to predict transport parameters of phthalate esters from biosolid amended soil in corn cropfields using an inverse solution approach. However, they did not consider the interaction of biosolids with organic contaminants (Sayyad et al., 2017). Different soil structures due to tillage and compost are accounted for in HYDRUS-2D for the purpose of simulating water, Cu and Cd transport in amended soils (Filipović et al., 2016a). A similar approach was used to simulate the impact of compost application on isoproturon transport, although this substance was not added to soil via compost. After a calibration step, the HYDRUS-2D model was found to accurately simulate water and isoproturon fluxes in agricultural soil following repeated urban waste compost application (Filipović et al., 2014,2016b). The fate of organic contaminants could also be better predicted by accounting for soil heterogeneity at the soil profile scale generated by OW amendment (Vieublé-Gonod et al., 2009). Yet another means to improve the prediction of risk in soil following amendment with OW containing organic contaminants would be to differentiate non-extractable residues of biogenic and abiotic origin. Indeed, microorganisms incorporate carbon and in some cases carbon from organic contaminants, leading to the production of biogenic non-extractable residues (Kästner et al., 2014). Contrary to non-extractable residues formed from parent organic contaminants or metabolites, biogenic non-extractable residues do not present environmental risks (Kästner et al., 2014). Environmental risks related to the formation of non-extractable residues from organic contaminants are thus often overestimated (Nowak et al., 2011, 2013).

In summary, to improve risk assessment regarding organic contaminants in OW applied on soils, it would be essential to develop/improve process-based models that consider, in the long term: interactions between organic contaminants, the different processes involved in the fate of organic contaminants, such as sorption, degradation, generation of transformation products, volatilization, leaching, uptake, etc., and modifications in soil properties following OW application. Models such as those described here should also be able to represent a diverse range of OW (in terms of quantity and quality). The variability of the parameters/processes described above should also be considered. In addition, most of the models are 1-D models, but there is a need to extend risk assessment to larger scales, e.g., field to watershed, region, country, etc. Finally, impact assessment should be improved by taking chronic data, mixtures, etc., into account.

3.4 Pathogens and antibiotic resistance in RA: Limits and solutions

The methods used in RA for monitoring fate, exposure and infectious outcome (i.e., damage) (Table 3 and Section 2.4) have limitations with regard to the consideration of microbiological hazards during OW treatment and recycling, as they do not fully capture the complexity of the mechanisms and processes involved. LCA is not yet designed to consider pathogens, nor is its development in that direction foreseen in the near future (e.g., not mentioned in Fantke et al. (2018)). Combining LCA and RA has been suggested for situations where the environmental performance and pathogen-driven health risks are of joint interest (Jolliet et al., 2014).

3.4.1 Microbial fate during organic waste treatment

The main concerns regarding the microbiological hazards of anaerobic digestion processes are the survival and spread of zoonotic and human pathogens, as well as the antibiotic resistance dynamics, including ARG transfer from non-pathogenic organisms (including commensals) to pathogenic bacteria (Zhao and Liu, 2019). Moreover, OWs could also spread plant pathogens, but these considerations are beyond the scope of this review. The efficacy of OW sanitization depends on several parameters, with the most critical ones being the initial amount of pathogens, ARB, ARG and MGE in the OWs to be recycled and sanitized (Strauch, 1991), in addition to their respective infectious doses and die-off rates in relation with the environmental constraints that will develop in the bioreactor. Microorganism die-off rates during anaerobic digestion mainly depend on the time of exposure to unfavorable temperatures, pH or toxic substances such as hydrogen sulfide (Ottoson et al., 2008; Sahlström, 2003). Other parameters, such as the O_2 concentration, the presence of ammonium and short-chain fatty acids (e.g., acetate), mainly change the ratios in terms of numbers of cells per microbial taxa, but are not likely to increase their death rate. Biotic factors affecting microbial pathogens, such as predation through bacteria ingestion by microfauna or parasitism, or bacteriophage attacks on bacteria during anaerobic digestion, have not been documented. Predation is more likely to occur during the treated OW storage period, at the end of the process. Storage has therefore been suggested as a means for improving the microbiological quality of these end-products (Sahlström, 2003). Digestion processes are based on microbial ecological successions and synergies between key functional groups. By definition this process thus induces significant changes in OW microbiomes (Razaviarani and Buchanan, 2014). A highly diverse range of microbial pathogens, ARB, ARG and MGE can become involved in these digestion processes via cross-contaminations or fecal carriage by humans and livestock. The hydrolysis step during these processes seems to be compatible with the functional abilities of some bacterial pathogens such as *P. aeruginosa* and *Clostridium perfringens*. However, the die-off rates of human and zoonotic viruses are directly related to their susceptibility to the abiotic constraints accumulating from the beginning of the process. Predation or antagonism between bacteria might also have an impact on such reduction rates, but these interactions have yet to be documented. Die-off rates of a panel of pathogens have been reported over the years for the anaerobic digestion process (see Sahlström, 2003, for a review), which has led to the development of HACCP and QMRA scenarios (see Section 2.5.4). The high variation in reported die-off values led Westrell et al. (2004) to assume that pathogens occur in similar numbers in raw and digested OW when they developed their QMRA and HACCP scenarios. Note that digestate spreading with immediate burial is recommended in France (JORF, 2017). This practice is likely to increase microbial contaminant exposure to soil components, including bacterial grazers. However, digestate microbiota, especially pathogenic taxa, can affect the soil biota (Teglia et al., 2011a). Few ecotoxicological studies have been conducted to assess the ecological impact of digestate application on soil. Moreover, ERA studies (US EPA, 1998) have mainly been focused on specific chemicals contained in the digestate and their associated ecotoxicity. Risk assessment in ERA could be enhanced by including both chemical and biological contaminants in ecotoxicological assays. The coalescence of communities from digestates and soils should also be investigated to evaluate resistance/resilience to invading taxa.

During organic waste composting, *Actinobacteria*, *Bacteroidetes*, *Proteobacteria* and *Firmicutes* species are the key microbial players (Bru-Adan et al., 2009). High *Proteobacteria* population levels could then be observed in mature compost. The main genera identified are *Pseudomonas* (28%), *Serratia* (20%), *Klebsiella* (11%) and *Enterobacter* (5%) (Boulter et al., 2002). Several microbial species of human health concern could thus play a role in the composting process (Reynnells et al., 2014). Microbial RA of composted OW could be assessed by monitoring: (i) host-specific human/animal pathogens (or indicators of their occurrence) found in the initial organic matter but unlikely to develop during the process, and (ii) cells of pathogens such as *Listeria*, *Clostridium* and *Klebsiella* that could be enriched by this process.

Several QMRA models have been suggested, but predicting the behavior of zoonotic pathogens in OW is still a challenge. Including HACCP in RA model simulations is thus recommended. Westrell et al. (2004) proposed the first published HACCP approach for anaerobic digestion, involving identification of critical points to control health hazards combined with a preventative management and quality assurance approach throughout the production and distribution steps. This approach generates safety criteria for each control point. Corrective measures are required if this critical limit is reached (Bryan, 1990; Orriss and Whitehead, 2000). As a first step in any HACCP framework, exposure scenarios must be defined and ranked in order of severity (Westrell et al., 2004). These exposure routes can involve: (i) direct contact with the pathogen during the digestion process or while handling OW treatment products—the pathogens could enter the body through wounds, (ii) inhalation of contaminated air, and (iii) ingestion of contaminated matter, OW treatment products or amended soil. However, as for QMRA, thorough knowledge of the type of pathogens and doses that can lead to infection according to these routes is required to be able to accurately assess the relative incidence of the observed hazards. Yet their presence appears to be highly stochastic, likely because of our scant knowledge of the origin and nature of OW involved in such processes. The HACCP framework of Westrell et al. (2004) led to the identification of major critical points requiring consideration in anaerobic digestion processes. The fate of microbial pathogens is highly dependent on the efficacy of the main biochemical transformation processes involved (temperature, pH, duration). Inferences regarding the performance of these processes could also be made by monitoring bacterial groups likely to have die-off values related to those of the pathogens. Generally, indicator bacteria such as *E. coli* and intestinal Enterococci are used to monitor the microbiological quality of digested OW (JORF, 2017). Their numbers are considered satisfactory if they do not exceed 3 log/g (JORF, 2017).

System models based on Bayesian networks[1] are now emerging as an alternative to QMRA models to overcome uncertainty associated with the underlying datasets (Aguilera et al., 2011; Barton et al., 2012; Beaudequin et al., 2015). Bayesian networks have been used to make RA predictions from incomplete datasets or small samples (Fenton and Neil, 2012; Kontkanen et al., 1997). Furthermore, Bayesian networks, by their nature, can be used for "forward inference" (whereby the system variables are specified and the impact on the outcome can be observed) and for "backwards reasoning" (whereby the effect or outcome is specified and subsequent changes in the causal variables can be computed). Bayesian networks can hence reveal variables that are key drivers of an outcome or,conversely, the sensitivity of an effect to the system variables (Ben-Gal, 2008; Coupé et al., 2000; Pollino and Hart, 2006). A Bayesian network framework can be used to generate scenarios and reduce microbiological risks by performing simulations with modified variables. This can help identify key control areas in a process where microbiological risks could be reduced, and to propose interventions (Albert et al., 2008). However, representing the distribution of a variable in a Bayesian network as continuous or discrete series remains a challenge. Moreover, quantification of conditional probability tables underlying each variable in a Bayesian network is often difficult. These distributions can be assessed on the basis of observed data, published papers or reports, statistical models or simulations (Pollino et al., 2007). Bayesian network predictions could be bolstered by linkages with DALY models. It could be interesting to apply this approach to subpopulations such as workers in contact with OW and OW treatment products. These estimates could then be used in Bayesian network models to infer key drivers influencing life expectancy and quality.

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[1] A Bayesian network is a flexible graphical model with variables represented by nodes and connected by directed arcs indicating dependencies and strength of the causal links (Nielsen and Verner Jensen, 2007). Each variable is assigned a probability distribution conditional to its parent variables. Uncertainty in a Bayesian network model is thus represented by a probability distribution. By construction, Bayesian networks can characterize and describe complex relationships among variables associated with a complex outcome (Donald et al., 2009).

3.4.2 Role of antibiotics and non-antibiotic chemical stressors on antibiotic resistance selection and antibiotic resistance dynamics after treated OW spreading on soil

In treatment systems, stressors such as antibiotics are often in mixtures and at high enough levels to increase the likelihood of antibiotic resistance. It was shown that antibiotics can exert selection pressure at far below inhibitory concentrations (Gullberg et al., 2011; Lundström et al., 2016). Bengtsson-Palme and Larsson (2016) attempted to determine minimal selective antibiotic concentrations in complex systems and they predicted no-effect concentrations for resistance selection for 111 antibiotics based on available minimum inhibitory concentrations for clinically relevant bacteria. These authors suggested that "emission limits for antibiotics must be set individually for each compound, and that different antibiotics have very different potential to be selective." They also mentioned that antibiotic concentration limits must account for antibiotic effects on mutagenesis, transfer of genetic material between bacteria, chromosomal DNA mobilization and biofilm formation as subinhibitory antibiotic concentrations were shown to affect those mechanisms. In addition, the concomitant presence of non-antibiotic chemical stressors that have antimicrobial properties might contribute to the spread and selection of antibiotic resistance. Among them, trace elements (Baker-Austin et al., 2006; Seiler and Berendonk, 2012), biocides

(Capita et al., 2013; Pal et al., 2015), PAH and PCB (Chen et al., 2017; Gorovtsov et al., 2018) could co-select for ARG. This phenomenon exemplifies the so-called "cocktail effect" (see Section 3.5). The co-selection of resistance is based on: co-resistance (a resistance gene towards a chemical is selected because it is genetically linked to another resistance gene under positive selection; this occurs when genes are co-located on the same genetic element, i.e., plasmid, genomic island, integron, transposon); cross-resistance (a resistance gene can confer resistance to various chemicals); and cross-regulation (different resistance genes conferring resistance to various chemicals are controlled by common/identical regulatory systems) (Bengtsson-Palme et al., 2016; Dickinson et al., 2019; Pal et al., 2017; Poole et al., 2019; Rutgersson et al., 2020; Yu et al., 2017).

In a meta-analysis, Goulas et al. (2020) addressed the effect of chemicals (effects of antibiotic administration to animals and spiking OW with antibiotics and/or metals) on antibiotic resistance markers after composting or anaerobic digestion of sludge or animal waste. They reported a "non-significant reduction of ARG/MGE after composting—regardless of whether the animals had received antibiotics or not—and no significant effect of antibiotic use on anaerobic digestion. When OW was spiked with antibiotics and/or metals before treatment, the ARG/MGE relative abundance was still reduced (but not significantly) compared to the absence of spiking (significant) after composting, and the ARG/MGE reduction was significant in both cases after anaerobic digestion." They related these observations to the "variability originating from the diversity in the duration of the exposure and/or in the concentrations of spiking molecules, which could affect the bacterial response to contamination, as well as the variation in the latency of measurement affecting the [antibiotic resistance] measurement. Another bias could explain the heterogeneity in results, which is linked to the range of ARG/MGE chosen by authors."

Soil acts as a resistance reservoir and high-throughput sequencing technology has been used to conduct metagenomic analyses of soil bacterial communities and the findings have helped describe ARG, their origins and potential to be transferred between species (Nesme and Simonet, 2015). Human activities such as spreading OW on soil might alter their intrinsic resistome, thereby introducing allochthonous ARB, ARG and exogenous chemical stressors. Resistome changes are determined: (i) by the survival and growth ability of ARG-bearing bacteria, (ii) potential gene exchanges between ARG-bearing bacteria and the autochthonous soil population (i.e., probability of contact, phylogenetic relationships), and (iii) by the nature, speciation, bioavailability and bioaccessibility of input chemicals as well as those already present (i.e., trace metals and pesticides in agricultural soils). Few data are currently available regarding the specific survival of ARG-bearing bacteria in terms of competition, predation or adaptation to soil environmental conditions (van Veen et al., 1997), or regarding horizontal gene transfer efficiency in situ. Moreover, further investigations are needed to determine whether ARG are carried by potential pathogens or co-located on mobile elements. The co-selection of resistance in agricultural soils mostly involves data related to the role of trace elements. These elements accumulate and can persist in soil for long periods because they are non-degradable and hard to remove. Their presence in animal waste consecutive to their use for growth enhancement and disease control, as well as in biosolids, inorganic fertilizers and pesticides (Hölzel et al., 2012; Mortvedt, 1996; Rangasamy et al., 2017; Singh and Agrawal, 2008), could exert selection pressure on antibiotic resistance in soils (Singer et al., 2016; Zhu et al., 2013). Studies by Berg et al. (2010, 2005) using both culture-based and culture-independent approaches demonstrated that Cu exposure in agricultural soils led to the selection of Cu-resistant bacteria and indirect selection of ARB. Various studies have shown a positive correlation between the presence of trace elements and the abundance of some ARG in agricultural soils receiving manure amendments. For instance, significant positive correlations were noted between some *sul* genes and various trace elements, i.e., Cu, Zn and Hg, in manure and soil samples collected from multiple feedlots in Shanghai (Ji et al., 2012). In addition, these authors indicated that the presence of ARG was relatively independent of their respective antibiotic inducers. Similarly, Hu et al. (2017) found that changes in ARG abundance were independent of the antibiotics present and were affected by long-term Ni contamination in agricultural soils. Based on a nationwide sampling campaign across China (Zhou et al., 2017) showed significant co-selection between trace elements and antibiotic resistance genes among Cu, Hg and *sul* genes. Arsenic in swine manure has also been shown to increase ARG and MGE abundance (Zhu et al., 2013). The impact of applying ARG-containing fertilizers on already trace element-contaminated soils (e.g., vineyard soils known for their high levels of Cu due to fungicide applications) should be taken into account, especially because trace elements may influence ARG mobility (Hu et al., 2016, 2017). Unlike in RA, in LCA these factors could only be taken into account in the inventory phase, since antibiotic resistance and other pathogen-related mechanisms are not accounted for in fate, bioavailability and effect modeling. Studies on bacterial communities in the gut of earthworms exposed to As and sulfamethoxazole contamination revealed synergistic interactions of both contaminants, leading to an increased incidence of ARG and MGE and changes in the bacterial community structures correlated with ARG profiles (Wang et al., 2019). These results suggested that the gut of soil microfauna is a neglected hotspot of antibiotic resistance. Furthermore, these authors highlighted an ARG/MGE co-occurrence pattern, indicating that horizontal gene transfer via MGE may occur in the earthworm gut (Ding et al., 2019). However, correlation-based analyses were carried out in most studies, but this may not reveal causal evidence of patterns in complicated systems. Laboratory experiments should be conducted under controlled conditions in micro- or mesocosms so as to validate the role of trace elements in antibiotic resistance dynamics and to quantify the role of the various co-selection mechanisms. Furthermore, as these studies were mainly based on total trace metal concentrations, further studies are needed to also take speciation, bioavailability and bioaccessibility at the microscale into consideration.

3.5 Contaminant mixtures in LCA and RA: Limits and solutions

Few examples were found in the literature of RA of OW treatments and recycling focused on the possible effects of physicochemical interactions among trace elements, organic contaminants and pathogens (i.e., co-toxicity), as well as on their joint fate after OW spreading. In-depth discussions on the so-called "cocktail effect" of the environmental emission of mixed contaminants are ongoing, while the limitations of current RA approaches to address this effect have been analyzed and some authors calling for a change of paradigms to take this issue into full account (Backhaus and Faust, 2012; Bopp et al., 2016; Svingen and Vinggaard, 2016). The cocktail effect is not considered in LCA as, by design, it deals with thousands of substances in a cumulative fashion. Under the current paradigms, substance mixtures would have to be treated as new inventory items, and toxicity data would be needed for the mixtures to be considered in LCA.

Bopp et al. (2016) reviewed 22 case studies of RA applied to chemical mixtures and found that the main shortcomings of current frameworks that would have to be overcome to perform mixture risk assessments include: (i) the difficulty of determining the exact composition of unintentional mixtures (e.g., in wastewater and sludge), (ii) the lack and high uncertainty of exposure and toxicity data, as well as of information on the mode of action of mixtures. The authors highlighted that "Data gaps seem to be the major hurdle when it comes to deal with risk assessment of chemical mixtures [...]" (Bopp et al., 2016). Pesticides are among the most commonly studied mixtures. The study concluded that the Information Platform for Chemical Monitoring data (IPCheM) should be further populated to assist future chemical mixture RA (further explored in Bopp et al. (2019), as outlined below). They provided recommendations for future case studies: i) compare different populations and vulnerable groups, (ii) include new chemicals and substance groups, iii) address interactions at low exposure concentrations, (iv) develop criteria for assessing interactions, (v) investigate approaches for substance grouping (e.g., per effect or mode of action), and (vi) examine the relevance of assessing mixtures across regulatory regimes. Bopp et al. (2019) discussed a number of further challenges and potential solutions associated with RA of chemical mixtures, disaggregated by hazard, exposure, risk and risk management. One challenge highlighted concerned the simultaneous vs. sequential exposure to multiple chemicals, which entails the mechanics and timing of exposure and the cumulative effect of concentrations that may individually be below the level at which the effect is observed. The authors, based on previously published findings, proposed a combined adverse outcome pathway/aggregate exposure pathway[m] framework to "put into context exposure models, biokinetic and dynamic modelling, the results from monitoring, biomonitoring, and *in vitro* testing." This framework is designed to integrate a variety of models (multimedia fate models, in vitro fate mathematical models, physiologically based kinetic models, etc). There is published evidence that this framework is being built and applied (e.g., Clewell et al., 2020; Price et al., 2020).

4. Potential environmental assessment enhancement and the prospect of a comprehensive framework for agricultural organic waste recycling assessment

In the light of the literature on LCA and RA applied to OW treatments and their recycling, a life cycle based approach covering both waste processing and recycling is clearly lacking. LCA toxicity methods do not account for the transformation/degradation/combination of trace elements, organic contaminants and pathogens, or their fate following the spreading of untreated or treated OW on cultivated soils. These methods are hampered by high uncertainty regarding human and ecotoxicity characterization factors, which are usually based on total concentrations and not regionalized, apart from a few very recent regionalized LCA methods (Bulle et al., 2019; Verones et al., 2020). Moreover, available characterization factors exclude a plethora of substances that may be present in OW. RA methods fail to consider a number of biophysical processes that determine the fate of emitted contaminants, including trace elements, organic contaminants and pathogens. Moreover, methods such as QMRA rely on datasets featuring high data uncertainty, and combinations of contaminants are not considered in RA. Both frameworks could benefit from additional models and approaches (including those used in other disciplines) to integrate overlooked biophysical processes and thus bridge the assessment gaps. Existing frameworks and models need to be combined to be able to accurately assess the environmental and human health impacts of regional strategies for recycling OW in agriculture. Indeed, no single framework/model currently encompasses all pathways via which contaminant-bearing OW could affect the environment and living organisms. Moreover, the overall dynamics of given contaminants after OW spreading are not taken into account.

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[m] An adverse outcome pathway "describes a logical sequence of causally linked events at different levels of biological organization, which follows exposure to a chemical and leads to an adverse health effect in humans or wildlife" (online OECD resource https://doi.org/10.1787/2415170X); an aggregate exposure pathway is a similar concept, proposed as a framework to organize dispersed exposure data (Tan et al., 2018).

A combination of environmental and risk assessments may have to be applied to recycling scenarios which need to be defined and, ideally, co-constructed with impacted stakeholders. Conventional LCA, which considers the fate of contaminants applied to agricultural soils, might be insufficient for comprehensive environmental assessment. LCA deals only with systems in equilibrium (steady state), while excluding the dynamics of substances during a given study period (generally a year), and also it deals with absolute quantities (flows, stocks). LCA should therefore be combined with tools that account for all relevant flows and stocks of all materials and specific substances to ensure comprehensive and exhaustive assessments. Material and substance flow analyses (Allesch and Brunner, 2015; Bouman et al., 2000) are the natural candidates for such integration because, together with LCA, both tools are included in industrial ecology toolboxes and share key features. Material flow analysis encompasses all flows while substance flow analysis takes substances of interest into account in a given system (e.g., a region). Combining both of these tools with LCA would require additional models to estimate not only direct emissions due to OW spreading on soil, but also the fate of contaminants of interest (e.g., cocktail effect, available vs. total concentrations, speciation, etc.). This modeling should rely on both empirical knowledge (e.g., soil experiments) and existing models. Table 6 summarizes a few novel or complementary approaches that

Table 6 Key aspects of biophysical processes overlooked in RA and LCA, and suggested models to address them

Key aspects	Proposed models and approaches	Readiness of approaches	References
Trace elements			
Trace element speciation in organic waste	Creation of a qualitative typology of OWs based on their basic characteristics related to physicochemical parameters driving trace element speciation in OW, such as pH and redox potential.	Relatively easy to implement, but would require a research project to develop a classification method similar to TyPol (Servien et al., 2014).	Tella et al. (2016)
Colloidal transfer of contaminants	Models for simulating the colloid facilitated transport of trace elements in fate modeling (e.g., HYDRUS 1D).	Fully functional model.	Šimůnek et al. (2012)
Multiple soil layers for the prediction of trace element fates in soil	Empirical or semi-mechanistic models to determine the fate of trace elements per soil layer over a given period.	Would require a review and validation of existing models.	Jacques et al. (2008)
Characterization of the binding properties of dissolved organic matter	Empirical regressions based on soil physicochemical parameters to predict specific dissolved organic matter binding properties.	Fully functional approach, yet requiring a literature review to identify models for specific trace elements. Implemented in LC-IMPACT (Verones et al., 2020).	Owsianiak et al. (2013)
Changes in trace element availability over a time course and consequences in terms of ecotoxicological endpoints	Data acquisition with DGT. Ecotoxicological endpoints based on DGT-available trace elements.	Fully functional approach, requiring empirical analyses and exploration of toxicity databases to identify suitable ecotoxicological endpoints.	Zhao et al. (2006) Thakali et al. (2006b)

Influence of soil organisms on trace element (bio)availability	Data acquisition with a biotest (e.g., RHIZOtest). Models to predict bioavailability (e.g., WHAM-F_{TOX}).	Fully functional approach, requiring empirical analyses and model calibration to specific conditions.	Bravin et al. (2010b) Tipping and Lofts (2015)
Organic pollutants			
Fate of organic contaminants post spreading (mineralization, bound residues)	Plant uptake models (e.g., SimpleTreat 3) coupled with models for water and solute transport in soil.	Fully functional approach, requiring some model coupling and calibration. Data intensive.	Legind et al. (2012) Polesel et al. (2015)
Interactions between organic contaminants and organic matter after spreading	Models describing organic contaminants and organic matter interactions (e.g., COP-Soil).	Fully functional approach, requiring some model calibration. Data intensive.	Geng et al. (2015) Goulas (2006) Brimo et al. (2018a,b)
Heterogeneity in the fate of organic contaminants spread on soils due to: interactions between organic contaminants and OW, various processes involved in the fate of organic compounds (sorption, degradation, production of transformation products, volatilization, leaching, uptake, etc.), the modification of soil properties following OW application, and the diversity of quantities and qualities among OW	Models used in the context of European pesticides registration.	Fully functional approaches, requiring some model selection and calibration. Data intensive.	ECHA (2016)
	Agricultural management models featuring water, chemicals, and heat transport modules; a plant growth module; an evapotranspiration module; an equilibrium chemistry process module; an organic matter-N cycling module; a pesticide fate module; and a management practices module including crop rotations, tillage, irrigation, fertilizer, pesticide and manure applications (e.g., RZWQM, STICS).	Fully functional approaches, requiring some model selection and calibration. Data intensive.	Ma et al. (1998) Malone et al. (2004) Brisson et al. (2003)

Continued

Table 6 Key aspects of biophysical processes overlooked in RA and LCA, and suggested models to address them—cont'd

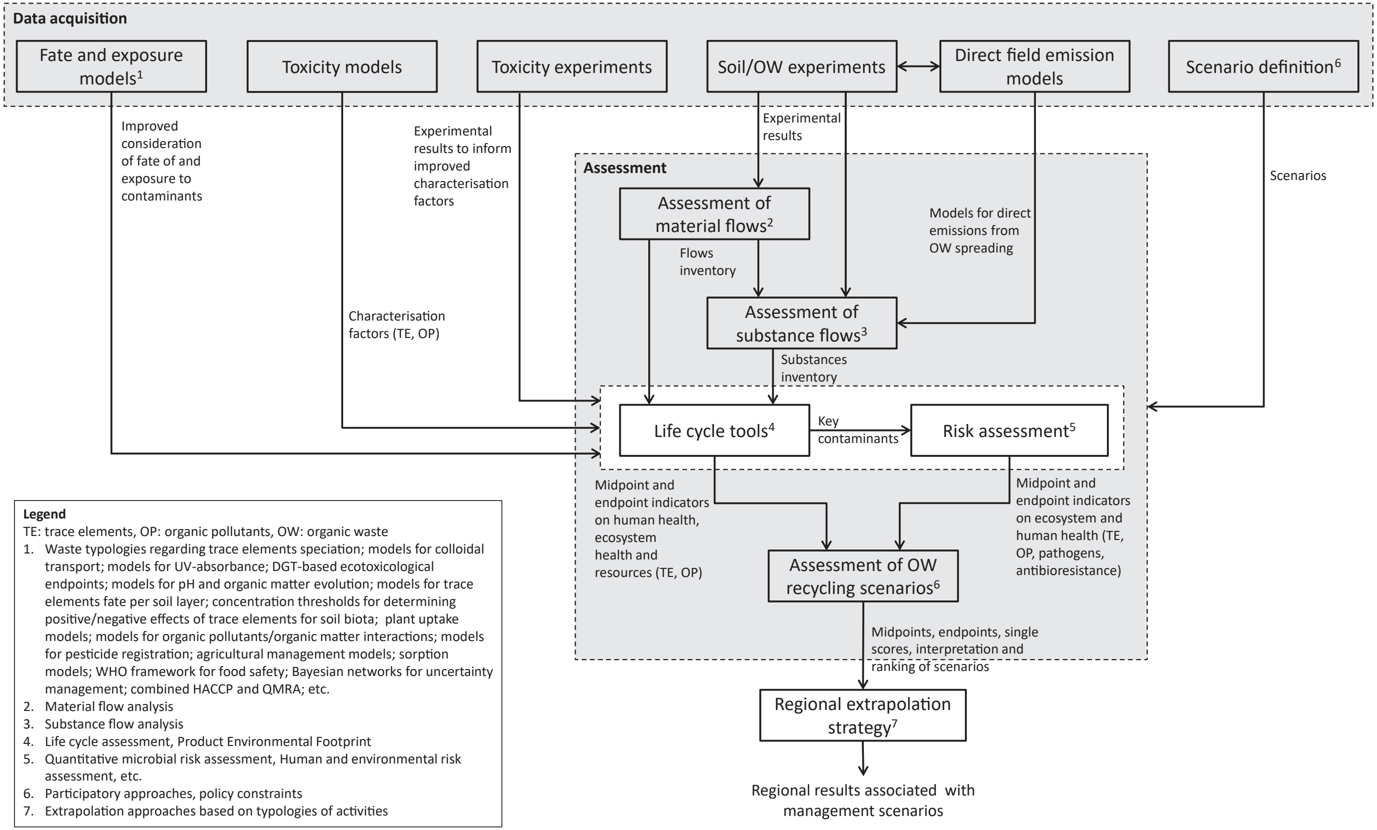
Key aspects	Proposed models and approaches	Readiness of approaches	References
	Sorption models (e.g., HYDRUS-2D).	Fully functional model.	Šimůnek et al. (2012) Filipović et al. (2016a, 2016b), Filipović et al. (2014)
Pathogens and antibiotic resistance			
Direct exposure to antibiotic-resistant pathogens or to resistance determinants (and subsequent horizontal gene transfer to bacterial pathogens on or within a human host)	WHO framework for food safety. Microbiological risk analysis (MRA).	Fully functional approach.	Manaia (2017); WHO (2010)
Antibiotic resistance	Explore the gut of soil microfauna as a hotspot of antibiotic resistance; apply metagenomic analyses of soil bacterial communities to describe ARG, their origins, and their potential to be transferred between species.	Quite well described approach, requiring empirical analyses and selection of specific models to fit observational data.	Ding et al. (2019) Nesme and Simonet (2015)
	Explore specific survival of ARG-carrying bacteria regarding competition, predation, and adaptation to soil environmental conditions.	Quite well described approach, requiring empirical analyses and selection of specific models to fit observational data. Data seems scarce to date.	van Veen et al. (1997)
Uncertainty management, quality of dose-response datasets	Bayesian networks.	Fully functional approach.	Fenton and Neil (2012)

Behavior of a zoonotic pathogens in OW	Combined HACCP and QMRA.	Fully functional approach.	Westrell (2004); Westrell et al. (2004)
Other aspects			
Mixture effects	No specific model, but further population of the Information Platform for Chemical Monitoring data (IPCheM) and a number of areas of further study have been suggested as a way forward	Immature approach.	Bopp et al. (2016)
Effect of repetitive and long-term applications of organic waste	Models and databases to predict/fit pH and organic matter patterns over time.	Various semi-mechanistic models exist, which are rather data intensive, thus requiring empirical analyses and model calibration to local conditions.	Clivot et al. (2019); Schädel et al. (2019)

could be used to enhance LCA and RA, including their levels of "readiness" (i.e., the extent to which such approaches could be applied or integrated today). The body of empirical and modeling knowledge on contaminants is vast, but the extension/complementation of LCA and RA would be a complex task, considering the data requirements at different levels as well as model complexity and suitability for a diverse range of situations. Additional toxicity experiments focused on terrestrial ecotoxicity could enrich the body of characterization factors used in LCA to assess the toxicity impacts of target contaminants.

A comprehensive framework (Fig. 4) could also include the set of approaches and models compiled in Table 6, depending on the goal and scope of the intended assessment. This theoretical framework could help guide the integration of models and approaches to be able to achieve comprehensive assessments of OW recycling in soils.

For instance, in region X, animal effluents and sewage sludge constitute a surplus that would have to be dealt with at a cost. In parallel, region X features vast periurban agriculture areas requiring fertilization at a cost (mineral fertilizers are imported from outside the region). An assessment is sought by stakeholders, and required by legislation, regarding potential impacts on the environment and human health associated with agricultural recycling of a portion of the surplus OW. The team entrusted with performing the analyses starts by designing and proposing stakeholders various industrial ecology-inspired possibilities for OW recycling in crop fields, i.e., a so-called "plausible promise" (Wassenaar et al., 2014). This systemic change strategy—to be elaborated in detailed scenarios with stakeholders via participatory approaches (e.g., as described in Queste and Wassenaar (2019))—is underpinned by the idea that the recommended recycling would bring overall improvements to the regional system (namely cheaper OW management and fertilization without worsening current impacts on the environment and human health, despite changes in agricultural practices and logistics). The team must demonstrate the environmental soundness of the plausible promise by comparing the "conventional" (i.e., impact addressed by current LCA and RA methods) environmental impacts of both of the proposed scenarios with the current situation, while exploring and quantifying additional environmental and human health impacts associated with the increased transfer of contaminants to agricultural soils. This is done first by performing an MFA (see Table 1) to establish the flows and stocks of "matter" (Wassenaar, 2015) in the system, and then estimating those that would occur under the proposed scenarios. Given the specificities of the region and the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TE: trace elements, OP: organic pollutants, OW: organic waste
1. Waste typologies regarding trace elements speciation; models for colloidal transport; models for UV-absorbance; DGT-based ecotoxicological endpoints; models for pH and organic matter evolution; models for trace elements fate per soil layer; concentration thresholds for determining positive/negative effects of trace elements for soil biota; plant uptake models; models for organic pollutants/organic matter interactions; models for pesticide registration; agricultural management models; sorption models; WHO framework for food safety; Bayesian networks for uncertainty management; combined HACCP and QMRA; etc.
2. Material flow analysis
3. Substance flow analysis
4. Life cycle assessment, Product Environmental Footprint
5. Quantitative microbial risk assessment, Human and environmental risk assessment, etc.
6. Participatory approaches, policy constraints
7. Extrapolation approaches based on typologies of activities

Fig. 4 Diagram of a comprehensive framework for environmental assessment of agricultural recycling of organic waste.

available OW, the team determines that further insight into the fate of specific substances of interest is needed and they perform an SFA for this purpose (Wassenaar et al., 2015). Based on the MFA and SFA findings, the team performs LCA of a sample of the current and prospective systems (OW generation, treatment and utilization), as well as RA targeting the substances of interest in the context of OW treatment and utilization. The team discovers that LCA—despite estimating a battery of conventional impact categories—is not well equipped to consider the fate of certain target substances due to limitations in the underlying terrestrial ecotoxicity and human toxicity models. The team thus decides to mobilize additional models to more accurately simulate the fate and bioavailability of the target substances. These models include: (i) the approach described in Owsianiak et al. (2013) to determine the terrestrial ecotoxicity of trace elements, informed by experiments conducted on soil and OW (e.g., chemical extractions), (ii) the COP-Soil model to determine interactions between organic contaminants and organic matter, and (iii) QMRA to predict potential exposure to pathogens in tandem with an assessment of the extent of survival ARG-bearing bacteria regarding their adaptation to the soil environmental conditions. The team also deploys: (i) STICS (Brisson et al., 2003) to model the proposed agricultural systems in which a considerable share of the crop nutrient needs are supplied by organic fertilizers via the application of treated OW—the idea is to improve the quality of mineral fertilizer substitution estimations based on static indicators such as mineral fertilizer equivalents (Brockmann et al., 2018; COMIFER, 2013), and (ii) the AMG soil organic carbon model (Clivot et al., 2019) to predict the effects of repetitive long-term OW applications on soil organic carbon. The team finally uses the overall available experimental and modeling results to assess the environmental soundness of the proposed scenarios, in consultation with the stakeholders via participatory approaches. Finally, results derived from a sample of systems are extrapolated to the regional scale, as described by Avadí et al. (2017).

5. Conclusion

The present review demonstrates that some aspects of organic waste treatment and recycling and some contaminant families have received far more attention than others. For contaminants, as trace elements have been studied to a greater extent than other contaminants, this largely relates to their much longer research history, which in turn could be explained by the respective analytical capacities. Organic contaminant and (to a lesser extent) pathogen research is slowly catching up, but environmental assessment frameworks are slow to follow. Combined OW treatment and recycling is less studied in combination, due to the complexity of these processes and the multidisciplinary scope. Common approaches for ecosystem and human impact assessment still fail to consider all relevant pathways and mechanisms involved when organic waste-borne contaminants are applied on soil. A number of refinements have thus been proposed to at least partially bridge these divides. Such refinements—consisting of models and approaches at different "readiness" and application complexity levels—are discussed regarding their suitability to fill gaps in conventional LCA and RA practice. In principle, most elements required for comprehensive consideration of trace contaminants in the environmental assessment of agricultural recycling of OW are available in one form or another, and their application would depend on the assessment needs and resources, as certain approaches may be resource (e.g., data, modeling skills) intensive. A comprehensive framework combining several complementary approaches has been proposed, which could help generate comprehensive environmental assessments of agricultural recycling of organic waste. The overall framework is a theoretical instrument, mainly designed to fuel discussion while providing directions for further research.

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CHAPTER THREE

Precise quantification of plant nutrient bioavailability: The relevance of the nutrient buffer power concept[☆]

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[☆] **Dedication:** This chapter, written under very trying times, because of the covid pandemic, is dedicated to my wife, Pankajam, a Nematologist trained in Europe, but one who gave up her profession and, instead, chose to be a homemaker, almost four decades ago, when we had our son and daughter. She is my all, and she sustains me in this difficult journey, that life is.

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Abstract

Efficient soil nutrient management is the key factor in sustainable crop production. Routine soil tests fail to precisely quantify plant nutrient bioavailability, from which economically viable fertilizer prescriptions can be made for field crops. The chapter discusses a revolutionary idea based on soil nutrient buffering. Employing thermodynamic principles, the author describes how the buffer power of a soil nutrient can be precisely quantified. Once this is done, the nutrient buffer power values can be integrated into computations, along with routine soil test values, from which economically viable fertilizer prescriptions can be made. A number of test crops, such as, Rye (*Secale cereale*), in Central Europe (Germany), for phosphorus, Maize (*Zea mays*) in Northern Europe (Belgium) for zinc, Wheat (*Triticum aestivum*) in Central Asia (Turkey), Black pepper (*Piper nigrum*) in South Asia (India) for znc, Cardamom (*Elettaria cardamomum* Maton) for potassium also in India, and White clover (*Trifolium repens*) in central Africa (Cameroon) for phosphorus and potassium, have been used to test the validity of the "The Nutrient Buffer Power Concept." Results are discussed with a new perspective for a fresh insight into soil testing for efficient and economically viable fertilizer management.

Many years ago, in one of the early editions of Advances in Agronomy, the *magnum opus* of agricultural science, or what is popularly known as the "Bible of Agricultural Science," Roy W. Simonson writing a chapter entitled "Concept of Soil" noted: "Someone has said that the fabric of human life is woven on earthen looms—it everywhere smells of the clay." Almost a half century later, we agronomists and soil scientists have come very far in our understanding of the "fabric of human life" which "everywhere smells of the clay." That the "fabric of human life" which is so very intimately linked to soil has dramatically changed is beyond dispute. Yet, there is no denying the fact that the "fabric of human life" will always be linked to soil which is the "pragmatic, the reality, the entity that dictates much of what societies can do" (Boul, 1994). Soil, in my opinion, is that invaluable gift of God to life on planet Earth and can aptly be termed "The Soul Of Infinite Life." Though the basic concept of soil, since its early description as a "thin mantle over the land surface" has vastly changed over the years, this thin mantle has always been the focal point since it is the medium for plant growth. For early man it was nothing more than a physical support for his predation. Quite likely, some areas were known to provide better footing than others, and some were to be avoided if possible. It is amazing that even after decades of research in soil science, which has provided such invaluable information on this "thin mantle over the land surface" so crucial to the existence of life, human, plant and animal, on planet Earth, this basic instinct of predation has remained unchanged. How else can we explain the disdain and callousness so often witnessed in modern societies, propelled by an insatiable greed to acquire unlimited wealth, which leads to the abuse of soil, the invaluable gift of God to man? Undoubtedly, the earliest shift in attitude toward soils must have originated at a time when man began to grow food, rather than gather it as his ancestors did. In many ways, the shift in attitude was the precursor to modern-day soil science. Though this shift must have occurred in pre-Christian times, about 9000 years ago, and focused on the inevitability of a proportionally smaller land surface supporting larger human populations, it is only in recent times that we have witnessed the magnitude of the impact of this shift in attitude of human existence. Much of land has become degraded and unsuitable for agriculture since a century ago. The 1992–93 World Resources Report (Stammer, 1992) from the United Nations on the status of world soils contains very alarming conclusions. For example, nearly 10 million ha of the best farm lands of the world have been so ruined by human activity since World War II that it is impossible to reclaim them. Over 1.2 billion ha have been seriously damaged and can be restored only at great cost. The loss in soil capability could mean that there will be enormous food shortages in the next 20–30 years and, as is but natural, the people of disadvantaged nations will suffer the most. Many factors have contributed to this alarming state of affairs, one of the prime factors being the "high-input agriculture" or more specifically the "chemical agriculture, euphemistically called the "green revolution," where unbridled use of chemical fertilizers coupled with carcinogenic herbicides and pesticides have ruined the soil resources. South Asia, in particular India, is a prime example. The state of Punjab known as the "cradle of green revolution" is a living example where hundreds of acres of once fertile land have turned barren, where even a blade of grass will not grow anymore. The ground water is so polluted with nitrogenous residues from excess of urea and water is no more potable. Nair (2019a,b) has reported that the unbridled use of urea has led even to global warming, because of the loading of stratosphere with nitrous oxide (N_2O), a byproduct of urea hydrolysis—a fact hitherto hidden by vested interests of the fertilizer industry. Dried aquifers, and vanishing bio diversity Nair

(2019a,b) due to continuous monoculture of wheat and rice is an environmental hazard. There are hundreds of acres of land stretches that have become barren, where once stood lush wheat and rice fields. Crop yields have plateaued or drastically declined. Two-thirds of the seriously eroded land is in Asia and Africa. About 25% of the cropped land in Central America is moderately to severely damaged. In North America, this is a small percentage—only 4.4%. Since the time of the green revolution, food production has declined dramatically in 80 developing countries during the past decade. Soil degradation is the major factor. In India of the 328.73 mha of geographical area, as much as 120.40 mha (nearly a third) has degraded soils, all due to the after effect of green revolution. Nearly 40% of the world's farming is done on very small parcels of 1 ha or less (Robison et al., 1981). Ignorance and poverty characterize this situation. Yet, emphasis on agriculture has always been confined mostly to large-scale farming. Large-scale farming, grand projects at huge costs and huge profits have been the order of the day of "development" for many decades. In a lighter vein, it can be said that even the "lebens raum" concept of Adolf Hitler, the master military strategist, who set out to conquer the world, had an echo in the inevitability of this modern-day fact. What else can justify the ruthless conquest of vast territories of land by the master military strategist, who set out to conquer the world or, more appropriately, the world's soils?

Despite the complexity of soil science and the emergent soil management practices, the basic concept of soil as a medium of plant growth can be expected to persist for an indefinite length of time. But, it is becoming increasingly clear that the earlier views on soil as merely the "supportive medium" for plant growth is giving place to newer ones on "intelligent managerial concepts" of this supportive medium Nair (2019a,b). This is amply illustrated by the shift in focus from the green revolution phase of the 1960s to mid-1970s, where application of increasing quantities of soil inputs, such as chemical fertilizers and pesticides was emphasized, to the "sustainable agriculture" phase from the early 1980s to the present (probably to continue?). Sustainable agriculture places more reliance on biological processes by adopting genotypes to adverse soil conditions, enhancing soil biological activity and optimizing nutrient cycling to minimize external inputs, such as fertilizers, and maximize their efficiency of use Nair (2019a, b). In fact, the paradigm of the earlier phase has given way to the emergent new paradigm (Sanchez, 1994) and this is clearly reflected in the dialogue of the world leaders during the Earth Summit in 1991 in Rio de Janeiro, Brazil, where Agenda 21 has incorporated six chapters on soil management issue (Keating, 1993). The focus of this review will be on the second paradigm inasmuch as prescriptive soil management is concerned with regard to understanding the dynamics of soil nutrient bioavailability, with specific focus on "The Nutrient Buffer Power Concept."

1. Efficient plant nutrient management: The key factor in sustainable crop production

Agricultural systems differ from natural systems in one fundamental aspect: while there is a net outflow of nutrients by crop harvests from soils in the first, there is no such thing in the second (Sanchez, 1994). This is because, nutrient losses due to physical effects of soil and water erosion are continually replenished by weathering of primary minerals or atmospheric deposition. Hence, the crucial element of sustainability of crop production is the nutrient factor. But, of all the factors, the nutrient factor is the least resilient (Fresco and Kroonenberg, 1992). The thrust of "high input technology," the hallmark of the green revolution, in retrospect, or the moderation of the" low input technology", the foundation stone of sustainable agriculture, in prospect, both dwell on this least-resilient nutrient factor. If the pool of the nutrients in the soil, both native and added, could be considered the "capital," efficient nutrient management might be analogous to raising the "interest," accrued from this capital in such a way that there is no great danger of the erosion of this capital. Hence, sound prescriptive soil management should aim at understanding the actual link between the "capital" and the "interest" so that meaningful management practices can be prescribed.

2. Soil tests and nutrient "bioavailability"

It is universal knowledge that soil tests are the basis for predicting nutrient "bioavailability." There are, perhaps, as many soil tests for each nutrient as there are nutrients. This review will not dwell on the merits or demerits of any single soil test or a group of them. Suffice to say that fertilizer recommendations traditionally are made at the point where marginal revenues equal marginal costs, which involve some positive synergism (De Wit, 1992). The most common result of this approach is the vast build-up in the soil nutrient pool in intensively cultivated soils (Whitmore and van Noordwijk, 1994). Data in the following Table (Table 1) indicate

Table 1 Nutrient balance (kg/ha/year) in intensively managed arable soils.

	N	P	K
Inputs			
Fertilizers	156	39	119
Other	32	–	9
Total	188	39	128
Outputs			
Harvest	103	16	91
Removal	24	–	–
Other	–	–	–
Total	127	16	91
Balance	61	23	37

After Frissel, M.J. (Ed.). 1978. Cycling of Mineral Nutrients in Agricultural Ecosystems. Elsevier. Amsterdam.

positive balances (in kg/ha/year) for N (61), P(213), and K(37) in intensive crop production systems (Frissel, 1978).

Over several decades, such positive balances can lead to a huge build-up of the nutrient capital, especially in the case of high-input, intensive agricultural systems, as in the case of many European, North American, and Scandinavian countries. A dangerous consequence of such huge soil build-up is nutrient contamination of ground water to such extremes that “environmental soil tests” become necessary to assess critical limits of nutrient pollution (Sharpley et al., 1993). In a state like Punjab in India, the “cradle” of Indian green revolution, ground water has been rendered non potable (Nair (2019a,b)). Nitrogen is a prime candidate for this scenario, especially in the temperate zone. At the other end of the spectrum are the marginal areas of tropical zone where inadequate replenishment of nutrient removal by crop growth and also nutrient loss by soil and water erosion has left that capital “in the red.” Initially fertile Alfisols of much of Africa with subsequent severe depletion of N and P (Yates and Kiss, 1992) are an example of this “nutrient bankruptcy.” Either way, contemporary soil tests are the basis on which prescriptive management practices are formulated.

3. Rating soil tests to define nutrient bioavailability and a fertility index

Most soil test laboratories around the world use some kind of "rating system" to evaluate soil test values. These rating systems invariably use qualitative terms, such as, "low," "medium" and "high" to describe the bioavailability of a specific soil nutrient. Admittedly, these terms denote different meanings in the context of soil nutrient bioavailability of a particular plant nutrient, and, at best, are empirical technologies. This problem has been recognized by researchers over the years. Morgan (1935) suggested a scale of 1–10 with 8 equal to the point of no response. Bray and Kurtz (1945) used relative yield or percentage sufficiency to describe the degree of deficiency, with 100 defined as the point of no response. The index below 100 follows the curvilinear relationship between soil test values and yield without the addition of the element. Above 100, the index displays a straight—line relationship indicating the relative margin of adequacy or the proximity to an excessive level. To eliminate the need for a percent sign, the values are referred to as "Fertility Indices" and they are reported to the nearest multiple of 10 from 0 to 9990 (Cope and Evans, 1985). In addition to ratings, most laboratories use some method of reporting results more precisely, mainly for use by farmers in record keeping and monitoring soil fertility. Some report kg/ha or lb./a or ppm extracted, but, these would be confusing to farmers, because each element has a different level for a specific degree of adequacy (Cope and Evans, 1985). For instance, the adequate or critical level for one soil may be 25 ppm P, 120 ppm K, 200 ppm Ca and 30 ppm Mg. Adequate levels in other soils and from other extracting procedures would be different for each element (Cope and Evans, 1985).

Despite the fact that a number of soil tests and others such as Diagnosis and Recommendation Integrated Systems (DRIS) are in vogue to predict nutrient bioavailability, it must be said that a universal picture is yet to emerge in this field with regard to precise bioavailability prediction. This is primarily because a soil test in the laboratory can never simulate plant root absorption of a specific nutrient in a field soil, though most of the time the assumption is that it does. In the final analysis, it is the plant and plant alone which will decide whether or not the nutrient is bioavailable. This review examines the important question, whether there is an alternative and more precise approach to quantify the nutrient bioavailability. And, it is in this context that "The Nutrient Buffer Power Concept" comes under focus.

4. The buffer power and effect on nutrient bioavailability

4.1 Basic concepts

In any nutrient management approach that is sound and reproducible, one must start with a basic understanding of the chemical environment of plant roots. When we consider this, the first term we come across is the "soil solution," because the plant roots are bathed in it and is most affected by its chemical properties. The Soil Science Society of America (1965) defines soil solution as "the aqueous liquid phase of the soil particles and other soluble materials." Adams (1974) has given a simple definition. "The soil solution is the aqueous component of a soil at field-moisture contents." Perhaps, it is important to emphasize here that much of contemporary soil testing has considered a soil extract as synonymous with the soil solution. Since soil extraction is supposed to simulate plant root extraction, it is pertinent to consider the chemical environment of the root, though briefly, from this angle. It is worth noting that the chemical environment of roots in natural soil systems is so obviously complex that both soil scientists and plant physiologists have been unable to provide a precise definition. If this complex chemical system is to be accurately quantified, thermodynamic principles will need to be used to evaluate experimental data. Even then, limitations are obvious, as in the case of K, one of the major nutrients in plant nutrition, where the thermodynamic investigations are quite often inapplicable under field conditions. This is because, although a quasi-equilibrium in K exchange can be achieved in the laboratory, these conditions are seldom, if ever, attained in field conditions (Sparks, 1987). Agricultural soils are for the most part, in a state of disequilibrium owing to both fertilizer input and nutrient uptake by the plant root. It thus appears that a universal and accurate definition of a root's chemical environment awaits the proper application of thermodynamics for the root's ambient solution (Adams, 1974), or even kinetics, as in the case of K (Sparks, 1987), where thermodynamics has been found inadequate.

Soil extractions with different extractants provide a second approach in defining the root's chemical environment. This approach has been particularly successful in understanding cases like P solubility, soil acidity, and K fixation. However, this approach also fails to define precisely the root's chemical environment. Though this approach also suffers from deficiencies, such as the extractants removing arbitrary and undetermined amounts of solid-phase electrolytes and ions (or the extractants causing precipitation of salts or ions from the soil solution) and the soil–plant interrelationship defined in terms of the solid-phase component of the soil, even though the sold phase is essentially inert as it maintains thermodynamic equilibria with the solution-phase (Adams, 1974), the latter part could be researched more to understand how the solid phase-solution phase equilibrium can be interpreted to give a newer meaning to quantifying nutrient bioavailability. It is in this context that the role of the plant nutrient's "buffer power" assumes crucial importance.

The close, almost linear, relationship in a low concentration range of less than 0.5 mM for NO_3^--N, NH_4^+-N, K^+, $H_2PO_4^-$, and HPO_4^{2-}, which has been established by numerous solution culture experiments, can be quantitatively described by the following Equation

$$U = 2\pi r\alpha\, C_r$$

where U is the uptake of a 1-m root segment, r is the root radius in centimeter, C_r is the concentration of the ion at the root surface, and α is the root absorbing power (Mengel, 1985). The metabolic rate of the root determines its absorbing power. A high root absorbing power would imply that a relatively high proportion of nutrient ions coming in contact with the root surface is absorbed and *vice versa*. The nutrient ion concentration at the root surface (C_r) depends on α since a high root absorbing power tends to decrease C_r; it also depends on the rate of movement of the nutrient from bulk soil toward the root surface (Mengel, 1985). Diffusion and/or mass flow controls this movement. But, it is now established that nearly 95% of the movement for nutrients such as P, K and Zn, (the last among heavy metals), and, possibly NH_4^+, is by way of diffusion. When root uptake of an ion species is less than its movement toward it, accumulation of the ion species on the root surface is bound to occur, as has been shown in the case of Ca^{2+}, where mass flow contributes to this accumulation (Barber, 1984). The diffusive path for ions, such as P and K, which plant roots take up at high rates but which are in low concentration in the soil solution near the root, is the concentration gradient. In a sense, the effective diffusion coefficient which quantifies the diffusive path and the buffer power are analogous to each other because the diffusive flux across the root surface is integrally related to the nutrient buffer power. This has been shown to be true in the case of P where a highly significant positive correlation between the two was found to exist in 33 soil samples obtained from experimental sites in the United States and Canada (Kovar and Barber, 1988). However, in a routine laboratory set up, it is far more easier to measure the buffer power than the effective diffusion coefficient and this review will further focus on the question how buffer power can be quantified without recourse to cumbersome analytical techniques and how its integration into routine soil test data will considerably improve predictability of nutrient uptake.

5. Measuring the nutrient buffer power and its importance in affecting nutrient concentrations on the root surface

The ability to predict the mobility of dissolved chemicals, such as fertilizers, in the soil is of considerable value in managing fertilizer applications. Soil testing, for the most part, in its essence, aims to achieve this. While modeling transport and retention of ions from thermodynamic (Selim, 1992), kinetic (Sparks, 1989), and mechanistic (Barber, 1984) angles could be very informative, the importance of translating this information into practically feasible procedures in crop production calls for an understanding not only of the basic concepts, but, of their intelligent field application as well with test crops. In a dynamic state of plant growth, the concentration of any nutrient on the root surface is nearly impossible to measure precisely, since both the nutrient in the plant tissue and the root absorbing power which directly affects it, change quickly due to root metabolic processes. The inability of even mechanical-mathematical models to accurately predict nutrient influx rates has recently been highlighted (Lu and Miller, 1994). Hence, if an effective soil testing procedure is to be devised for a nutrient, one must resolve the problem of quantifying the nutrient concentration on the root surface rather indirectly, even if it is impossible to resolve it directly, for the reasons mentioned above.

Using Fick's first law,

$$F = -D(dC/dx)$$

where F is the flux, dC/dx is the concentration gradient across a particular section, and D is the diffusion coefficient, Nye (1979) has suggested that the formula can be applied to both ions and molecules. The negative sign for D implies net movement from high to low concentration. Although for molecules in simple systems like dilute solutions D may be nearly constant over a range of concentrations, for ions in complex systems like soils and clays D will usually depend on the concentration of the ion, and on that of other ions, as well (Nye, 1979). Nye (1979) has further suggested that though Fick's first law may be derived from thermodynamic principles in ideal systems, in a complex medium such as the soil, the above equation may be regarded as giving an operational definition of the diffusion coefficient. Thus, Nye (1979) defines the diffusion coefficient as

$$D = D_1\,\theta\,f_1\,(dC_1/dC) + D_E$$

where D_1 is the diffusion coefficient of the solute in free solution, θ is the fraction of the soil volume occupied by solution and gives the cross-section for diffusion, f_1 is an impedance factor, C_1 is the concentration of solute in the soil solution, D_E is an excess term which is zero when the ions or molecules on the solid have no surface mobility, but, represents their extra contribution to the diffusion coefficient when they are mobile. D_E can generally be ignored since only in rare instances will it play any role in diffusion of plant nutrient ions in soil (Mengel, 1985). From the point of view of nutrient bioavailability, dC_1/dC, which represents the concentration gradient, assumes crucial importance, as we shall see below.

The term dC_1/dC, where C_1 is the concentration of the nutrient ion in the soil solution and C is the concentration of the same ion species in the entire soil mass, assumes considerable significance in lending a practical meaning to nutrient bioavailability. If we ascribe the term "capacity" or "quantity" to C and "intensity" to C_1, we have in this term an integral relationship between the two parameters that may crucially affect nutrient bioavailability. Since the concentration gradient of the nutrient depletion profile in the zone of active nutrient uptake depends on the concentration of the ion species int the entire soil mass, (represented by "capacity" or "quantity") in relation to the rate at which this is lowered on the plant root surface by the uptake process (represented by "intensity"), it could be argued that a quantitative relationship between the two should represent the rate at which nutrient depletion and/or replenishment in the rooting zone should occur (Nair, 1984a,b). This relationship has been functionally quantified by Nair and Mengel (1984) for P in eight widely differing central European soils (Table 2), and the term dC_1/dC has been referred to as the "nutrient buffer power." Nair and Mengel (1984) used electro-ultra-filtration (EUF) to quantify C_1, while using an incubation and extraction technique to quantify C. For P, C it was found to closely approximate isotopically exchangeable P (Keerthisinghe and Mengel, 1979), but, in the experiments conducted by Nair and Mengel (1984), it was estimated by the extraction of incubated soil

Table 2 Comparison of the P buffer power of 8 widely differing central European soils (determined by two different techniques).

	Regression function		**Correlation coefficient ("r")**	
Soil	**(1)**	**(2)**	**(1)**	**(2)**
Benzheimer Hof	Y = 18.8× + 7.94	Y = 0.23× +8.98	0.912	0.995
Hungen	Y = 38.2× - 1.03	Y = 4.32 + 0.25×	0.967	0.997
Oldenburg B6	Y = 49.8× + 0.52	Y = 0.72 + 0.26×	0.994	0.999
Wolfersheim	Y = 70.3× +0.03	Y = 0.11 + 0.27×	0.998	0.983
Obertshausen	Y = 70.5× +2.66	Y = 2.89 + 0.30×	0.966	0.998
Oldenburg B3	Y = 73.6× +2.07	Y = 0.61 + 0.31×	0.994	0.997
Klein-Linden	Y = 75.0× +0.38	Y = 1.81 + 0.32×	0.999	0.991
Gruningen	Y = 75.4× +0.89	Y = 3.62 + 0.36 x	1.000	0.996

Notes: The *b* values in the regression functions represent the P buffer power of each soil. In regression functions (1) (after Nair and Mengel, 1984) Y = CAL-P (Schuller's method) and in regression functions (2) (after Nair, 1992a,b) Y = the author's method. x in both regression functions refers to electro-ultra-filterable- P. Note the very high "r" values in all the cases, (Significant at 99% confidence level). In fact, in Gruningen soil it attains unity, which is a remarkable statistical observation, hardly obtained in biological relationships, unlike in physical ones. The soils are arranged in their sequential ascending P buffer power.

with an extractant which was a mixture consisting of 0.1 M Calcium lactate + 0.1 M Calcium acetate + 0.3 M Acetic acid at pH 4.1. The extractant exchanges adsorbed phosphate and dissolves Calcium phosphates, except apatites; the method known as "CAL-Method," developed by Schuller (1969), is now widely used in central Europe. In the case of K^+ and NH_4^+—N, C denotes the concentration of exchangeable, and to some extent non exchangeable fractions (Mengel, 1985). Since only very low concentrations in the range of 2.0 μ M may be attained on the root surface for both P and K (Classen et al., 1981; Classen and Barber, 1976; Hendriks et al., 1981), Nair and Mengel (1984) had to use EUF technique to quantify C_1. Thus, the nutrient ion depletion around the roots which is caused by the diffusive flux of the nutrients toward the root surface is related to both the "quantity" and "intensity" parameters, a quantifiable relationship between both represents the buffer power specific to the nutrient in question and the soil. A growing root will at first encounter a relatively high concentration of P which is in the range of the concentration of the soil solution (Nair and Mengel, 1984). As uptake continues, a depletion will occur at the root surface. This depletion profile gets flatter with enhanced nutrient uptake

(Classen et al., 1981; Hendriks et al., 1981; Lewis and Quirk, 1967). But, it is the capacity of the soil to replenish this depletion which ensures a steady supply of nutrient ions to the plant root without greatly depressing its average concentration on the root surface. It is the nutrient's buffer power that decides these depletion and/or replenishment rates. A soil with a high P buffer power implies that the P absorbed from the soil solution is rapidly replenished. In such a case, P concentration at the root surface decreases only slowly and mean P concentration at the root surface remains relatively high. In soils with a low P buffer power, the reverse is true and P concentration at the root surface is rapidly diminished and remains relatively low. This has been experimentally proved for P (Nair, 1992a,b; Nair and Mengel, 1984). This phenomenon also holds true for Zn^{2+} (Nair, 1984a,b), K (Nair et al., 1997), and NH_4^+-N (Mengel, 1985).

6. Quantifying the buffer power and testing its effect on nutrient bioavailability

6.1 Example of phosphorus

When the exchangeable and desorbable nutrient ions are plotted on the Y-axis and the corresponding concentrations of same ions in the equilibrated solution on the x-axis, we obtain a slope, the steepness of which will represent the buffer power of that ion. The P buffer power of the 8 central European soils, mentioned earlier, are given in the following table (Table 2).

The "quantity" factor (C) was determined by two techniques (1) by an incubation and extraction technique (Nair and Mengel, 1984) and (2) by an adsorption-desorption equilibrium technique (Nair, 1992a,b), while the "intensity" factor (C_1) was determined by the EUF (Nemeth, 1979) technique. It is highly remarkable that the correlation coefficients, in the case of all soils investigated, between C (represented by Y) and C_1 (represented by x) are very highly significant as indicated by the r values, which in all cases were close to unity and in one case (Gruningen soil) it was unity, a remarkable relationship in biological systems, unlike in physical ones. This very clearly establishes the fact that the techniques employed will accurately quantify the concentration gradient for P in the soils investigated when plants are grown in these soils. If this hypothesis is true, the impact of P buffer power will clearly be reflected in the P uptake by the test plant since the P buffer power becomes the most crucial factor in predicting P bioavailability to growing plant root. This can be tested by correlating P uptake with the routine soil test data, without integrating the P buffer data and with

Table 3 Correlation coefficients for the relationship of P uptake *vs* routine P soil tests without (A) and with (B) integration of the P buffer power.

Details	A	B
P uptake *vs* EUF-P	0.393[a]	0.8870[b]
P uptake *vs* CAL-P	0.714[b]	0. 9415[b]

[a] Significant at 5% confidence level.
[b] Significant at 1% confidence level.
Notes: After Nair and Mengel (1984). Uptake was measured using the Neubauer seedling technique using summer Rye (*Secale cereale*) as test plant. Electro-Ultra-Filterable P (EUF—P) and Ca lactate + Ca acetate + Acetic Acid mixture (CAL—P) (Schuller, 1969).

integrating the same in the computations, using a multiple regression function Y = a + bx + cz, where Y=P uptake by the test plant, x = the routine soil test data, and z = P buffer power, and, a and b are constants. The impact of the P buffer power on P uptake *vis-a-vis* P bioavailability is shown in the following table (Table 3).

In both cases of routine soil test data, the predictability of uptake was remarkably improved by incorporating the P buffer power data. The coefficient of determination (CV), which is a measure of the precision of these computations, increased from 15% to 79% in the case of EUF-P ad from 51% to 89% in the case of CAL—P. This, in effect, means that by integrating the P buffer power data, the precision of P uptake predictability increased by 427% in the case of EUF-P and 74% in the case of CAL—P. Obviously, the increase has been very remarkable in the case of EUF—P. This also shows that the quantification of either the intensity factor alone (as in the case of EUF-P soil test data) is insufficient to precisely predict P bioavailability. A substantial proportion of the variance in P uptake is contributed by the P buffer power. From the above arguments, it follows that soils with a low buffer power for a particular nutrient requires a high initial concentration of the ions and vice vera, to maintain optimal supply to the plant roots. Mengel and Busch (1982) provided experimental evidence to substantiate this in the case of K^+ of Rye grass growing in 9 central European soils widely differing in physiological properties. This would also point to the fact the relationship between the buffer power of the nutrient and the "critical" or "cut off" limit where plant yield is perceptibly reduced have an inverse relationship—a soil with a low buffer power for the nutrient resulting in a higher critical concentration in the plant tissue as compared to a soil with a relatively high buffer power for the nutrient having lower critical concentration in the plant tissue for the same nutrient. This has been found to be true in the case of K^+ (Mengel and Busch, 1982) and Nair (unpublished data). Nair(unpublished data) found a very highly significant negative correlation between the plant top critical concentration for P and the P replenishment rate in the soil substrate which the P buffer power represents in summer Rye (*S. cereale* L.).In the case of dry matter yield this relationship was significant, but positive. This suggests that the P buffer power controls the P depletion and/or replenishment in the rooting zone and its accurate measurement would be the key to a precise quantification of P bioavailability. Remarkably, the P buffer power of the soils had no direct relationship to clay or humus content, or soil pH (Nair and Mengel, 1984).

7. P buffer power measurement vs soil test P data for dependability of nutrient bioavailability prediction

The important question on which the choice between P buffer power and/or contemporary or routine soil tests has to be made depends on what one aims to achieve inasmuch as prescriptive soil management practices are concerned. Contemporary soil tests are based on philosophies and procedures which were developed several decades ago, with essentially no change in the general approach. In order to be accurate, a soil test must measure both solution concentration of nutrients and their rates of movement through the soil. The buffer power approach seems to accomplish this. Virtually no soil test provides information about the most important factors which govern phosphate bioavailability, which are phosphate concentration in the soil solution and the phosphate buffer power. In the widely used bicarbonate method (Olsen et al., 1954) or using water extraction (van der Paauw, 1971), the P quantities recovered may be 10–100 times more than that found in the soil solution (Mengel, 1985). Thus, all the methods which use an acid extraction extract much more phosphate from the “labile pool” (Larsen, 1967). Acid extractions, in certain instances, can also extract phosphate that under normal crop growth will be found unavailable to plant roots. The discrepancy between contemporary soil tests and crop response to P application has been highlighted (Nair, 1992a,b). In an extended study comparing 8 central European soils with extremely differing physico-chemical properties, Nair (1992a,b) found that the response to a wide range of P application to summer Rye grass (*S. cereale* L.) had no relevance at all to routine soil test data. Three routinely used soil tests, namely, the 0.01 M $CaCl_2$ test

(Mattingly et al., 1963), the CAL-P test (Schuller, 1969) and EUF-P test (Nemeth, 1979), were considered. The fluctuations in shoot P concentration with regard to P application were not at all reflected by the soil test values. Two of the soils which were at either extremes of "availability" (as characterized by the soil tests) showed totally divergent responses to P application, while the response was found to be very consistent when the soil's P buffer power data was incorporated in the computations. This proves that the accuracy of routine soil tests can be vastly enhanced by integrating the corresponding P buffer power of the soil in the computations.

Buffer curves are extremely important in determining phosphate bioavailability. The equilibrium of a soluble P fertilizer incorporated into a soil is not merely a function of adsorption and/or precipitation, but, also, of diffusion. Even if the fertilizer source is soluble and well mixed with the soil, the phosphate distribution is not homogenous, resulting in areas of high or low phosphate concentrations. Since phosphate diffusion is a slow press, an even distribution brought about by diffusion takes time. The contact period between phosphate fertilizer and the soil has an impact on P bioavailability, which has practical importance, and this can be depicted by buffer curves (Barekzai, 1984). He has plotted P quantity (Ca lactate soluble) on y-axis and P intensity (EUF—P) on the x-axis. The curve showed that the solubility of applied P fertilizer decreased considerably during 6-weeks of incubation as compared to the time immediately after application. In fact, such curves show the aging process of P and reflect the phosphate concentration of the bulk soil solution. The steepness of the curve ("b" values in the regression functions) at a given phosphate concentration reflects the P buffer power. The data in Table 2 show this relationship for 8 representative central European soils, varying widely in their physico-chemical characteristics (Nair and Mengel, 1984). Considerable differences can be found among soils in their P buffer power (Table 2); acid tropical soils invariably have a high P buffer power, meaning that at a given quantity of bioavailable P, the P concentration in the soil solution is relatively low (Pagel and van Huay, 1976). With soils widely differing in their P buffer power, at an identical quantity bioavailable P, the P concentration of the soil solution can differ by a factor of 100 (Barekzai, 1984).

8. Example of potassium

As discussed with regard to P, the dynamics of K bioavailability follows a similar pattern to that of P, especially in the range of low concentrations. Becket (1971) has used the activity ratio for K^+ and Ca^{2+} to determine K bioavailability. Since interlayer K would play an important role in K bioavailability, it would be more logical to consider K buffer power in determining K bioavailability. Routinely, it is the ammonium acetate extraction which is widely used to characterize K bioavailability. The reason that this may not be suitable to characterize exchangeable K is that in the routine extraction, only the top layer is extracted, while interlayer K from which deep-rooted plants can feed is ignored (Nair et al., 1997). There is extensive evidence to substantiate this (Mengel, 1985). The importance of interlayer K in the nutrition of deep-rooted and perennial crops, such as, Cardamom (*E. cardamomum* M.), the world's most valuable spice crop, next to only Black pepper, has been highlighted by Nair et al., 1997.

9. The importance of K buffer power determination in predicting K bioavailability in perennial crops

As in the case of P, the K buffer power assumes great importance in predicting K bioavailability, especially with regard to deep-rooted and perennial crops. With annual or biennial crops, K bioavailability has been studied with reference to the exchangeable K. However, with perennial and deep-rooted crops non-exchangeable and interlayer K^+ play a crucial role in K bioavailability. Three soil parameters that control the rate of K supply to the plant roots which have been used to predict the K absorption by plant roots are (1)the K intensity in the soil solution (2) the K buffer power and (3) the effective diffusion coefficient (Becket, 1971; Classen et al., 1986; Mengel and Kirby, 1980)). K buffer power can be directly obtained from the K-quantity-K intensity relationship. The effective diffusion coefficient depends on, among other factors, the K buffer power. Plants feed not only from exchangeable K but also from nonexchangeable K, which mainly consists of K^+ trapped in the interlayers of nonexpanded 2:1 clay minerals (Hoagland and Martin, 1933; Schachtschabel, 1937).

Exchangeable K comprises that which can be exchanged with NH_4^+ ion, and is primarily planar K^+, the interlayer K^+ of expanded 2:1 clay minerals and some of the K^+ at the interlayer edges of nonexpanded 2:1 clay minerals. Interlayer K^+ of nonexpanded clay minerals such as illites and interlayer and lattice K^+ micas (present in feldspars) constitutes the nonexchangeable K^+. The interlayer K^+ is of particular importance in the nutrition of deep—rooted and perennial crops, such as, cardamom, as demonstrated by Nair et al. (1997), and also for annual crops such as rye grass (*Lolium perenne* cv.Taptoe) (Mengel and Uhlenbecker, 1993).

In most of the soil tests for K bioavailability, nonexchangeable K is not considered. For cereals such as wheat (*T. aestivum*), 80% of the K^+ extracted by the crop came from nonexchangeable K pool. This is one of the most important reasons for the poor soil test-crop response relationship with regard to K fertilizer application based on such tests (Kuhlmann and Wehrmann, 1984). The contribution of nonexchangeable K to plant bioavailability was assessed by 1 M HCl extraction by Schachtschabel (1961), similar to the 1 M HNO_3 extraction proposed by Pratt (1965) and McLean and Watson (1985). However, the efficiency of 1 M HCl extraction to quantify plant available K from the nonexchangeable pool has been disputed (Boguslawski and Lach, 1971; Grimme, 1974; Kuhlmann and Wehrmann, 1984). Soils containing primarily 2:1 clay minerals, such as, vermiculite and illite have interlayer K in excess of crop demand. However, the bioavailability of interlayer K of nonexpanded minerals is independent of the quantity of interlayer K as such, but, dependent on its release rate depending on the type of K^+ bearing minerals (Sparks, 1987). Release of K from interlayer positions is an exchange and diffusion process (von Reichenbach, 1972). While exchange depends on the cation species and their concentration near the surface of the mineral, diffusion depends largely on the expansion of the mineral and therefore on soil moisture. Net release of K will only occur if the K concentration of the adjacent solution is low (Mengel, 1985). Martin and Sparks (1983), while studying the release of nonexchangeable K^+ from sandy and loamy sand extracted with an H^+ charged ion exchanger resin, found large release of K^+ with a K^+ concentration of about 1–2 μ M in the contact solution. The concentration may approximate the rhizosphere concentration level. Under submerged conditions, as in rice, there can be a depletion zone for K in the rhizosphere (Xu and Liu, 1983). Plant roots act as a sink for K and maintain the K solution concentration at very low levels (Kuchenbuch and Jungk, 1984). This would cause further release of interlayer K (Mengel, 1985). These considerations point to the important fact that a precise quantification of K bioavailability, where non exchangeable interlayer K is concerned, hinges primarily on its release rate, which the K buffer power attempts to quantify, as we shall see in the following discussion.

Nair et al. (1997) selected cardamom (*E. cardamomum* M.) as the test plant to demonstrate the importance of nonexchangeable and interlayer K on K bioavailability *vis-à-vis* K buffer power. The choice of cardamom was because it is a very deep-rooted perennial crop, which can grow in the field for more than 50 years. The K buffer curves were constructed by a two-step extraction in which 1 N HNO_3 was used to determine the K "quantity" (Wood and De Turk, 1941), and, 1 N NH_4OAc to determine K "intensity". The NH_4OAc extraction is universally used to determine the exchangeable K. The contribution of nonexchangeable K to plant roots has been assessed by 1 M HCl extraction (Schachtschabel, 1961) and also by 1 M HNO_3 extraction (McLean and Watson, 1985; Pratt, 1965). Nair et al., 1997regressed 1 N HNO_3 extractable K (y) over 1 NH_4OAc extractable K (x) to obtain the K buffer given in the following table (Table 4) .

Data in Table 4 clearly indicate that the Coorg soils, which has a much higher K buffer power, produced cardamom yield which was twice of that obtained in Idukki soils. The higher K buffer power of the Coorg soils was clearly reflected in the cardamom yield. By comparison, the 1 N NH_4OAc extractable K content had no significant relationship with leaf K (Table 5)

Table 4 K buffer power of cardamom growing soils from two regions of southern India (Kerala and Karnataka) extensively growing the crop as a plantation crop

Region	Regression function (Y = a + bx)	r	Crop yield(kg/ha)
Coorg (Karnataka State)	142.38 + 1.4443x	0.8561[a]	155
Idukki (Kerala State)	592.46 + 0.9172x	0.5799[b]	80

[a] Significant at a confidence level of 1%.

[b] Significant at a confidence level of 5%.

Notes: b values in the regression functions refer to the K buffer power of the soils. The K buffer power refers to the poled data of the soil samples obtained from 94 locations covering an area of about 24,000 ha. Yield data refer to the same regions.

After Nair, K.P.P., Sadanandan, A.K., Hamza, S., and Abraham, J. 1997. The importance of potassium buffer power in the growth and yield of cardamom. J. Plant Nutr. 20, 7 & 8, 987–997.

Table 5 Correlation coefficients and regression functions for the relationship leaf K (Y) *vs* exchangeable K (x, NH_4OAc extraction)

Details	Regression function Y = a + bx	Correlation coefficient®
Leaf K *vs* exchangeable K	Coorg	
	Y = 1.2701 + 0.0004	0.2064
Leaf K *vs* exchangeable K	Idukki	
	Y = 1.6448 + 0.000006	−0.006

Notes: The correlation coefficients refer to the leaf samples from 94 locations from which soil samples were drawn to calculate the K buffer power. In cardamom, the 5th pair of leaves from the top of each panicle bearing tillers are sampled for K analysis.

After Nair, K.P.P., Sadanandan, A.K., Hamza, S., and Abraham, J. 1997. The importance of potassium buffer power in the growth and yield of cardamom. J. Plant Nutr. 20, 7 & 8, 987–997.

Table 6 Correlation coefficients ® for the relationship between leaf K (Y) and exchangeable K (x, NH_4OAc extraction) for the pooled data from 94 locations from two regions (Coorg, in Karnataka State) and Idukki (in Kerala State) without (A) and with K buffer power data integration in the computations.

	Correlation coefficient	
Details	**A**	**B**
Leaf K *vs* Exchangeable K	0.2510	0.4367[a]

[a]Significant at 1% confidence level.

and further the integration of the K buffer power in the computations with the routine K soil test data (NH_4OAc extractable K) remarkably improved the relationship (Table 6).

Cardamom is a heavy feeder of K, and in India, which grows most of this valuable cash spice crop, and in other countries of the Asian and Africa continents, where cardamom is grown, its K fertilizer needs are almost always based on exchangeable NH_4OAC extraction. Data in Table 5 unequivocally show the ineffectiveness of this extraction to precisely predict K bioavailability; further, data in Table 6 show how the situation is remarkably improved by the integration of the K buffer data into the computations. A substantial variation (302.7%) in leaf K is attributable to the K buffer power. These results have been obtained from a very extensive area (20,000 ha) and demonstrate the true effectiveness of scheduling K fertilizer applications based on K buffer power data, in addition to routine soil K test data, rather than simply based only on the latter.

The K buffer power in this instance integrates both exchangeable (NH_4OAc extraction and nonexchangeable and/or interlayer K (HNO_3 extraction) and this provides an accurate estimation of K depletion around the plant roots. In a recent study (Mengel and Uhlenbecker, 1993) on K bioavailability from interlayer K to rye grass (L. *perenne* L. cv.Taptoe) it was observed that the rate constant (*b* values) obtained by correlating K released (from the interlayers of clay minerals) and time periods by a modified EUF technique was closely related to K uptake and represented the K bioavailability index from nonexchangeable K. These rate constants, according to the authors, are of utmost importance because they provide information on the bioavailability of nonexchangeable K in attaining maximum yield; and a set of "critical *b*" values toward attaining this objective have been reported. It appears that the rate constants of Mengel and

Uhlenbecker (1993) are analogous to the K buffer values reported by Nair et al. (1997), because, though the techniques differ in their details, they have accomplished the same objective of precisely predicting K bioavailability from the nonexchangeable pool and/or interlayer K. The capability of tapping interlayer K varies among plant species. For instance, Steffens and Mengel (1979) found that rye grass (*L. perenne*) could feed from the interlayer K^+ for a longer period without yield depression, while red clover (*Trifolium pratense*) could not. These authors reported that since L. *perenne* had a longer and deeper root system compared to *T. pratense*, the former could grow satisfactorily, while relatively low K^+ concentration at which the latter would already suffer from K deficiency (Steffens and Mengel, 1981). The differences in root mass, root length, and root morphology between monocots and dicots explain the better K^+ feeding capacity from interlayer K^+ of the former compared to the latter (Mengel, 1985).

Cotton (*Gossypium hirsutum* L.) is another deep-rooted long-duration plant on which K buffer power exerts considerable influence on K acquisition. Brouder and Cassman (1994) evaluated K uptake by cotton in a vermiculite soil using mechanistic models and observed that initial model output produced both substantial under-and overpredictions of whole plant K accumulation. Model predictions were greatly enhanced by estimating the K buffer power. They further concluded that the contribution of the fixed K pool on the plant bioavailable K pool was likely to be substantial and that this influence must be captured in estimates of the soil K buffer power. These studies were conducted after observing in a San Joaquin Valley cotton field in California that cotton exhibited late season K deficiency while other crop species remained unaffected. In such cases, the precise estimation of K buffer power will lead to far more dependable K fertilizer recommendations than by routine NH_4OAc extractions.

Though it has been long recognized (Schachtschabel, 1937) that the soil K fraction which is not exchangeable by NH_4 ions (nonexchangeable K) may be important for the supply of K to plants, it is only of late that researchers have paid more attention to this aspect. The work of Sparks and Huang (1985) has very carefully examined the release mechanism from nonexchangeable source and the factors controlling it. Considerable portions of initially nonexchangeable K can be utilized by plant roots even within a few days (Kuchenbuch and Jungk, 1984). The depletion zone, however, extends into the ambient soil for 2 mm only. Hinsinger et al. (1992) embedded phlogopite in agar and observed that the interlayer K of this mineral was entirely lost in the close vicinity of ryegrass roots within 4 days.

Since the process limiting the rate of K uptake in the rhizosphere may be K transport through the soil, rather than the release from minerals as such, some researchers have focused their attention on this aspect. One such example is the mechanistic mathematical model of Classen and Barber (1976). Classen et al. (1986) and Classen (1990) have successfully applied the model referred to above to predict K depletion profiles in soil around plant roots. Meyer and Jungk (1993) have used these models to predict K uptake by test plants from exchangeable and nonexchangeable K sources. They reported that 64–79% of the K taken up by wheat (*T. aestivum* L.) and sugar beet (*Beta vulgaris* L.) was derived from the rapidly released exchangeable and 21–36% or less from the nonexchangeable or less mobile soil K fraction.

The buffer power describes the relationship between adsorbed K and the K concentration of the ambient solution. In simulation models it is assumed that this relationship is linear, and hence, independent of soil solution concentration. However, in desorption studies with soil a sharply curved buffer relationship could be found, and, Meyer and Jungk (1993) have referred to it. Very near the plant roots the soil can be subjected to a curved buffer function since plant roots strongly reduce the soil solution concentration.

An important aspect to be considered in the utilization of nonexchangeable K is the role of plant roots. Plant species differ in their ability to utilize nonexchangeable K and this has been attributed to the differences in root length (Mengel and Steffens, 1985). When radial distance between two single roots decreases, consequently increasing root density, this would result in the overlapping of the depleted soil volumes between these roots. This would lead to decrease in the rate of K uptake per unit root. In the case of rapidly diffusing K fraction, which has a higher mobility, the competition effect between roots would be very intense. There is evidence to support this view, as shown by the work of Mitsios and Rowell (1987), who observed that the contribution of nonexchangeable K increased with a corresponding increase in root density. Additionally, the differences in root hair length and density among plant species (Fohse et al., 1991) affect their ability to acquire soil K. Accordingly, the work of Meyer and Jungk (1993) has shown that K uptake was higher when they included root hairs as well in their model calculations. Since root hairs contribute to an increase in root absorbing surface, a reduction in the distance of diffusion from the site of K release to the site of K uptake, and an increase in the K concentration gradient, they can be expected to exert a pronounced effect on K bioavailability from the less mobile K fraction.

10. The commercial significance of K buffer power determination in K fertilizer management for perennial crops

The commercial significance of K buffer power determination for accurate and reproducible fertilizer recommendations for perennial crops like cardamom assumes great importance in those countries which are faced with the situation of importing these fertilizers, for lack of manufacturing capacity domestically, because such imports are a great pecuniary stress on the national exchequer. India is a case in point. The recent decontrol of both phosphatic and potassic fertilizers in India by the central government resulted in the escalation of prices of both overnight. In a situation like that, the farmers become extremely wary of their field use and unless the fertilizer application is cost-effective, faith in their use would be shattered, more so in the scientists who make such recommendations.

The K fertilizer recommendation for cardamom has been based exclusively on NH_4OAc extraction. The investigation of Nair et al. (1997) showed its ineffectiveness. Though the importance of K buffer power in predicting K bioavailability has been reported earlier, these research reports related mainly to annual crops such as white clover (During and Duganzich, 1979) and rye grass (Mengel and Busch, 1982); the work of Nair et al. (1997) was the first of its kind in a perennial crop like cardamom.

11. Case studies with African soils

In Central Africa, The Republic of Cameron is a small country. This author had the opportunity to test the effectiveness of "The Nutrient Buffer Power Concept," while he held the position of the Professor & Head of the Department of Soil Science at The University Center, Dschang, in The Republic of Cameroon.

Soils are lateritic, highly acidic, with the pH between 4.5 and 5.0. The country's agricultural scenario is mainly confined to cocoa, coffee and rubber. Among the cereals, both rice and maize are popular. The country has a huge animal (cattle) population; hence, good, palatable and nutritious fodder is a great necessity for the country's dairy industry. With this view in background, an attempt was made to introduce white clover (*T. repens* L.) from the United States, and the following investigation with regard to the nutrition of white clover was taken up at The University Center, Dschang.

Table 7 Physico-chemical characteristics of the experimental soils.

Details	**Soil 1**	**Soil 2**
Sand(%)	48	7
Silt(%)	18	41
Clay(%)	34	52
Organic carbon(%)	5.6	8.2
Total N(%)	0.37	0.48
pH (1 N KCl)	4.4	5.0
CEC (meq/100 g soil)	9.5	20.7
Base saturation (%)	21.8	32.2
Available P (ppm)	2.1[a]	13.0[a]
Available P (ppm)	3.7[b]	4.7[b]
Available P (ppm)	Traces[c]	3.2[c]
Available K (mequiv./100 g soil)	0.18[d]	0.27[d]
Available K (meqiv/100 g soil)	0.17[c]	0.21[c]

[a] Olsen's test.
[b] Bray II test.
[c] 0.01 M $CaCl_2$ extraction.
[d] NH_4OAc test.

Notes: All of the below-mentioned soil tests are "routine" soil tests for available P and K. The only exception is the 0.01 M $CaCl_2$ extraction which gives the P concentration in the equilibrium suspension of soil (Mattingly et al., 1963).

Experimental Soils: The soils investigated are widely varying. Their physico-chemical characteristics are listed in the following table (Table 7).

The main objective of the investigation was to examine how well the "Buffer Power Concept" explains the soil bioavailability of P and K in very problematic African soils. And, white clover was chosen as the test crop because there is acute shortage of palatable and nutritious fodder for the cattle livestock in the country. What is generally fed to the cattle is the post-harvest waste of either rice or maize. This does not ensure good milk yield. It was thought that livestock industry had a tremendous potential in the country and so white clover was chosen as the test crop, for its production potential. The seeds were obtained through a collaborative Memorandum of Understanding between The University Center, Dschang, The republic of Cameroon, and Institute of Food and Agricultural and Forest Sciences, the University of Florida, Gainesville, Florida, USA.

Table 8 Linear regression functions (Y = bx + a) and correlation coefficients (“r” values) for the interrelationship between Olsen’s P test (Y=P “quantity”) *vs* (0.01 M $CaCl_2$ extractable P (x = P “intensity”), and NH_4OAc extractable K (Y = K “quantity”) *vs* 0.01 $MCaCl_2$ extractable K (x = K “intensity”).

Nutrient (“r”)	Soil	Regression function (bx + a)	Correlation coefficient
P	1	0.41x + 0.24	0.994[a]
	2	0.47x + 2.37	0.890[a]
K	1	0.17x + 0.10	0.960[a]
	2	1.28x + 0.17	0.940[a]

[a]Significant at a confidence level of 99.9%.

Notes: “b” values in the regression functions refer to the buffer power of the nutrient in question, a = a constant. Remarkably, in both cases of P and K, soil 2 has a higher buffer power than soil 1. But, most significantly, in the case of K it is much higher. Soil 2 has a K buffer power higher by 752.9% than soil 1, while for P it is only 14.6%.

Table 9 Correlation coefficients for plant top concentration and plant top uptake of P and K without (A) and with (B) the P and K buffer power of the experimental soils.

Details	A	B
P concentration *vs* Olsen’s soil test	0.61[a]	0.69[a]
K concentration *vs* NH_4 (OAc) soil test	0.05	0.62[a]
P uptake *vs* Olsen’s soil test	0.17	0.77[a]
K uptake *vs* NH_4OAc soil test	0.18	0.78[a]

[a]Significant at 99.9% confidence level.

Results in the following table (Table 8) clearly indicate that the experimental technique devised by this author had resulted in a remarkable positive interrelationship between the Q/I measurements. The very highly significant “r” values (at 99.9% confidence level) substantiates this contention. Also, soil 2 has much higher P and K buffer power compared to soil1. What follows is the further examination of the question whether integrating the P and K buffer power data into the computations enhances predictability of the P and K concentration in plant top, and, eventually, P and K uptake. Answers to this question are presented in Table 9.

Data in Table 9 unequivocally establish the important fact that integration of the buffer power, of the concerned nutrient into the computations, remarkably improved the predictability of both P and K concentration in the test plant top and also their uptake. The predictability rate was as high as

99.9%. More than this, there are other very important additional features of the results, which follow. That is, first, in as much as P and K uptake process is concerned, neither of the widely practiced routine soil test for P, that is the Olsen's test, nor the NH_4OAc test for K, showed any positive statistically significant relationship. This is reflected in the very low "r" values (Table 9). But, most remarkably, the "r" values shoot up to very highly significant ones (at a confidence level of 99.9%) when the corresponding buffer power values of P and K are integrated into the computations. In fact, in the case of Olsen's soil test, for P uptake, the coefficient of determination increases from a mere 2.9% in the absence of the P buffer power to 59.3% when the corresponding buffer power data was integrated into the computations. In the case of K of the routine NH_4OAc extraction for K uptake, the corresponding values are 3.2% and 60.8%. The coefficient of determination is a precise measure of the accuracy of prediction. In other words, these results unequivocally demonstrate that by integrating the respective P and K buffer power values in the computations, a substantial variance in P and K uptake can be explained. This is, indeed, a very remarkable observation of this investigation, which has considerable practical significance in white clover production in The Republic of Cameroon. This is, because, once the P and K buffer power values of the soils in question are determined, to begin with, the application of these important nutrients through the respective chemical fertilizers carrying them could be appropriately designed. This has very extensive practical consequence in white clover production in The Republic of Cameroon. Most remarkably, in the case of K, the coefficient of determination for plant top K concentration increased from a mere 0.25% to 38.4%. This translates to 15.36% increase in variance prediction. This, without doubt, is not a small increase at all, demonstrating the effectiveness of the "The Nutrient Buffer Power Concept". Results in the following tables (Tables 10 and 11) have an important practical bearing of white clover production in The Republic of Cameroon, *vis-a-vis* "The Nutrient Buffer Power Concept." The most important conclusion is that among the two nutrients investigated, namely, P and K, response to P fertilizer application has shown a consistent pattern, with both higher dry matter production and P uptake. With enhanced P fertilizer application rates, there has been consistent increase in dry matter production and P uptake. The magnitude of dry matter production and P uptake in response to enhanced P fertilizer application rates has been more in the case of soil 2 as compared to soil 1. When we come to K fertilizer application and crop response, it has been quite inconsistent. The consistently better response

Table 10 Plant top dry matter production (kg/ha) and P uptake (kg/ha) from the experimental soils as a function of P fertilizer application.

	Dry matter production (kg/ha)				**P uptake (kg/ha)**			
	P application rate (kg/ha)				P application rate (kg/ha)			
Soil	0	12.5	25	37.5	0	12.5	25	37.5
Soil 1	29	62	78	76	43	95	152	191
Soil 2	67	96	99	93	106	154	176	181

What are the implications of this finding in white clover production in The Republic of Cameroon?

Table 11 Plant top dry mater production (kg/ha) and K uptake (kg/ha) from the experimental soils as a function of K fertilizer application (kg/ha).

	Dry matter production (kg/ha)				**K uptake (kg/ha)**			
	K application rate (kg/ha)				**K application rate (kg/ha)**			
Soil	0	50	100	200	0	50	100	200
Soil 1	32	24	27	20	1371	959	1071	737
Soil 2	65	73	76	87	2989	3675	3815	4576

in soil 2 as compared to soil 1 can be traced to the much higher buffer power of soil 2 as compared to soil 1 for both P and K (Table 8).

The Republic of Cameroon is an emerging country on the African continent, bilingual (French and English), politically stable, peace loving, with a small population and vast natural resources like oil, minerals (especially bauxite, raw material for aluminum, much sought after by the aviation industry), agriculture (especially cocoa, second highest producer next to Ghana, on the African continent, much sought out in the chocolate industry), and, a vast potential for tourism. It has a stable livestock industry (cattle production), which has a very bright future. Though on the countryside natural grazing is the common route for cattle feeding, things are giving way to supplemental feeding. It is here the potential for white clover production in the country emerges. This author imported white clover seeds from the United States and the results of the experiments reported here are from the imported seeds. The objective behind the investigation was to popularize the cultivation of white clover in The Republic of Cameroon, and it is seen that the “Buffer Power Concept” has a major role to play in its nutrition, inasmuch as P and K nutrition of the plant is concerned, consequently fertilizer management of these two nutrients carrying fertilizers, as can be clearly deduced from the experimental results discussed above.

This research formed part of a Master's thesis, of one of the author's students, Ms. Che Felicitas, while the author held the position of Professor and Head of the Soil Sciences Department at The University Center, Dschang. The thesis of Ms. Felicitas was selected as the best thesis submitted to the University for the Master's degree and she received a sum of 400,000 CFA (equivalent to US $ 1000) awarded in recognition of the academic excellence of the research she carried out under the supervision of this author by the Organization for Advancement of Science on the African continent. The award was given by the Minister of Higher Education and Scientific Research, on behalf of the, President Mr. Paul Biya, of The Republic of Cameroon, and was celebrated as a very important national event.

12. Experimental evidence in black pepper

The following discussion would pertain only to Zinc, the most important micronutrient in Black pepper cultivation, with some reference to wheat, as well, from Central Asia, for the sake of comparison.

12.1 Quantifying the buffer power for precise bioavailability prediction: Heavy metals

Zinc: Since Zn, among the heavy metals, has become the most problematic, in agricultural production, and human nutrition, on a global scale, the scope of this review is confined to this very important plant nutrient. There is a great paucity of published material on the effect of buffer power on bioavailability of heavy metals.

Plants obtain most of their fertilizer Zn from reaction products and not applied sources as such, implying that any source of Zn added to soil has to necessarily conform to a chain reaction involving adsorptive, desorptive, and resorptive processes that govern the maintenance of an equilibrium between adequate Zn concentration in the soil solution nearest to the zone of Zn depletion on the one hand and plant uptake on the other. The Zn buffer power defines this. As Zn concentration in soil solution is normally very low, the supply to plant roots by mass flow can only account for a very small fraction of plant demand. For instance, with a transpiration coefficient of 300 L/kg dry matter and corresponding Zn concentration of 10^{-7} M in the soil solution, approximately 2 mg of Zn can be supplied by mass flow against a demand of 10–30 mg of Zn/kg dry weight of plant tissue. In calcareous soils, as the Zn concentration is of a much lower order of approximately 10^{-8} M, the supply by mass flow could be very much lower (Marschner, 1994) indicating that mass flow can only contribute very negligibly to meet plant needs of Zn. Hence, Zn movement to the plant root surface is principally by diffusion and is essentially confined to a zone around the plant root, which hardly extends beyond the root hair cylinder (Marschner, 1994).

Though published papers on the relevance of Z buffer power in soils to Zn bioavailability are very limited, indeed, there is no dearth of the same on other aspects of Zn nutrition. Genotypic differences to Zn nutrition in a very important crop, such as maze, with regard to its hybrids, inbreds, and composites, were reported more than four decades ago (Nair and Prabhat, 1977); this investigation focused on the importance of genetic engineering for tailoring maize varieties for better efficiency of Zn utilization, while the complicated mechanism of Zn-P-Fe interaction was researched prior to this (Nair and Babu, 1975). In a recent review on the mechanism of Zn uptake, (Marschner, 1994) indicated that flow culture experiments with various species showed adequate ranges of Zn concentration in the range of 6×10^{-8} to 8×10^{-6} M which are concentrations greater than those that would be expected in the soil solution of most soils. He further pointed out that although work using chelate—buffered solutions has indicated adequate Zn concentration between 10^{-10} and 10^{-11} M, extremely low adequate Zn concentrations required a concomitant excess of about 100 μ M Zn-chelate as buffer at the plasma membrane of the root cells. This implies a need for an unlimited Zn pool for replenishment of Zn^{2+} at the plasma membrane. When plants grow in soil it is impossible to expect a Zn buffer of this size to exist, and free Zn^{2+} and chelated —Zn concentration will be at least threefold lower. Hence, critical deficiency or sufficiency concentrations obtained through research employing chelate-buffered solutions cannot be applied to soil-grown plants.

Most of the work on Zn bioavailability to plants in soil is based on chemical extractions, among which, DTPA extraction is the most frequently used. The DTPA extraction quantifies a labile fraction of soil Zn comprising water-soluble, exchangeable, adsorbed, chelated and some occluded Zn. The critical soil level of DTPA-extractable Zn can vary from 0.3 to 1.4 mg/kg soil, which equates to about 900–4200 g/ha of Zn in heavy soils and about 600–2800 g/ha Zn in light soils in the plow layer (0–20 cm depth). The crop requirements on the other hand are quite small, in the range of 100–300 g/ha for a total dry matter production of about 10 t/ha (Marschner, 1994). The inadequacy of DTPA extraction to reflect plant Zn demand shows that other important factors, such as replenishment of soil solution (Nair, 1984a,b), mobility, and transport to the root surface (Nair et al., 1984; Wilkinson et al., 1968), and also the activity of the roots themselves (Marschner, 1994; Wilkinson et al., 1968) are involved. Since the Zn buffer power is intricately involved in all these three factors, the focus of this review is mainly on that attribute.

As early as five decades ago, it was suggested that colloidal Zn was released by some specific processes associated with root activity (Wilkinson et al., 1968). Conditions in the rhizosphere and, in particular, root-induced changes, markedly affect Zn bioavailability. A difference in the rhizosphere pH of as much as 2, higher or lower compared to bulk soil, can be expected to occur as a result of imbalance in ionic uptake. For instance, any acidifying fertilizer such as $(NH_4)_2\ SO_4$ can result in a net excretion of H^+ ions ions and others such as $NH_4\ NO_3$ can result in net excretion of HCO_3^- or OH^- ions. Additionally, secretion of organic acids and enhanced CO_2 production, as well, will affect rhizosphere pH, and all of the above-mentioned changes will markedly affect Zn bioavailability. However, the scope of this review is confined to the kinetic/dynamic aspects of the changes occurring in the rooting zone mirrored in the Zn buffer power changes, rather than changes in soil reaction in the rhizosphere *per se* on Zn bioavailability.

The distribution of Zn between the solid and solution phases can be described by its buffer power. The bioavailability of soil Zn to the plant root depends on the Zn concentration, Zn buffer power and effective diffusion coefficient (Barber, 1984). The Langmuir equation gives the relation between B and C_1 as follows.

$$\frac{C1_1}{(x/m)} = \frac{1}{aB} + \frac{C1_1}{B}$$

where C_1 is the Zn concentration in the soil solution, x/m is the amount of Zn adsorbed per unit of soil, B is the adsorption maximum, and a is a constant related to the soil's bonding energy for Zn. A straight line is obtained when $C_1/x/m$ is plotted against C_1 with a slope of 1/B and intercept of 1/aB. The inverse of $C_1/(x/m){=}b$, the Zn buffer power, where C_1 and x/m are both expressed in volume units (Barber, 1984). Using this approach, Shuman (1975) estimated the buffer power values varying from 5 to 100 for four soils representing different major physiographic regions of Georgia. Based on the diffusion model of Drew et al. (1969), Nair (1984a,b) has argued that the $\bar{c}$ in the Eq. $U = 2\pi\ \alpha\ \overline{ac}\ t$ (Drew et al., 1969), where U is the quantity of Zn absorbed per centimeter of root length, *a* is the root radius in cm, α is the root absorbing power, c is the average Zn concentration on the root surface, and *t* is the duration of the absorption period, in fact, represents an indirect measure of the Zn buffer power. As we already know, the bulk of Zn uptake is by diffusion (Barber, 1984; Elgawhary et al., 1970, Wilkinson et al., 1968). This diffusive process will maintain a concentration gradient in the rooting zone. This concentration gradient will directly affect the Zn uptake by plant root because of its effect on the average Zn concentration on the root surface. The Zn buffer power will affect this concentration gradient, because the rate of Zn depletion and/or replenishment is mirrored by it. In a sense, the effective diffusion coefficient and the buffer power are analogous for nutrients which are principally absorbed by the plant root through diffusive processes (Nair, 1989). Hence, the crucial question to examine would be the role of Zn buffer power in influencing Zn bioavailability for plant uptake.

12.2 Quantifying Zn buffer power

Nair (1984a,b) used a novel method to quantify Zn buffer power. Nair (1990) has demonstrated the importance of Zn and P buffer power in affecting their plant uptake *vis-à-vis* their bioavailability. Heavy metal pollution is a major environmental hazard in Europe, especially on the highways due to automobile exhausts; as a consequence, a number of soils are very highly contaminated. Such soils are unsuitable for a precise study on the impact of Zn buffer power on plant Zn uptake, and the choice of soil was narrowed to a heavy clay soil in the northern part of Belgium containing 1.1 ppm total Zn, 5.5 ppm DTPA extractable Zn, and, 0.13 ppm electro-ultra-filterable (EUF) Zn. The soil was acidic (pH 6.6, 1 N KCl), low n organic carbon (1.8%), high in $CaCO_3$ (16.5%), containing beidellite as the predominant clay mineral. Zn buffer power was quantified by regressing DTPA extractable Zn (y) on electro-ultra-filterable Zn (x) by a stepwise extraction of incubated soil, and the *b* value in the regression function represented the Zn buffer power. EUF has been employed for a rapid estimation of the "intensity" of a range of heavy metals, especially in central, western, and eastern European soils (Nemeth, 1979; Nemeth and Recke, 1982). However, earlier investigations of these authors did not give satisfactory results; analysis of only the alkaline cathode filtrate is insufficient to give precise information about bioavailability indices, primarily due to the fact that the heavy metals are collected by the cathode filter as hydroxides and hydrated oxides, which are hardly soluble in the alkaline cathode filtrate. However, as these oxides comprise soluble and desorbable ions of the heavy metal in question, they are of importance in plant nutrition. Nair (1984a,b)

Table 12 Correlation coefficients ("r") between Zn intensity and maize top Zn concentration and total Zn uptake by plant top at harvest without (A) and with (B) Zn buffer power integration.

Details	**Correlation Coefficients ("r")**	
	A	**B**
Zn intensity *vs* maize top Zn concentration	0.290	0.812[a]
Zn intensity *vs* total Zn uptake by maize top	0.356	0.618[b]

[a] Significant at 0.1% confidence level.

[b] Significant at 1% confidence level.

After Nair, K.P.P. 1984a. Towards a better approach to soil testing based on the buffer power concept. In: Proc. 6th. Int. Colloquium for the Optimization of Plant Nutrition, 2–8 September, Pierre-Martin Prevel (Ed.). Montpellier, France, vol 4, pp. 1221–1228, Nair, K.P.P. 1984b. Zinc buffer power as an important criterion for a dependable assessment of plant uptake. Plant and Soil 81, 209–215.

used a modified procedure to bring the oxides into an acid medium for subsequent analysis. The studies indicated that Zn "intensity" alone is insufficient to precisely predict Zn uptake by maize used as a test plant, as it is widely grown as a food crop, in Europe, in this investigation. Data are given in the following table (Table 12).

Data in Table 12 show that the precision of predicting Zn concentration in the maize top increased remarkably, as substantiated by the increase in the coefficient of determination which works out to 65.9%. With regard to total Zn uptake by the maize plant, the increase is less marked, yet, substantial. The data clearly show that the major factor responsible for the variance in Zn concentration in the maize top and total Zn uptake by the maize top is the Zn buffer power, and not Zn intensity as quantified by EUF extraction. In a separate experimental set up Nair et al. (1984) monitored Zn transport by simulation experiments in a laboratory setup using the same field soil and obtained proof to support the hypothesis that it is essentially the buffered Zn that contributes to the major uptake process by the test plant. Dissolved salts in a field soil must move with the liquid, the net movement from a given reference plane being dependent on the activity gradient of salt and water. This naturally brings us to the important question of solute movement within the soil matrix which is dependent on the soil conductivity. Buffered Zn would be in the bulk soil solution to be further transported to plant roots. This transport, though dependent on the soil conductivity, would also be linked to the quantum of Zn *per se* in the bulk soil solution, which in turn, would be dependent on the Zn buffer power, of the soil in question. Nair et al. (1984) quantified these relationships. In a field soil, it is the buffered Zn which maintains a concentration gradient between the bulk soil solution and the root surface sufficiently conducive for optimal plant uptake. The investigation also showed the ineffectiveness of DTPA extraction as a reliable soil test for Zn bioavailability. EUF is being put to use increasingly for commercial soil testing in many European countries, notably for sugar beet cultivation in Austria. Determination of Zn intensity singly may not provide reliable information regarding plant bioavailable Zn. Besides Zn intensity and Zn buffer power, other soil factors have only a very minor influence on Zn absorption. EUF has the advantage of a rapid assessment of the Zn intensity factor. Combining this advantage of rapid assessment of the intensity factor of the nutrient with its corresponding buffer power might greatly enhance the reliability of fertilizer recommendations not only for Zn, but, perhaps, for other heavy metals, as well, making EUF a reliable tool in soil testing for heavy metals.

13. Case studies with Asian soils

13.1 South Asian soils

The 3rd International Zinc Symposium in Hyderabad, India, attended by 195 delegates from 30 countries, focused on the cruciality of Zn in both plant and human nutrition. Zn has become a major constraint in crop production. There is widespread Zn deficiency in tropical soils. This section of the review is divided into two parts, where the focus will be first on South Asian soils, India being a classical example and second, Central Asian soils, Turkey, where severe Zn deficiency in the main wheat growing belt of the country (Anatolia) is threatening wheat production and adversely affecting human nutrition.

13.2 Investigation in Indian soils

The red soil of the lateritic belt of Kerala State, in southern India, was chosen as the test soil. The economic mainstay of the State is Black pepper (*P. nigrum* L.). The crop is very susceptible to Zn deficiency, and, among the major diseases of Black pepper it is the "Quick Wilt," caused by the fungus *Phytophthora* spp. (*Phytophthora capsici*), attributed to severe soil Zn deficiency, that is ruining pepper plantations in Kerala State. The disease onset is sudden and within a week the entire plantation can be devastated, hence the name "Quick Wilt." The "official" recommendation to correct this is based on the classical, routine, DTPA extraction. A "blanket" recommendation is made for the entire State, where the Black pepper farmers are advised to apply Zn fertilizer at the rate of 25 kg/ha, as $ZnSO_4$ for the entire State. This recommendation emanates from the research carried out by the scientists (Agronomists and Soil Scientists) affiliated to the Indian Institute of Spices Research, at Calicut, Kerala State, under the administrative umbrella of the Indian Council of Agricultural Research, New Delhi, India. This author, has, for long, suspected the advisability of such blanket recommendation, and had suggested, in its place, investigating the Zn buffer power of the soils and base the Zn fertilizer recommendation based on the Zn buffer of the soil concerned. Zn fertilizer is quite expensive in India, and at the current price of INR 500/kg of Zn SO_4 it works out to approximately US $ 8/kg (75INR (Rupees) make one US $) for a farmer to apply Zn fertilizer to his pepper garden to control/preempt the disease. This price is quite prohibitory on the scale of monetary value for a poor or marginal Black pepper farmer.

13.3 Quantifying the Zn buffer power of pepper-growing soils

Nair (1984a) has used Electro Ultra Filtration (EUF) technique to measure the Zn "ïntensity" and an adsorption-desorption equilibrium technique to measure the Zn "quantity." Because the EUF technique is a highly sophisticated instrumental procedure, where an expensive Electro Ultra Filtration instrument has to be set up, only rich European and North American countries can afford to employ such techniques. For the developing countries, a simple adsorption-desorption equilibrium technique, developed by this author, has been used as follows (Nair, 2002).

200 g of representative soil samples from the principal Black pepper growing regions in the State of Kerala, India, were incubated at 60% of the maximum water holding capacity with graded rates of Zn over a fortnight, by maintaining the water regime to constancy through watering each day at the same time of the day. At the end of the period the soil samples were extracted with 0.01 M $CaCl_2$ solution over a 24-h period and the extract tested for Zn using atomic absorption spectrometry. This represented the Zn "intensity". Separate extractions were made with DTPA, which represented the Zn "quantity." The following table (Table 2) shows the Zn buffer power of the experimental soils (Table 13).

The results in the following table (Table 14) refer to the investigations carried out in Turkey in Anatolia the principal wheat growing region of the country.

The above results refer to farmers fields from Kerala State.

Table 13 Zinc buffer of the Black pepper growing soils from India.

Soil	"r" value"	"b" value
Peruvannamuzhi	0.8337***	0.7824
Thamarasseri	0.9304***	1.5786
Ambalavayal	0.9604***	3.0358

Note: All the "r" values are very highly significant, at a confidence level of 99.9% (***) implying that the adsorption-desorption equilibrium technique developed by the author provides an accurate measure of the Zn buffer power of the concerned soils. Further, the soils showed widely varying Zn buffer power, as shown by the "b" values, with the soils from *Peruvannamuzhi* region least buffered for Zn, while that from the *Ambalavayal* region most buffered, with the soils from *Thamarasseri* region intermediate in their Zn buffer power. These findings have remarkable impact, on Black pepper production, as we shall see from results incorporated in Table 15.

Table 14 Linear regression functions ($Y = a + bx$) and correlation coefficients ("r" values) for the relationship between DTPA extractable Zn (Zn "quantity," Y) and 0.01 $MCaCl_2$ extractable Zn (Zn "intensity," x).

Soil	Adsorption-Desorption Equilibrium	Soil Incubation	"r" values A	"r" values B
Konya (Central Anatolia)	$Q = 201bI + 5.3$	$Q = 679bI–5.9$	0.951[a]	0.978[a]
Koruklu(Gap region)	$Q = 17bI + 17.9$	$Q = 375bI - 8.7$	0.015	0.784[a]
German soil(reference soil)	$Q = 8bI + 6.5$	$Q = 11bI + 7.8$	0.972[a]	0.942[a]

[a]Significant at a confidence level of 99.9%.

Note: Q = Zn quantity, *I*=Zn intensity, *b* = Zn buffer power. A without the integration of Zn buffer power ("b" values) in the computations, B = with the integration. The experimental technique employed has resulted in very highly significant (99.9% confidence level) correlation coefficients ("r" values), except in the case of soils from the Gap region(Koruklu) in the case of the incubation experiments, which suggest the high accuracy of the adsorption-desorption equilibrium technique to determine Z intensity, which is a true reflection of the Zn buffer power. Note the remarkable improvements in the "r" values (B compared to A) which unequivocally show that the integration of the Zn buffer power remarkably improves the relationship. How this affects plant uptake, and, eventually wheat yields, will be discussed in the following tables and explanation of experimental details.

Results in all the three tables above (Tables 14–16) unequivocally establish the importance of Zn buffer power integration in the computations in the predictability of Black pepper plant top Zn concentration, plant top Zn uptake and, eventually, dry matter production. DTPA (Diethylene

Table 15 Black pepper yields from farmers' fields—the figures are weighted against the respective Zn buffer power of the representative soils.

Soil	Yield(kg/vine) Targeted	Actual	Deviation (%)
Peruvannamuzhi	0.241	0.401	+66
Thamarasseri	0.490	0.487	+0.6

Note: Target weighting was done against the highest vine yield obtained from the *Ambalavayal* region. Note the remarkable closeness between targeted and actual yields in *Thamarasseri* region, whereas in *Peruvannamuzhi* region, there is a huge deviation. Soils in the *Peruvannamuzhi* region are atypical Black pepper soils. Ironically, the "official" recommendation for Zn fertilizer application emanate from experiments conducted in *Peruvannamuzhi* region, as the Black pepper research station, affiliated to the Indian Institute of Spices Research, Calicut, Kerala State, affiliated to the Indian Council of Agricultural Research, New Delhi, is located here.

Table 16 The "r" values (correlation coefficients) for the relationship between routine DTPA soil test for Zn bioavailability, Zn uptake and dry matter production in Black pepper with (A) and without (B) Zn buffer power integration.

Details of the soil test	A	B
DTPA soil test *vs* Zn concentration in plant top	0.8[a]	0.9[a]
DTPA soil test *vs* Zn uptake by Black pepper plant	0.8[a]	0.9[a]
DTPA soil test *vs* Black pepper dry matter production	−0.7	0.8[a]

[a] Significant at a confidence level of 99.9%.

Triamine Penta Acetic Acid) is the universally adopted soil test for Zn bioavailability. Most remarkably, the overall relationship between DTPA soil test and Black pepper dry matter production not only improved very significantly, when the Zn buffer power was integrated into the computations, but, changed from a negative relationship to a positive one with the Zn buffer power integration into the computations (Table 16). This is a very remarkable scientific finding emphasizing the importance of "The Nutrient Buffer Power Concept." Further, it also demonstrates that the predictability of Black pepper yield can be remarkably improved by taking into consideration the Zn buffer power (Table 14). This finding will immensely help the Black pepper farmers of the State of Kerala and wheat farmers of Turkey.

As a reference investigation, the following one was conducted in Central Asia (Turkey) to examine the crucial question whether "The Nutrient Buffer Power Concept" holds the key to optimal Zn fertilization in wheat. Turkey is one of the major wheat producing countries of the world. Nearly

Table 17 Effect of Zn fertilization (100 kg $ZnSO_4$/ha) on mean and range of Zn concentration and wheat grain yield among 28 wheat genotypes grown in Konya soils and 25 grown in Gap soils in Turkey.

	Tissue concentration (ppm)				Grain yield (kg/ha)		Percentage increase		
	Without Zn		With Zn		Without Zn		With Zn		
Soil	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Konya	7–10	9	10–19	14	1550–4010	2710	248–5900	4570	69
Gap	16–23	19	22–31	25	1530–5260	3500	1550–5300	3510	0

The Zn buffer power is very clearly reflected in grain yield increase. Note that the "b" value (Zn buffer power, Table 14) for both the adsorption-desorption equilibrium technique (developed by the author) and incubation technique for Konya soils are 201 and 679, respectively. The corresponding values for Koruklu soils (Gap region) are 17 and 375, respectively. The percentage increase in wheat grain yield in Konya soils is 69 while that in Koruklu soils it is 0. In other words, the Konya soils are highly Zn buffered, and, hence, the Zn bioavailability to wheat plant is very high, which has reflected in high wheat yield.

Table 18 Interrelationship between Zn bioavailability parameters and wheat grain yield and shoot tissue concentration of Zn in Turkey.

Parameter investigated	Correlation coefficient ("r" values)
DTPA soil test *vs.* Zn concentration in shoot tissue	0.672***
Zn buffer power *vs* percentage increase in wheat grain yield	0.860***

Notes: Note the very highly significant (at a confidence level of 99.99% ***) "r"values between Zn buffer power and percentage increase in wheat grain yield. Though DTPA soil test seems to have a positive influence on Zn concentration in plant top, it is the Zn buffer power that yields far greater influence on wheat grain yield.

Important Note: The most remarkable aspect of the above results is that the coefficient of determination increased from 45.16% to 74% when the computations were done against the Zn buffer power in the case of wheat grain yield as against the shoot Zn concertation estimated only by Zn extraction values. *Per se* 63.9% of the variation in wheat grain yield can be attributed to the Zn buffer power rather than merely the routine DTPA extraction values. This finding has immense practical importance in Zn fertilizer management in wheat production in Turkey.

45% (4.5 million ha) of the wheat producing area in Turkey is located in the highly calcareous region of Central Anatolia. Central Anatolia is semi arid, being the driest region of Turkey. Scanty annual rainfall (only about 325 mm) and low water supply greatly limit wheat yields. Zn bioavailability (as per the common DTPA test) has been found to be very low and the farmers have been advised to apply as much as 100 kg of Zn fertilizer/ha, as $ZnSo_4$.

Very recently Nair (2019, unpublished data) conducted an investigation into the above-mentioned problem and the results are summarized in the following tables (Tables 17 and 18).

14. Experimental evidence in cardamom

Cardamom is a commercial crop, and, it has a great commercial significance for a country like India. In India, it is mainly grown in the States of Kerala and Karnataka, in Southern India. The crop is also grown in Guatemala, but, the Indian cardamom is the world's choice. The main problem in cardamom cultivation is one of precisely quantifying its K fertilizer needs, as the crop is a very heavy feeder of Potassium. The recent decontrol of prices of both potassic and phosphatic fertilizers in India has put the cardamom farmers in jeopardy and it was thought necessary to explore whether "The Nutrient Buffer Power Concept" has any significant relevance in precisely quantifying the Potassium fertilizer needs of Cardamom. As of now, the routine NH_4OAC (Ammonium acetate) test is used for formulating a Potassic fertilizer recommendation for cardamom. Hence, an extensive investigation was taken up in the States of both Kerala and Karnataka to obtain soil samples, and leaf samples and examine how the Potassium (K) buffer power determines potassium uptake by cardamom and consequently affects cardamom yield. The experimental techniques are discussed elsewhere (Nair et al., 1997). The salient results are incorporated in the following tables (Tables 19–21).

The experimental results show that the Coorg region had a very high yield of 155 kg/ha as compared to that from Idukki region at 80 kg/ha—almost a 100% increase. This is simply due to the better K buffered soils of Coorg compared to that of Idukki region reinforcing the validity of "The Nutrient Buffer Power Concept." Results in the above three Tables (19–21) substantiate this conclusion.

Table 19 The K buffer power of cardamom growing soils.

Region	Regression Function ($Y = a + bx$)	Correlation coefficient ("r")
Coorg (Karnataka State)	$Y = 142.38 + 1.443x$	$r = 0.856$[a]
Idukki (Kerala State)	$Y = 592.46 + 0.917x$	$r = 0.580$[b]

[a] Significant at 95% Confidence level.

[b] Significant at 99% Confidence level.

Notes: "b" values in the regression functions represent the K buffer power of each soil. The K buffer power refers to the pooled values of soil samples obtained from 94 locations covering an area of more than 20,000 ha in the Cardamom growing regions of Southern India, from Kerala and Karnataka States. After Nair, K.P.P., Sadanandan, A.K., Hamza, S., and Abraham, J. 1997. The importance of potassium buffer power in the growth and yield of cardamom. J. Plant Nutr. 20, 7 & 8, 987–997.

Table 20 The relationship between leaf Potassium and Exchangeable potassium.

Details	**Regression Function (Y = a + bx)**	**"r" value**
[a]Potassium in leaf *vs* Exchangeable potassium	$Y = 1.27bx + 0.0004$	0.206
[b]Potassium in leaf *vs* Exchangeable potassium	$Y = 1.65 + 000006$	−0.006

[a] Coorg soils.

[b] Idukki soils.

After Nair, K.P.P., Sadanandan, A.K., Hamza, S., and Abraham, J. 1997. The importance of potassium buffer power in the growth and yield of cardamom. J. Plant Nutr. 20, 7 & 8, 987–997.

Table 21 Relationship between Potassium in leaf and exchangeable Potassium in soil for the pooled data from 94 locations for both soil regions without (A) and with (B) buffer power integration in the computations.

	"r" values	
Details	A	B
Potassium in leaf *vs* exchangeable Potassium	0.25	0.44[a]

[a] Significant at a confidence level of 99%.

Important Note: There is a remarkable (76%) increase in the coefficient of determination when the K buffer power is also integrated into the computations between leaf K and soil exchangeable (NH_4OAc extractable) K.

15. Concluding comments and future imperatives

Historically, soil testing has been employed to quantify bioavailability of essential plant nutrients to field—grown crops. However, contemporary soil tests are based on philosophies and procedures developed several decades ago, without significant changes in their general approach. For a soil test to be accurate, one needs to clearly understand the physico-chemico-physiological processes at the soil–root interface, and, an understanding of soils and plant root systems as polycationic systems is essential. It is this knowledge that leads to sound prescriptive soil management practices inasmuch as nutrient bioavailability *vis-a-vis* chemical fertilizer management is concerned, because, of all the factors which govern sustainability of crop production, the nutrient factor is the most important, and yet, it is the least resilient to management. This review focuses on the buffering of important plant nutrients, such as, phosphorus, potassium and zinc, on their bioavailability to a number of annual and perennial field crops. Experimental evidence is presented from research carried out on temperate soils(Central European and North European) and tropical soils (Central Asian, Central African and South Asian) soils, which, unequivocally establishes the important fact that precise quantification of the concerned nutrient's buffer power holds the key to a clearer understanding of plant bioavailability of some of the major plant nutrients, such as phosphorus and potassium, and micronutrients, such as, zinc. "The Nutrient Buffer Power Concept" attempts to explain bioavailability of plant nutrients on the basis of the diffusion model, as it is the principal process by which these nutrients are taken up by the plant roots. Possibly, other nutrients, not included in these investigations, but, also, taken up by the diffusive process would also conform to the principles of this concept. To substantiate this hypothesis, supportive experimental evidence is needed.

There are similarities between the "Buffer Power Concept" and "Quantity/Intensity" approach in predicting plant bioavailability of important plant nutrients, such as phosphorus and potassium. While the Q/I approach has met with a fair measure of success in predicting P bioavailability, with regard to K bioavailability the Q/I relationship does not enjoy universal acceptance, since, a single relationship for all soils between plant uptake by a given crop and AR_K does not exist, perhaps due to the nature of the soil components regulating AR_K.

In substance, soil testing in a laboratory is meant to simulate what a plant root would accomplish in a field soil. All soil tests meet this requirement with different degrees of success. But, for a soil test to be universal in scope, it must attempt to quantify, as precisely as possible, factors which most crucially affect plant root uptake. Of all the factors involved in nutrient uptake, the most crucial is the average concentration of the specific nutrient on the root surface. In a dynamic state of plant growth, it is virtually impossible to precisely quantify the average plant nutrient concentration on the root surface. The concerned nutrient's buffer power is an indirect measure of the average nutrient concentration on the root surface and analytical methods which accurately quantify the nutrient buffer power would render the soil test in question dependable; hence, the fertilizer recommendation which emanates from such a procedure would be reproducible. It is against this background that "The Nutrient Buffer Power Concept" merits wider application for field use. Fertilizer prices have dramatically increased over the years due to the oil crisis of mid 1970s, and, field experience shows that recommendations emanating from routine soil tests have met with only limited success. A number of countries on the Asian and African continents spend enormous sums of money on fertilizer import, for lack of infrastructure for fertilizer manufacture in their own countries, which is great strain on their national exchequer. Where there is the infrastructure for fertilizer manufacture, the soil testing support service is far from satisfactory. Since fertilizer is a crucial input, next to water, in modern farming, cost-effective fertilizer recommendations are an important prerequisite for successful crop production. In countries, such as India, fertilizer prices, especially of phosphatic and potassic, have skyrocketed over the years due to the Government of India Fertilizer Price Decontrol Order, centered on market economy. In such a situation, farmer confidence can only be instilled and maintained by reproducible fertilizer recommendations, which must be cost effective. If not, it would be a financial strain on the farmer, especially poor and marginal, which will have long range adverse effect on farming.

The success of a new approach, to a large measure, rests on the ingenuity of those applying it to the demands of a new situation. In a broad sense, this could be called a "shift in paradigm." This principle is no exception to making "The Nutrient Buffer Power Concept" a universal success. As compared to routine soil testing, this approach calls for the accurate determination of the buffer power of the nutrient in question, to begin with. Once this is accurately accomplished, done, the buffer power factor can be integrated with the routine soil test data and precise fertilizer recommendations can be formulated on the basis of this new information. This implies that, in addition to obtaining routine soil test data, one also needs to know the concerned nutrient's buffer power. This review has shown how the buffer power is determined based on analytical methods varying from a simple adsorption-desorption equilibrium technique, developed by the author, to elaborate Electro Ultra Filtrable technique (EUF). Only selected laboratories around the world have EUF facilities. Where they are absent, alternative analytical procedures, as for example, the one developed by the author, can be used. Developing appropriate analytical methods to quantify the buffer power and modification of the protocol for routine soil tests to integrate buffer power data for precise fertilizer recommendations calls for both ingenuity and drive on the part of the researcher, but, that will be the future imperative in accountable soil testing.

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CHAPTER FOUR

Stimulation of plasma membrane H$^+$-ATPase by auxins or fusicoccin and its relation to maize kernel setting, grain yield, and harvest index

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Abstract

Increase in kernel setting and decrease of vegetative shoot biomass have been suggested as two possibilities for improvement of maize harvest index. The kernel number at maturity is mainly determined at the time around pollination, when, particularly under stress conditions, kernel abortion occurs leading to grain yield depressions. Plasma membrane (PM) H$^+$-ATPase activity of vesicles derived from maize kernels shortly after pollination was shown to be significantly inhibited when plants were grown under drought or salinity. It is therefore hypothesized that with application of the phytohormone auxin or of fusicoccin, PM H$^+$-ATPase activity can be stimulated in the developing maize kernels, leading to an improved hexose uptake and thus to

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a better kernel set. In this review, we first focus on the auxin indole-3-acetic acid (IAA) and give an overview of the main studies on auxin-induced elongation growth with respect to stimulation of PM H^+-ATPase. Particular attention is paid to the IAA action in developing maize kernels, including interactions with cytokinins. The second part of our review addresses fusicoccin, its impact on PM H^+-ATPase, determined with various experimental approaches. With application of IAA at anthesis a stimulation of PM H^+-ATPase could be achieved, yet it did not result in a better kernel set at maturity. IAA was probably applied too early, disturbing the balance between cytokinins and auxins in the kernels. Applied at the appropriate growth stages, auxins and also cytokinins are promising measures to improve maize kernel development and grain yield, thus finally increasing the harvest index.

Abbreviations

2,4 D	2,4-dichlorophenoxyacetic acid
ABA	abscisic acid
AMs	axillary meristems
BAP	benzyl-amino-purine
CHX	cycloheximide
DAP	days after pollination
FC	fusicoccin
HI	harvest index = grain yield/total above-ground biomass at physiological maturity
IAA	indole-3-acetic acid
$NUtE_{grain}$	nitrogen-utilization efficiency grain = grain dry matter/nitrogen content of total above-ground biomass at physiological maturity
PAC	paclobutrazol
PM	plasma membrane
Thr	threonine
WUE_{grain}	water-use efficiency grain = grain dry matter/total water consumption

1. Introduction

Decrease of vegetative shoot biomass and increase in kernel setting have been suggested as two possibilities for improvement of maize harvest index (HI; Hütsch and Schubert, 2017). During the last decades, the HI of maize remained almost unchanged (Duvick, 2005; Russell, 1991; Tollenaar, 1989), whereas it was substantially increased for many small-grain cereals such as wheat (Brancourt-Hulmel et al., 2003; Hay, 1995; Rooney and Leigh, 1993; Siddique et al., 1989) and barley (Bertholdsson and Brantestam, 2009; Ortiz et al., 2002; Riggs et al., 1981). If a higher HI were also achieved for maize, this would be accompanied by improvements in water-use efficiency (WUE_{grain}) and probably also in nutrient-utilization efficiencies ($NUtE_{grain}$).

Promising results have already been obtained by application of the gibberellin biosynthesis inhibitor paclobutrazol (PAC) to various maize cultivars, which caused strong decreases in straw biomass resulting in significant increases in HI and water use efficiency (Hütsch and Schubert, 2018, 2021a, 2021b). In addition to reduced vegetative growth, kernel setting and thus the number of maize kernels at maturity is an important determinant of grain yield, and therefore this also has a strong impact on the HI. Although a small kernel number can be partly compensated by an increased single kernel weight (Hütsch et al., 2014, 2015; Jung et al., 2017; Schubert et al., 2009), high grain yields can only be achieved with high kernel numbers. The final kernel number is mainly determined at the time around pollination, when notable kernel abortion occurs under stress, but also to some extent under optimal growth conditions (Fig. 1; Andersen et al., 2002; Hütsch et al., 2014, 2015; Jung et al., 2017; Schussler and Westgate, 1995; Setter et al., 2001; Zinselmeier et al., 1995). Possible reasons for reduced kernel setting are insufficient sucrose availability and inhibited activity of the two enzymes, acid invertase and plasma membrane (PM) H^+-ATPase (Hütsch and Schubert, 2017).

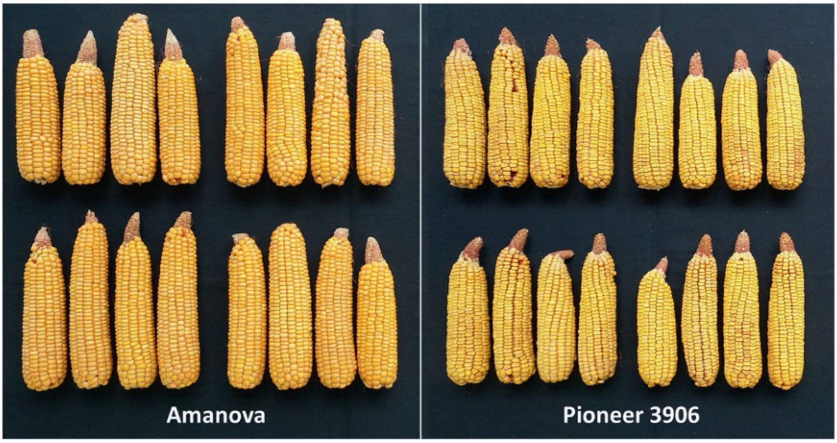

Fig. 1 Cobs with kernel abortion at the tip of the maize cultivars Amanova and Pioneer 3906, grown under optimal conditions and harvested at maturity. *After Hütsch, B.W., Schubert, S., 2021. Water-use efficiency of maize may be increased by the plant growth regulator paclobutrazol. J. Agro. Crop Sci. 207, 521–534.*

Even under drought or salt stress, maize kernel development was not source- but sink-limited with particular emphasis on these two enzymes as important determinants for sink activity (Cheng et al., 1996; Chourey et al., 2006; Hütsch et al., 2014, 2015; Jung et al., 2017; Miller and Chourey, 1992). Sucrose, transported to the maize cob *via* phloem, has to be hydrolyzed by acid invertase in order to supply hexoses for carrier-driven import into the ovaries, which is essential to keep the kernels alive (Andersen et al., 2002; Mäkelä et al., 2005; McLaughlin and Boyer, 2004; Schussler and Westgate, 1994; Zinselmeier et al., 1995, 1999). Although under drought and salt stress developing maize kernels showed decreased acid invertase activity shortly after pollination, the hexose concentrations were either increased or unchanged (Hütsch et al., 2015; Jung et al., 2017). Thus, the delivery of hexoses by acid invertase activity did obviously not limit kernel development under stress conditions. However, in the study of Jung et al. (2017) it was demonstrated that two days after controlled pollination maize kernel PM H^+-ATPase activity was significantly decreased under salt stress, pointing to a strong involvement in kernel abortion. The inhibited enzyme activity probably caused a pH increase in the apoplast, diminishing the pH gradient at the plasma membrane, which drives the H^+-cotransport of hexoses (Bihmidine et al., 2013; Sondergaard et al., 2004; Zhao et al., 2000). It is suggested that reduced uptake of hexoses resulted on one hand in their accumulation in the apoplast, on the other hand their lack in the kernels limited growth and development, and eventually resulted in kernel abortion and lower kernel numbers at maturity (Jung et al., 2017). It is hypothesized that with application of the phytohormone IAA, an auxin, or of fusicoccin, PM H^+-ATPase activity can be stimulated in the developing maize kernels, leading to an improved hexose uptake and thus to a better kernel set (Fig. 2; Hütsch and Schubert, 2017).

In this review, we first focus on auxins, their discovery and metabolism in plants, and we give an overview of the main studies on auxin-induced elongation growth. Particular attention is paid to the IAA action in developing maize kernels, including interactions with cytokinins and sugars as well as evaluation of effects of phytohormone applications to plants. The second part of our review addresses the fungal toxin fusicoccin (FC), its impact on PM H^+-ATPase, determined with various experimental approaches. Reasons for the unsuitability of FC use in practice to affect maize kernel development are discussed. Eventually, effects of auxins and FC on PM H^+-ATPase are compared, and perspectives for further research are given.

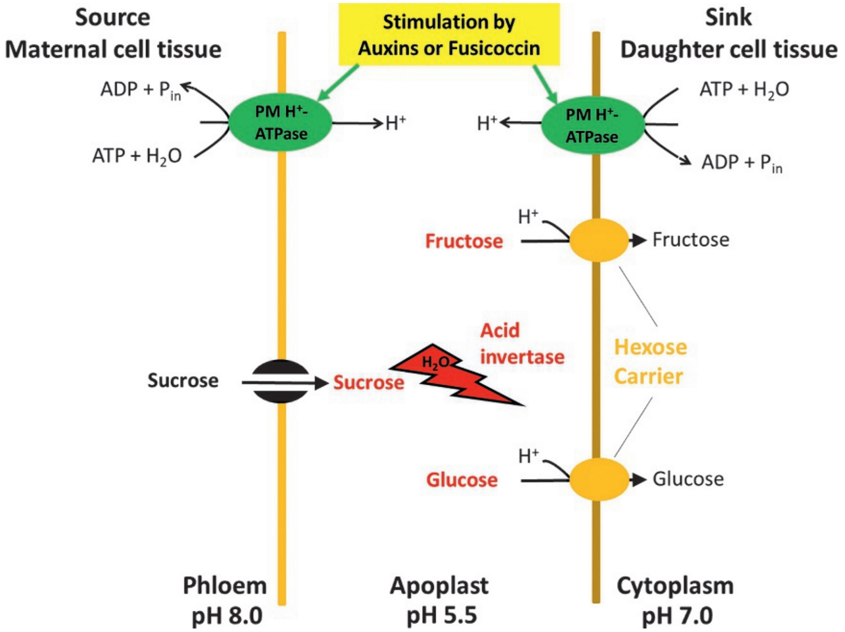
Source
Maternal cell tissue
Stimulation by
Auxins or Fusicoccin
Sink
Daughter cell tissue
ADP + P_{in}
ATP + H_2O
PM H^+-ATPase
H^+
H^+
PM H^+-ATPase
ATP + H_2O
ADP + P_{in}
H^+
Fructose
Fructose
Acid
invertase
Hexose
Carrier
H_2O
Sucrose
Sucrose
H^+
Glucose
Glucose
Phloem
pH 8.0
Apoplast
pH 5.5
Cytoplasm
pH 7.0

Fig. 2 Sucrose transport from source (leaves) to sink (kernels) of maize. Sucrose moves to the phloem terminus where it is released non-selectively through the plasma membrane (PM). In the kernel's apoplast it is hydrolyzed by means of acid invertase to glucose and fructose, which are selectively taken up by the daughter cells with hexose transporters. These transporters are energized with the pH gradient, established by the PM H^+-ATPase, which can be stimulated by auxins or fusicoccin. *Modified after Hütsch, B.W., Schubert, S., 2017. Harvest index of maize (*Zea mays *L.): are there possibilities for improvement? Adv. Agro. 146, 37–82.*

2. Auxins

2.1 Discovery of IAA and its metabolism in plants

Already in the late 19th century, a role for a growth-promoting substance in plants was postulated, which approximately 50 years later was termed auxin and identified as indole-3-acetic acid (IAA) (Went and Thimann, 1937, cited in Delker et al., 2008). In 1946, IAA was extracted for the first time from a plant material, namely immature maize kernels (Haagen-Smit et al., 1946, cited in Hager, 2003). IAA is the most abundant endogenous auxin in plants (Simon and Petrášek, 2011), where it is mainly required for oriented cell expansion.

Auxin metabolism is complicated not only by the fact that IAA is produced *via* multiple biosynthetic pathways, but also due to a complex metabolic network for conjugation of IAA to various metabolites (Delker et al., 2008). These IAA conjugates can serve as storage or transport forms of IAA, or contribute to its catabolic degradation for the removal of excess IAA. In addition to the dependence of auxin-regulated processes on biosynthesis and metabolism, the establishment of tissue-specific concentration gradients is also required for regulation of plant morphogenesis (Benkova et al., 2003; Cheng and Zhao, 2007; Simon and Petrášek, 2011). Such gradients may be formed by a combination of local sites of auxin biosynthesis and directional auxin transport, which involve specialized influx and efflux carriers (Delker et al., 2008). Most IAA is synthesized in young leaves by both tryptophan-dependent and tryptophan-independent pathways. IAA transport across the plasma membrane is either mediated by passive diffusion in the undissociated (protonated) form or by an active, carrier-mediated transport (auxin influx carriers) of the dissociated anion (IAA^-). Following the passive uptake, IAA dissociates in the more alkaline intracellular environment to the anion, which is trapped inside the cell and needs an efflux carrier for transport across the plasma membrane (Simon and Petrášek, 2011). Thus, multiple levels of regulation are involved in mediating the diverse physiological responses induced by auxin.

2.2 Auxin-induced elongation growth

While auxins were known to stimulate growth, it was not until the 1970s that the acid-growth theory proposed that some of this effect relies on apoplast acidification (Arsuffi and Braybrook, 2018). It is generally accepted that cell-wall loosening is the first auxin-induced process during elongation growth (Hager, 2003). If auxin controls the PM H^+-ATPase, it can also control the H^+-concentration of the apoplast and, as a consequence, the wall-loosening processes. Based on these assumptions, Hager et al. (1971) postulated the acid-growth theory with the following sequence of events: (1) PM H^+-ATPase pumps H^+ into the apoplast, (2) IAA enhances the activity of this H^+-ATPase causing a lowering of the apoplastic pH, (3) O_2 is needed to provide ATP as the substrate of the ATPase, (4) the extruded protons destroy Ca^{2+}-bridges, which stabilize the cell wall, and the lower pH activates cell wall-loosening enzymes (*e.g.*, expansins) initiating the enlargement of the cell, (5) the active H^+-secretion is compensated by an uptake of cations (*e.g.*, K^+), thus causing secondary auxin effects (*e.g.* increase of turgor for cell elongation). Growth induction by auxin (and by fusicoccin) requires potassium uptake through K^+ channels (Claussen et al., 1997; Siemieniuk and Karcz, 2015; Tode and Lüthen, 2001).

The main postulate of the acid-growth theory was the existence of a H^+-secreting, ATP-dependent enzyme in the PM. The PM H^+-ATPase was successfully isolated and purified by several researchers, starting in 1982 (Hager and Biber, 1984; Vara and Serrano, 1982). The PM H^+-pump exhibited a narrow pH optimum at 6.5 with a pronounced increase of activity between pH 7.5 and 6.5 (Hager and Biber, 1984). The activity of the PM H^+-pump can be regulated by the cytosolic pH while activation was observed due to a pH drop (Hager, 2003).

With measurements on maize coleoptiles, auxin rapidly increased the amount of antibody-detectable H^+-ATPase in the PM (significant already 10 min after IAA addition; Hager et al., 1991). The changes in the growth rate of the coleoptile segments in response to IAA exactly reflected the changes of the H^+-ATPase protein level in the PM. It is suggested that the auxin-enhanced H^+-extrusion is a gene-controlled process, responsible, *e.g.*, for the synthesis of PM H^+-ATPases, increasing the capacity for H^+-pumping into the apoplast as a precondition for wall enlargement ("acid growth"; Hager et al., 1991). Although there are strong indications that auxin-induced acid growth requires active transcription and translation (Arsuffi and Braybrook, 2018), contradictory results were also obtained (Cho and Hong, 1995; Jahn et al., 1996; Takahashi et al., 2012). Jahn et al. (1996) treated maize coleoptile segments *in vivo* with IAA, and found increased H^+-extrusion and elongation rates, whereas no increase in the amount of ATPase molecules was observed. They argued that the very short lag phases after auxin treatment, observed by Hager et al. (1991), seem to be incompatible with *de-novo* protein synthesis, thus pointing to its importance at the posttranslational level (Falhof et al., 2016).

A drawback of the study of Hager et al. (1991) is the missing of concomitant activity measurements of PM H^+-ATPase, thus it is unknown whether the activity showed parallel increases to the enhanced amount of PM H^+-ATPase enzyme (Cleland, 1995; Jahn et al., 1996). The auxin-induced increase in H^+-secretion could also be due to a greater activity of preexisting ATPases. According to Cleland (1995) there are various possibilities, how auxin can increase the activity of already existing PM H^+-ATPase molecules: (1) Reduction of cytosolic pH; a decrease in pH_c of 0.2 units results in a doubling in PM H^+-ATPase activity (pH optimum of PM H^+-ATPase: 6.5; cytosolic pH of most cells: 7.3–7.6);

(2) enhanced phosphorylation of the PM H^+-ATPase; (3) auxin activates a phospholipase, resulting in the formation of lysophospholipids in the PM, which are the most potent activators of the PM H^+-ATPase identified to date (Falhof et al., 2016). Finally, Cleland (1995) concluded that auxin-induced elongation is initiated when auxin binds to a receptor (auxin does not bind directly to the PM H^+-ATPase), probably located on the outside of the PM, and triggers a cascade of events leading to enhanced H^+-secretion by the PM H^+-ATPase.

Phosphatase-mediated changes in PM H^+-ATPase phosphorylation were identified as important determinants of auxin-regulated growth (Haruta et al., 2015). Phosphorylation of Thr-947 was stimulated in response to IAA, effects being evident within 10 min and peaked by 20 min (Takahashi et al., 2012). Spartz et al. (2014) proposed a mechanism for auxin-mediated PM H^+-ATPase activation involving SAUR proteins. *SAUR* genes represent the largest family of auxin-responsive genes, and several are rapidly induced following auxin treatment (Ren and Gray, 2015). SAUR overexpression results in both, increased PM H^+-ATPase activity and Thr-947 phosphorylation. These effects seem to be mediated by SAUR regulation of a family of protein phosphatases that dephosphorylate Thr-947; SAURs inhibit their activity. Since *SAUR* genes are rapidly upregulated by auxin, it is possible that the SAUR-mediated phosphatase mechanism may be fast enough to explain some of the rapid auxin effects on the H^+-pump (Haruta et al., 2015). The involvement of phosphatases and SAUR proteins in stimulation of PM H^+-ATPase by auxin could explain why after *in vitro* application of IAA to PM vesicles no effects were observed (Hager et al., 1991; Jahn et al., 1996). With isolation and purification, the phosphatases and SAUR proteins, which are normally located in the cytoplasm, are most likely removed from the vesicle samples, thus losing their regulatory function on PM H^+-ATPase.

Although the acid-growth theory is widely accepted by plant physiologists and has been supported by older studies (*e.g.*, Cleland, 1976: avena coleoptiles) and recent findings (Polak and Karcz, 2021: maize coleoptiles), nevertheless it is not without controversy. A critical inspection of the experimental basis of the acid-growth theory revealed that it is based on qualitative rather than quantitative arguments (Kutschera and Schopfer, 1985a). The authors reinvestigated four experimental predictions of the acid-growth theory of auxin action in inducing cell elongation, using abraded segments of maize coleoptiles. The coleoptile, the classical object of auxin research, is usually abraded or peeled off to remove parts of the waxy cuticle including the adhering epidermis in order to make the apoplastic space of the tissue experimentally accessible. A method to measure elongation growth and medium-acidification in the same tissue sample was established (Kutschera and Schopfer, 1985a). This is in contrast to previous studies, where the effects of IAA on H^+-secretion and cell elongation had been measured under different experimental conditions, thus making quantitative comparisons doubtful. The obtained results disagreed with the predictions in all four cases, thus Kutschera and Schopfer (1985a) concluded that these results are incompatible with the acid-growth theory of auxin action.

As peeled maize coleoptile segments failed to respond to auxin with normal growth and with H^+-secretion (Kutschera and Schopfer, 1985a), the function of the epidermis in auxin-mediated elongation growth of maize coleoptile segments was investigated in a further study (Kutschera et al., 1987). It was shown that the outer epidermis controls at least 85% of the IAA effect on elongation and H^+-extrusion of the intact coleoptile segment. These findings indicate that reception as well as action of IAA in this organ is predominantly localized in the epidermis. Strong support of this conclusion was brought about by the discovery and isolation of an IAA-binding protein (auxin receptor) which could be localized exclusively in the outer epidermis of maize coleoptiles (Löbler and Klämbt, 1985). The cooperation of functionally different tissues is emphasized ("systems-level" approach), and it is concluded that "cell elongation" can only be understood at the level of the entire organ that displays biochemical features not established by single cells (Kutschera et al., 1987; Kutschera and Khanna, 2020; Kutschera and Niklas, 2007).

2.3 Role of auxins during transition from vegetative to reproductive growth

Auxin signaling is essential for organogenesis and the generation of all primordia. Auxins are polarly transported to the site of primordia initiation (Delker et al., 2008), where they are perceived by the nuclear auxin receptor (Galli et al., 2015). During transition from vegetative to reproductive growth, the shoot apical meristem turns into an inflorescence initiating floral meristems. Grasses such as maize contain inflorescences with multiple types of specialized reproductive axillary meristems (AMs). In maize, these AMs give rise to two types of inflorescences: the tassel, which produces male florets optimized for pollen dispersal, and the ear, which produces female florets and finally form the kernel-bearing cob (Skirpan et al., 2009). Therefore, auxins are necessary for the initiation of floral primordia, and the disruption of auxin biosynthesis, polar auxin transport, or auxin signaling leads to the failure of flower formation (Cheng and Zhao, 2007). The inhibition of auxin transport may lead to accumulation of auxin in meristems to levels that are inhibitory for the formation of new primordia. This demonstrates particularly for auxins that the dosage can produce a poison.

2.4 Auxin action in developing maize kernels

2.4.1 Synthesis of IAA and interaction with cytokinins

Developing maize kernels contain levels of IAA several orders of magnitude greater than reported for vegetative tissues (Bandurski and Schulze, 1977). Maize endosperm, which constitutes the majority of kernel dry matter, was used to investigate the timing of developmental events and regulatory roles of auxins (Lur and Setter, 1993a). There are several stages of endosperm development: (a) cell division, (b) cell enlargement and differentiation, (c) accumulation of storage material, (d) desiccation and maturation. Shortly after pollination, developing cereal grains exhibit significant transient increases in two of the major plant hormones, auxins (IAA) and cytokinins (Locascio et al., 2014; Morris, 1997). In maize kernels, cytokinins (zeatin and zeatin riboside) showed maximal concentrations at an early stage (approximately 9–10 DAP), which coincided in time with the peak in endosperm cell division rate (Dietrich et al., 1995; Jameson and Song, 2016; Lur and Setter, 1993a, 1993b; Morris et al., 1993; Rijavec et al., 2011). The enzyme cytokinin oxidase increases shortly after the increase in active cytokinins and is responsible for decreasing cytokinins back to basal levels (Jones and Setter, 2000; Morris, 1997). In contrast, IAA concentration was low at 9 DAP and increased sharply thereafter (Lur and Setter, 1993a). Starting 10–15 DAP, a strong increase of total IAA in the content per kernel (up to 5000-fold) and in the concentration (up to 360-fold) were observed, reaching the maximum at about 45 DAP (Jensen and Bandurski, 1994). The maize endosperm is a site of IAA biosynthesis, containing all necessary enzymes required for *de-novo* aromatic biosynthesis of IAA and its ester conjugates (Jensen and Bandurski, 1994). The results of Glawischnig et al. (2000) strongly suggest that tryptophan-dependent IAA synthesis is the predominant pathway for auxin biosynthesis in the maize kernel. In addition, some IAA might be imported into the kernel from the mother plant. The sequence of events during auxin action is biosynthesis, polar transport, and perception/transduction of the signal (Locascio et al., 2014). By the time IAA begins to accumulate, cell division has ceased and growth occurs through cell expansion, an effect that is usually attributed to IAA (Jensen and Bandurski, 1994; Morris, 1997).

In addition to their absolute concentrations and timing of their accumulation, the cytokinin-to-auxin ratio and their interaction play an important role in regulating development (Lur and Setter, 1993b). The decrease in cytokinin concentration and the strong increase in auxin concentration at about 10 DAP created a sharp decline in the cytokinin-to-auxin ratio. This ratio is important for the regulation of several developmental processes, such as the start of starch and storage protein accumulation at about 10 DAP (Jones and Setter, 2000; Lending and Larkings, 1989; Ou-Lee and Setter, 1985). Gradients of hormones in the different seed compartments are generated and are important for communication. Correct seed development requires a coordinated crosstalk between the seed tissues, and failure in phytohormone communication can cause seed abortion (Locascio et al., 2014).

2.4.2 Integrated action of IAA with sugars, 14-3-3 proteins and nitrogen

In early maize kernel development, the integrated action not only of several hormones, but also of sugars is required (Doll et al., 2017). Sugars have a well-documented dual functionality, acting as metabolites and also as signaling molecules with multiple regulatory roles (Koch, 2004; LeClere et al., 2008; Rolland et al., 2006; Smeekens and Hellmann, 2014). Results indicate that sugar influx into sink tissues may influence sink size and strength by regulating auxin levels (LeClere et al., 2010). As there are no symplastic connections between the mother plant and the developing daughter kernel (Tang and Boyer, 2013), the apoplastic way is compulsory making the hydrolysis of incoming sucrose into hexoses a prerequisite for sugar uptake into the kernel. The key enzyme for this hydrolysis is acid invertase, located in the cell wall. The involvement of this enzyme in sugar metabolism and auxin biosynthesis was studied with cell wall invertase-deficient *minature1* maize kernels, which result from a loss-of-function mutation at the *MN1* locus that encodes a cell wall invertase (Chourey et al., 2010). The kernels are characterized by a small seed size, resulting from both, decreased cell size pointing to reduced cell enlargement, and decreased cell number due to less cell division in developing endosperm (Vilhar et al., 2002). The miniature kernels showed greatly reduced levels of IAA throughout kernel development, indicating that invertase-mediated sucrose cleavage directly or indirectly regulated the levels of this plant hormone during seed development (LeClere et al., 2008). Developing maize kernels may modulate growth by altering IAA biosynthesis in response to sugar concentrations (LeClere et al., 2010). Although auxins have been previously reported to regulate invertases and thus sugar levels (Roitsch et al., 2003), the studies of

LeClere et al. (2008, 2010) and of Chourey et al. (2010) give evidence to suggest the reverse that sugar levels affect auxin levels. In addition, it is assumed that some of the extensive crosstalk between auxin and cytokinin is mediated through sugar signals originating from invertase function (LeClere et al., 2008, 2010).

Apart from the importance of sugars and plant hormones for signaling networks, 14-3-3 proteins are also involved, as key players, in various aspects of plant hormone physiology. They are versatile regulators of IAA action (Camoni et al., 2018). In addition, the nutrient nitrogen can regulate plant development through the control of hormone metabolism (Krouk et al., 2011). Different N regimes in maize have been shown to alter IAA biosynthesis, transport, and accumulation (Tian et al., 2008). Increased biomass accumulation in maize grown in mixed N supply (75% nitrate/25% ammonium), in comparison to nitrate or ammonium alone, was mediated by increased auxin synthesis (Wang et al., 2019). Application of mixed N-forms (ammonium and nitrate) caused 11% maize grain yield increase compared to merely nitrate application due to a higher kernel number at maturity (Smiciklas and Below, 1992).

2.4.3 Application of cytokinins and auxins

Several researchers have attempted to influence grain yield by exogenous cytokinin applications, and could enhance grain set, sometimes leading to yield increases (Jameson and Song, 2016; Morris, 1997; Smiciklas and Below, 1992). However, when targeting increases in cytokinins the possibility of enhancing cytokinin degradation has to be considered, as the plant reacts by activating homeostatic mechanisms (Jameson and Song, 2016). The key to this reaction is the enzyme cytokinin oxidase, which catalyzes the irreversible degradation of many cytokinin forms (Gajdošová et al., 2011; Werner et al., 2006). In contrast, long-acting, synthetically produced cytokinins (*e.g.*, BAP, benzyl-amino-purine) cannot be degraded by cytokinin oxidase (Morris, 1997; Schopfer and Brennicke, 2010). The cytokinin metabolism of three different maize hybrids, grown under non-stressed field conditions, was investigated by Dietrich et al. (1995). Stalk infusions of BAP into intact plants at pollination increased the kernel number per cob at maturity by up to 30%, contemporarily kernel weight decreased significantly by 19%, resulting in an unchanged kernel yield per cob. In addition, applications at 3 DAP and 6 DAP did not result in significant alterations in yield or kernel number. The apical 10–15% of kernels were found to abort unless treated with cytokinins. Dietrich et al. (1995) suggested that BAP was allowing apical kernels (which would normally abort) to pass some critical stage so that, on pollination, they could develop normally. Thus, cytokinin affects two phases of grain development: an early phase at pollination when kernel set is improved, and a subsequent phase after pollination when the peak of endosperm cell division occurs.

IAA regulates fresh weight growth in many plant tissues (Cleland, 1995), and the synthetic auxin 2,4 D also stimulated fresh weight accumulation in maize endosperm (treatment at 11 DAP, endosperm sampling at 15 DAP; Lur and Setter, 1993b). In our own studies, we applied IAA to unstressed maize plants twice, 2 days before controlled pollination and at pollination day, by spraying the substance evenly onto the whole plant (application rate per plant: 1.9 mL of 1.5 mM IAA plus 0.1% Tween-20). The developing kernels were harvested at 2 DAP, the material was homogenized and plasma membrane (PM) vesicles were isolated and purified by two-phase partitioning as described by Jung et al. (2017). The *in vitro* hydrolytic activity of the PM H^+-ATPase (measured at the optimum pH 6.5) was significantly stimulated by 22% due to IAA application (Fig. 3A; B.W. Hütsch and F. Tscharn, unpublished). Also, the maximal pH gradient (ΔA_{492}) at the PM was substantially increased by 10% (Fig. 3B). The concentrations of sucrose and hexoses in the kernels were unaffected by the IAA treatment. We hypothesized that due to a stimulation of the PM H^+-ATPase hexose transport into the developing kernels will be favored, resulting in less kernel abortion. However, at maturity kernel numbers per cob were significantly decreased causing grain yield reductions of 19% (Fig. 3C and D; B.W. Hütsch and F. Tscharn, unpublished). Thus, increased PM H^+-ATPase activity could not be translated into grain yield improvements. Probably the auxin application occurred too early during kernel development. As initially upon pollination the cytokinins play the key role, auxin application at this stage might have disturbed the phytohormone balance, causing disruption of cell division (shorter period of mitotic activity and generation of less endosperm cells; Ma et al., 2019) and a rather early onset of cell enlargement due to increased IAA concentrations. In fact, individual kernel weight was increased by 11% due to IAA application (Fig. 3E; B.W. Hütsch and F. Tscharn, unpublished).

2.4.4 Involvement of phytohormones in kernel abortion under stress

ABA plays a central role as "master controller" in plant responses to stress, as reflected by the broad scope of processes over which it exerts substantial control (Liu et al., 2005; Setter, 2006). In response to water deficit

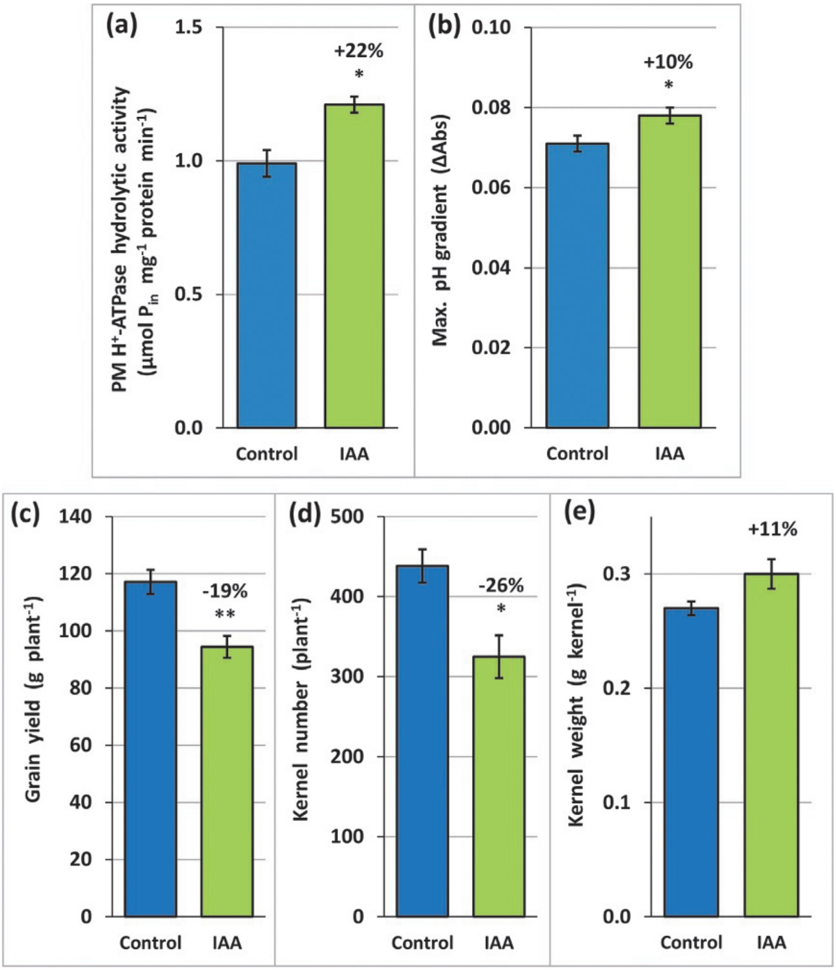

Fig. 3 Hydrolytic PM H$^+$-ATPase activity (A) and maximal pH gradient (B) of vesicles derived from developing maize kernels (cv. Pioneer 3906), harvested 2 days after controlled pollination, and grain dry matter yield (C), kernel number per cob (D), and single kernel weight (E) at maturity, as affected by IAA treatment during flowering; data show means of five replicates $\pm$ *SE*; differences in percentage between control and treatment are given and, if significant, indicated by $*P \leq 5\%$ and $**P \leq 1\%$. Dosage per plant: 1.9 mL of 1.5 mM IAA (B.W. Hütsch and F. Tscharn, unpublished).

ABA accumulated in maize kernels (Ober et al., 1991; Westgate et al., 1996), and kernel set is lost in response to exogenously supplied ABA (Mambelli and Setter, 1998; Myers et al., 1990). Additionally, the rise in ABA levels in maize seems to be specific to the kernels in apical cob regions

(Ober et al., 1991; Setter et al., 2001; Wang et al., 2002), which are most prone to abortion (Artlip et al., 1995), causing substantial grain yield losses. The negative impact which ABA exerts on PM H^+-ATPase activity (Falhof et al., 2016; Schubert and Matzke, 1985) could be counteracted by IAA application possibly enhancing kernel set and grain yield.

Although ABA is the most studied stress-responsive phytohormone, the role of cytokinins, ethylene, gibberellins, brassinosteroids, and auxins during environmental stress is emerging (Achard et al., 2006; Colebrook et al., 2014; Ha et al., 2012; Iqbal et al., 2011; Krouk et al., 2011; Peleg and Blumwald, 2011; Qin et al., 2011; Wang et al., 2008). Crosstalk between the different hormones results in synergistic or antagonistic interactions that play crucial roles in response of plants to abiotic stress (*e.g.*, Brugière et al., 2003). Reed and Singletary (1989) shaded maize plants during flowering to increase kernel abortion, and investigated the roles of carbohydrate supply and the phytohormones IAA, ABA, and the cytokinin zeatin riboside, the biologically dominant cytokinin in developing maize kernels. Kernel abortion was not initiated by an inadequate supply of carbohydrates, rather by an impaired transfer of sugars to the developing kernels, and it was also not initiated by a signal of the investigated hormones. After completion of abortion, aborted kernels contained higher concentrations of ABA and lower concentrations of IAA than non-aborted kernels (Reed and Singletary, 1989). According to the authors, kernel abortion in maize may occur by the following sequence of physiological events (see also Hütsch and Schubert, 2017):

- Ethylene, generated in the ear during pollination of silks, initiates abortion by inhibiting growth of slower-growing kernels at the cob tip.
- Reducing sugars accumulate in the cob of aborting kernels.
- ABA increases in aborting kernels, which may promote abortion by inhibiting both, kernel growth and sugar uptake by the kernels.
- Levels of growth-promoting hormones IAA and cytokinins in aborting kernels may be insufficient to counteract growth inhibition by ABA and ethylene.
- Completion of abortion is due to termination of sugar supply.

The importance of ethylene for maize kernel abortion was further strengthened by studies of Cheng and Lur (1996), Habben et al. (2014), Hanft et al. (1990), and Shen et al. (2020).

3. Fusicoccin

Almost 60 years ago, a toxin produced by the fungus *Phomopsis amygdali* (formerly known as *Fusicoccum amygdali* Del.) was identified to cause the wilting disease of peach and almond trees in Italy (Graniti, 1962, cited in De Boer and De Vries-van Leeuwen, 2012). The major active compound in the fungal extract was called fusicoccin-A (FC), which is the best-studied member of the fusicoccanes, a class of diterpenes (De Boer and De Vries-van Leeuwen, 2012). A compilation of the historical milestones in FC research is given by Camoni et al. (2019). The first comprehensive review on fusicoccin as a tool in plant physiology was published by Marrè (1979). FC is able to stimulate a number of important physiological processes such as H^+-extrusion, K^+ uptake, and cell enlargement, effects strikingly similar to that induced by auxins. FC is therefore sometimes called "super-auxin" (Hager, 2003). The FC action is in agreement with the acid growth theory (Kutschera and Schopfer, 1985b). It is suggested that several, probably all, effects of FC can be interpreted as consequences of the primary direct activation of the H^+-pump in the plasma membrane: *e.g.*, uptake of cations and various anions, of amino acids and sugars, and also of the increase in malate synthesis as a consequence of the rise in cytosolic pH (malate/oxal-acetate buffer system). Thus, it is concluded that the observed effects depend on the interaction between FC and the PM H^+-ATPase, although *in vitro* studies on isolated membrane vesicles showed unsatisfactory reproducibility and high variability of stimulation due to FC (Marrè, 1979).

3.1 *In vitro* effects of FC on PM H^+-ATPase

In the early *in vitro* studies, microsomal vesicles were used which constitute a mixture of various membranes containing at least three distinct ATP-dependent H^+-pumps: ATPases located at the tonoplast (inhibition by nitrate), the plasma membrane (inhibition by vanadate), and mitochondrial and chloroplast membranes (inhibition by azide). This problem was partly overcome by using microsomal vesicles from 24-h-old radish seedlings, which showed an 80% vanadate-sensitive ATPase activity as compared to about 30% in 72-h-old seedlings (De Michelis et al., 1983; Rasi-Caldogno et al., 1985). At this stage, two-phase partitioning for purification of the membrane suspension had not been introduced, and the percentage of sealed inside-out vesicles and right-side out vesicles was variable

(De Michelis et al., 1983). This could partly explain variations of results between different studies on *in vitro* effects of FC on PM H^+-ATPase of isolated vesicles. In addition, in several studies the vesicles were preincubated without and with FC between 25 °C and 33 °C for up to 1 h prior to measurements of hydrolytic or pumping activity of the PM H^+-ATPase (Blum et al., 1988; De Michelis et al., 1989, 1991; Rasi-Caldogno et al., 1986, 1993; Rasi-Caldogno and Pugliarello, 1985). According to Rasi-Caldogno et al. (1986), pretreatment was necessary to obtain maximal stimulation of the H^+-pumping activity by FC, the reasons for the requirement still being unknown.

However, during this preincubation uncontrolled enzymatic reactions can take place. It is argued that FC binding possibly protected its receptor from degradation during PM extraction and purification, or FC prevented the loss of essential components (De Michelis et al., 1991; Rasi-Caldogno et al., 1993; Schulz et al., 1990). It is questionable which effects were measured after preincubation. There exists uncertainty whether an increase in PM H^+-ATPase activity after preincubation with FC is in fact caused by a real stimulation, or whether it is rather an increase relative to the strong decrease in activity in the control vesicles without FC. Indeed, the difference relied only on the decrease in activity of the control PMs (from pH 6.6 to pH 7.5); after FC treatment the activity was identical at both pH values (Rasi-Caldogno et al., 1993). Overall, it can be concluded that the results of *in vitro* FC effects on PM H^+-ATPase obtained after preincubation at room temperature and above are not convincing. The conclusion that FC is able to stimulate the PM H^+-ATPase in isolated plasma membranes is therefore doubtful.

In order to prevent uncontrolled enzymatic reactions prior to measurement of PM H^+-ATPase activity, we conducted *in vitro* experiments pretreating isolated PM vesicles from developing maize kernels with 100 μM FC for 15 min on ice. This should allow electrostatic binding of FC to its partners, which does not involve enzymatic reactions and thus also takes place at low temperatures. Subsequently, the hydrolytic H^+-ATPase activity of the samples was measured with 5 μM FC in the assay. FC showed no effect at the four assay pH values tested (Fig. 4; B.W. Hütsch et al., unpublished). Even though the FC pretreatment on ice did not result in a stimulation of the PM H^+-ATPase, at least during activity measurements at 30 °C for 30 min an effect would have been expected as FC-induced activation was shown to occur within a few

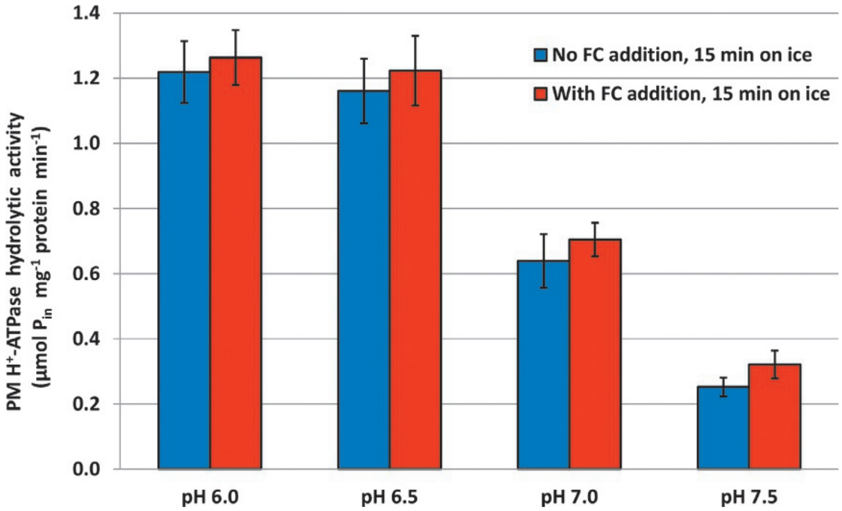

Fig. 4 Hydrolytic PM H$^+$-ATPase activity of vesicles derived from developing maize kernels (cv. Amadeo), grown under optimal conditions and harvested 3 days after controlled pollination; the vesicles were pretreated without or with 100 µM FC on ice for 15 min prior to activity measurement at 30 °C for 30 min; the FC concentration in the assay was 5 µM and the pH was adjusted to the desired values; data show means of three replicates ± *SE*; within each pH value, differences between untreated control and FC application were not significant at the 5% level (B.W. Hütsch et al., unpublished).

minutes (De Michelis et al., 1991; Hager et al., 1991; Johansson et al., 1993). Therefore, as long as decomposing processes in the isolated vesicles can be excluded during pretreatment, *in vitro* FC application does not affect PM H$^+$-ATPase activity.

3.2 Physiology of FC action on PM H$^+$-ATPase

The PM H$^+$-ATPase contains a C-terminal autoinhibitory domain (Palmgren et al., 1991) which has been found to be associated with a 14-3-3 protein (Jahn et al., 1997; Oecking et al., 1997). In eukaryotic cells 14-3-3 proteins are abundant cytosolic proteins, that bind tightly to other proteins resulting in stabilization of conformations (Ferl, 2004; Wilson et al., 2016). In plants, 14-3-3 proteins have been suggested to play a role also in the binding of FC, which is able to stabilize the active ATPase/14-3-3 complex (Falhof et al., 2016; Korthout and De Boer, 1994; Marra et al., 1994; Oecking et al., 1994). The physiological factors involved in controlling the PM H$^+$-ATPase activity were investigated in detail by employing a FC-responsive yeast expressing *Arabidopsis* PM H$^+$-ATPase AHA2 (Baunsgaard et al., 1998). Acidification of the external medium indicated that FC activates the plant PM

H^+-ATPase in this system. As the 14-3-3 protein binds directly to the C-terminus of the H^+-ATPase, this interaction apparently creates a FC-binding site (Baunsgaard et al., 1998; Oecking and Hagemann, 1999). In the presence of FC, addition of 14-3-3 protein caused an increase in the hydrolytic PM H^+-ATPase activity of AHA2 in the yeast system, whereas FC in the absence of exogenously added 14-3-3 protein had no effect. Apparently, the 14-3-3 protein already associated with the membrane was insufficient to produce any detectable activation of AHA2 (Baunsgaard et al., 1998). In order for the 14-3-3 protein to bind to the PM H^+-ATPase and release C-terminal autoinhibition, phosphorylation of the penultimate threonine (Thr-947 in AHA2) is a prerequisite (Falhof et al., 2016; Fuglsang et al., 1999; Olsson et al., 1998; Svennelid et al., 1999). FC application to plants increased phosphorylation levels of the penultimate Thr, most likely resulting from bound 14-3-3 protein, protecting the pThr from phosphate removal by protein phosphatases (Falhof et al., 2016). Yet, it was shown that FC-induced stabilization occurs also in the absence of phosphorylation (Fuglsang et al., 2003). Posttranslational modifications of the PM H^+-ATPase such as phosphorylation of certain amino acid residues, mainly clustered in the autoinhibitory domain, play crucial roles in its regulation (Falhof et al., 2016; Haruta et al., 2015). Phosphorylation at Thr-881 or Thr-947 increases AHA2 activity, whereas phosphorylation at Ser-899 or Ser-931 decreases the activity (Haruta et al., 2015).

As a large number of 14-3-3 and PM H^+-ATPase isoforms exists in Arabidopsis (13 and 11 expressed genes, respectively), the binding between 14-3-3 and ATPase isoforms may be rather specific (Alsterfjord et al., 2004). FC treatment of Arabidopsis leaves induced strongly increased binding of 14-3-3 to the ATPase (Alsterfjord et al., 2004), which is much more than previously stated that FC binds to and stabilizes the already activated H^+-ATPase/14-3-3 complex (Jahn et al., 1997; Oecking et al., 1997). FC promotes 14-3-3 protein binding to the PM H^+-ATPase in an essentially irreversible manner (Olsson et al., 1998; Svennelid et al., 1999). Thus, the FC molecule fits in a cavity in the interaction surface between PM H^+-ATPase and 14-3-3 protein to tightly bridge the two partners (Fig. 5; Falhof et al., 2016). It is calculated that under conditions without FC less than 1% of total 14-3-3 is attached to the ATPase, whereas after FC treatment several percent of total 14-3-3 may be engaged in activation of the PM H^+-ATPase (Alsterfjord et al., 2004). A decrease in specificity upon FC treatment is suggested, resulting in recruitment of additional 14-3-3 isoforms to the PM (Alsterfjord et al., 2004; Würtele et al., 2003).

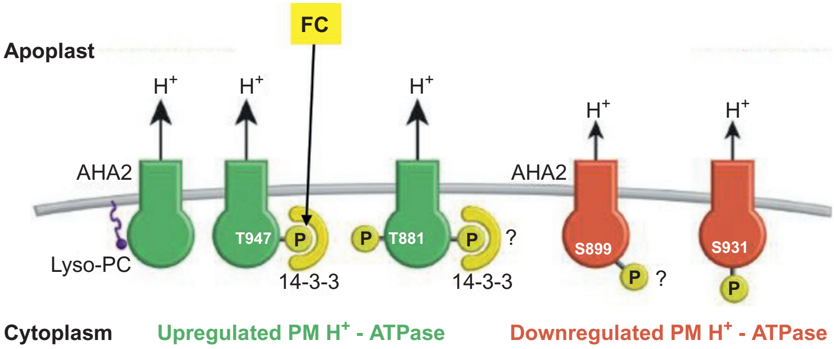

Fig. 5 Posttranslational regulation of the PM H^+-ATPase: in the downregulated state the pump can still hydrolyze ATP, but the coupling efficiency between energy consumption and transport of H^+ is low. In the upregulated state the coupling efficiency and H^+-transport rates are high. Phosphorylation (P) of the C-terminal penultimate threonine residue (Thr-947 in the Arabidopsis pump AHA2) creates a binding site for activating 14-3-3 protein. FC fits in the cavity between (P) and 14-3-3 and causes an irreversible binding of the two partners *Modified after Falhof, J., Pedersen, J.T., Fuglsang, A.T., Palmgren, M., 2016. Plasma membrane H^+-ATPase in the center of plant physiology. Mol. Plant 9, 323–337.*

Hence, the main factors for the failure of *in vitro* FC effects on PM H^+-ATPase can be summarized as follows: (1) After two-phase partitioning and several centrifugation steps, the vesicle samples most likely do not contain free 14-3-3 proteins anymore. (2) If the vesicle samples are kept ice-cold during the whole preparation procedure (during isolation and prior to activity measurements), decomposition of the active ATPase/14-3-3 complex by proteases or dephosphorylation by phosphatases is neglectable. (3) A stabilization of the still intact complex by *in vitro* addition of FC to the vesicles is therefore not needed to stimulate H^+-ATPase activity, and (4) FC cannot support additional 14-3-3 bonds because of the lack of free 14-3-3 proteins. Thus, as a logical consequence it is concluded that stimulation of PM H^+-ATPase activity by FC supply to the isolated, purified vesicles cannot be expected. In order to support this conclusion, it should be tested if the supply of appropriate 14-3-3 proteins to the vesicle sample, in addition to FC, causes a stimulation of PM H^+-ATPase.

3.3 Kinetic parameters of PM H^+-ATPase and pH dependence of FC action

The hydrolytic PM H^+-ATPase activity of membrane preparations from cell-suspension cultures showed typical Michaelis-Menten kinetics, and when the cells were incubated with FC for 30 min prior to homogenization, FC doubled V_{max} and lowered k_m by a factor of 2 (Schulz et al., 1990). Similar results were obtained by Johansson et al. (1993) after FC treatment of spinach leaves prior to PM vesicle isolation. Oat roots, treated with FC prior to PM isolation, showed significantly increased V_{max} by 1.4-fold and 1.9-fold when hydrolytic H^+-ATPase activity was measured at pH 7.0 and 7.5, respectively, whereas no effect was observed on k_m (Lanfermeijer and Prins, 1994). FC *in vivo* treatment of maize coleoptile segments led to a 2-fold increase in V_{max} and a decrease in k_m for ATP from 1.5 to 0.24 mM (Jahn et al., 1996). The FC- and 14-3-3-activated PM H^+-ATPase AHA2 expressed in yeast exhibited about a 2-fold increase in V_{max}, whereas the apparent affinity for ATP remained unaffected ($k_m = 0.7$ mM measured at pH 7.0; Baunsgaard et al., 1998). Thus, an increase in V_{max} was frequently observed after FC treatment, whereas k_m was either decreased or unaffected. In addition, FC stimulated H^+ pumping more than it stimulated ATP hydrolysis, suggesting that the coupling between hydrolysis and H^+-pumping became more efficient, which may be an important part of the regulatory process (Babakov et al., 2000; Johansson et al., 1993; Palmgren et al., 1991).

Several authors reported pronounced stimulatory effects of FC at pH values around 7, thus typical for the cytosolic cell compartment, but at values around the pH optimum of the PM H^+-ATPase (pH 6.5), FC effects were hardly detectable (Baunsgaard et al., 1998; Jahn et al., 1996; Johansson et al., 1993; Lanfermeijer and Prins, 1994; Olivari et al., 1998; Schulz et al., 1990).

3.4 *In vivo* effects of FC on PM H^+-ATPase

Considerable stimulation of PM H^+-ATPase activity was only observed when intact plants or plant organs were treated with FC *in vivo* or prior to PM isolation by adding FC to the tissue homogenization medium (De Michelis et al., 1996; Johansson et al., 1993; Lanfermeijer and Prins, 1994; Oecking et al., 1994; Rasi-Caldogno et al., 1986, 1993; Schulz et al., 1990). Thus, in subsequent studies plant seedlings were treated *in vivo* with FC prior to membrane isolation (De Michelis et al., 1996; Olivari et al., 1998). After *in vivo* treatment of Arabidopsis, binding of FC to the PM and stimulation of hydrolytic H^+-ATPase activity were detectable after 15 min, and increased with the length of treatment up to 3 h (De Michelis et al., 1996). The slow penetration of FC was explained by the rather compact tissues of the seedlings, and could be accelerated by higher FC concentrations or vacuum infiltration of FC (as used by Johansson et al., 1993). In addition, FC bound during *in vivo* treatment was still bound to isolated PMs (De Michelis et al., 1996), and FC-activated H^+-ATPase was sufficiently stable in its activated state to withstand membrane isolation and purification (Jahn et al., 1997; Lanfermeijer and Prins, 1994; Schulz et al., 1990). It was demonstrated that the 14-3-3 protein interacts directly with the C-terminal region of the H^+-ATPase (Jahn et al. (1997). An increased association between the 14-3-3 protein and ATPase when treated with FC suggests that FC in some way stabilizes the ATPase/14-3-3 protein complex, making the association irreversible (De Boer, 1997; Fullone et al., 1998; Olsson et al., 1998; Svennelid et al., 1999). Thus, FC application strongly facilitates purification of the H^+-ATPase/14-3-3 protein complex (Jahn et al., 1997).

We tried to stimulate PM H^+-ATPase activity of developing maize kernels *in vivo* by application of FC onto the two leaves adjacent to the maize cob. Treatment with 1.5 mL of a 73 μM FC solution per plant at time of controlled pollination did not affect PM H^+-ATPase in isolated vesicles derived from kernels which were harvested 2 DAP (results not shown). Probably, FC transport from the leaves to the developing kernels was not fast enough or did not take place at all, as penetration of FC through the intact epidermal cuticle seems to be very slow (Radice et al., 1980). After entering the plant, FC is mainly transported *via* the transpiration stream in the xylem, whereas phloem transport is of minor importance (De Boer, 1997; Radice et al., 1980). In addition, phloem transport of metabolites is driven by source/sink relations, the maize cob being not really a sink for FC. In order to overcome these transport problems, we injected a FC solution (1 mL of 20 μM FC per cob) by syringe and needle into the rachis of the developing maize cob at time of controlled pollination. At maturity, the kernels on the FC-treated cobs were somehow out of alignment combined with size increase of single kernels (Fig. 6A). Thus, the injected FC obviously had an impact on kernel growth, although the distribution of FC was still unsatisfactory. FC application did neither significantly affect grain yield nor its determinants, number of kernels per cob and single kernel weight (Fig. 6B–D). Additionally, the results are far from our original purpose to improve kernel setting and thus grain yield by stimulation of PM H^+-ATPase. Application of FC onto the leaves is obviously no useful approach to achieve this goal, in contrast to auxin application, as described in Section 2.4.3 of this review.

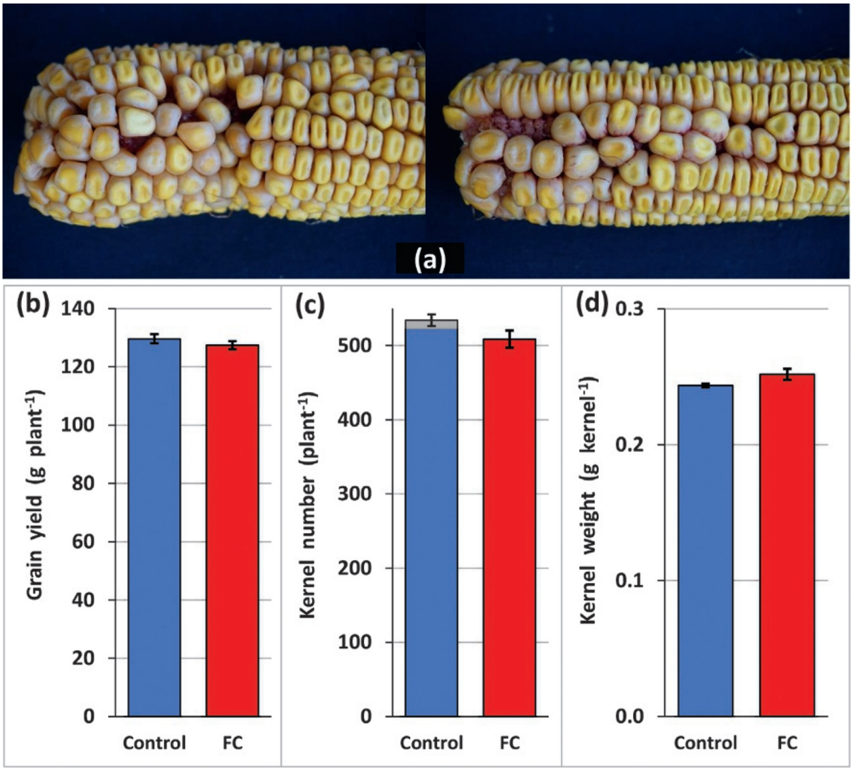

Fig. 6 Maize cobs as affected by FC injection during flowering (A), grain dry matter yield (B), kernel number per cob (C), and single kernel weight (D) of cv. Pioneer 3906, harvested at maturity; data show means of five replicates ± *SE*; differences between control and FC-treated plants were not significant at the 5% level (B.W. Hütsch et al., unpublished).

3.5 Comparison of FC and auxin action on PM H^+-ATPase

The early effects of natural hormones often involve protein synthesis and long chains of intermediary events, whereas FC seems to interact directly with its physiologically active target (Marrè, 1979). FC is relatively monotonous in its action and shows little or no tissue or organ specificity, while hormones display a large variety of tissue-specific effects. The action of IAA or ABA closely repeats (IAA) or antagonizes (ABA) the main features of FC action on the various aspects of plant physiology (Marrè, 1979).

Activation by FC, in contrast to activation by auxin (Hager et al., 1991), is not likely to proceed *via* regulation at the transcriptional or translational level, as the observed activation by FC was relatively rapid and largely completed within 4 min of incubation (Johansson et al., 1993) or without a lag-phase (Hager et al., 1991). FC treatment had no effect on the amount of H^+-ATPase molecules within the PM (Hager et al., 1991; Jahn et al., 1996; Lanfermeijer and Prins, 1994). These results are supported by observations that FC action is insensitive to inhibitors of protein synthesis (Kutschera and Schopfer, 1985b; Marrè, 1979; Rubinstein and Cleland, 1981). Cycloheximide CHX (inhibitor of protein synthesis) has been shown to completely inhibit auxin-induced growth and proton extrusion, whereas the effect upon FC treatment was much weaker (Kutschera and Schopfer, 1985b).

4. Conclusions and perspectives

Stimulation of PM H^+-ATPase by *in vitro* application of IAA or FC to isolated PM vesicles is most unlikely. During isolation and purification important components such as 14-3-3 proteins and phosphatases are probably lost, making the activation of PM H^+-ATPase by FC and IAA, respectively, improbable. In order to support this conclusion for FC, it should be tested if the supply of appropriate 14-3-3 proteins to the vesicle sample, in addition to FC, causes a stimulation of PM H^+-ATPase. *In vivo* activation of PM H^+-ATPase by addition of FC or IAA to intact plants or to plant organs was shown in numerous studies. However, activation of PM H^+-ATPase in developing maize kernels by FC treatment is a difficult task, as FC is poorly phloem-mobile making its transport into the maize cob problematic. On the contrary, IAA, sprayed onto the whole maize plant at anthesis, was able to stimulate PM H^+-ATPase activity in the maize kernels shortly after pollination. Yet, this stimulation did not result in a better kernel set and increased grain yield at maturity, instead significant decreases were obtained. The growth stage, when IAA was applied, was probably too early, disturbing the balance between cytokinins and auxins in the kernels.

Future studies could try to improve kernel setting by application of cytokinins at flowering. Cytokinins are mainly responsible for cell division, but presumably decrease PM H^+-ATPase activity (Falhof et al., 2016). A stimulatory effect of IAA, not only on PM H^+-ATPase but also on kernel growth, can be expected when applied later in kernel development towards the end of the cell division phase (approximately at 10 DAP). Auxins are also responsible for the formation of flower primordia and floral initiation which starts at the 5-leaf-stage (V5) and determines the potential kernel number.

Application of auxins at this early growth stage would be particularly interesting for maize plants grown under stress conditions such as drought or salinity. Auxins could counteract the stress hormone ABA, alleviating growth depressions and favoring the development of floral meristems. Higher potential kernel numbers make yield improvements more probable. Auxins and cytokinins, applied at the appropriate growth stages, are promising measures to improve maize kernel development and grain yield, thus finally increasing the harvest index.

Acknowledgments

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CHAPTER FIVE

Overview and application of the Mitscherlich equation and its extensions to estimate the soil nitrogen pool fraction associated with crop yield and nitrous oxide emission

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Abstract

Natural levels of soil nutrients are spatio-temporally variable and insufficient for agricultural purposes. Artificial fertilizers are applied to achieve greater crop growth rates and yield. Mitscherlich's equation and Boule's fertilizer units are described and illustrated in relation to crop yield then applied to estimate the nitrogen (N)-pool fraction in the soil

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that contributes to a component of greenhouse gas (GHG) emission, specifically the nitrous oxide (N_2O) flux. Mitscherlich (1909) proposed a diminishing returns model to extract information about soil N status for production responses. Mitscherlich's equation was generalized by Baule (1918) and modified by Bray (1945) to account for soil nutrient contributions for multiple fertilizers. These models are examined in this chapter. Their application results in the extraction of further information on soil nutrient variability and N_2O emission across various geo-positions (specific global locations). It is concluded that Mitscherlich's equation and Boule's fertilizer units are useful tools to investigate soil-fertilizer interaction and compare soil fertility and GHG emission.

1. Introduction

Our climate's nitrogen (N) cycle supports all biogeochemistry processes and products and is fundamental for sustaining plant and animal life on earth. The cycles and activities of our planet with the sun control the interplay among earth-related phenomena, which include photosynthesis, biological N cycling (incorporating nitrification, ammonification, denitrification, N mineralization), wind, clouds, thunder, rainfall and lightning (Tie et al., 2002; Vagstad et al., 1997). These are all contributory factors in determining the extent of reactive nitrogen (N_r) as part of the soil nutrient pool. Fowler et al. (2013) determine a figure of 413 Tg N year^{-1} of N_r due to the global N fixation of terrestrial and marine ecosystems. A substantial proportion of this figure, 240 Tg N year^{-1}, can be attributed to terrestrial anthropogenic activities via soil or vegetation. For details and thorough reviews of the N-cycle and impact and interactions of various factors (positive and negative) see, e.g., Thomas (1992), Galloway et al. (2004), Gruber and Galloway (2008), Ollivier et al. (2011), Fowler et al. (2013), van Groenigen et al. (2015).

A continuing supply of N_r is needed for nature's food web. Liebig's law of the minimum is a principle originally developed in agricultural science by Sprengel (1828) and later popularized by von Liebig (1855). It states that "growth is dictated not by total resources available but by the scarcest resource (limiting factor)." This principle has also been applied to biological populations and ecosystem models for factors such as sunlight or mineral nutrients (Gorban et al., 2011). To work out the necessary proportion of nutrients for soil nutrition, Liebscher conducted many experiments with the main nutrients [N, phosphorus (P) and potassium (K)] at the end of 19th century. Based on the results of these experiments he formulated his law of the optimum (Liebscher, 1895). This principle states that "a production factor that is in minimum supply contributes more to production the closer other production factors are to their optimum" (also see de Wit, 1992).

Along with historical studies of soil-plant interaction and fertilizer use, Mitscherlich (1909) developed his model, often referred to as the law of diminishing returns, to quantify crop response to fertilizer. Spillman (1923) also worked on this idea independently, hence the response model sometimes being referred to in literature as the Mitscherlich-Spillman equation. Baule (1918) generalized the Mitscherlich equation for two or more nutrients; this is known as Baule-Mitscherlich limiting factor equation (Verduin, 1988). To study nutrient interactions, Baule (c. 1920 while working with Mitscherlich in Germany) also developed the idea of half-way points, which are generally called Baule units. Bray (1945) used the Mitscherlich model to study soil nutrient status via soil tests. He extended Mitscherlich's equation to study soil nutrient roles (both from soil and fertilizer) in the production of various crops. He showed how the extended model can be used to predict fertilizer requirement. Following the development of these mathematical models much research was undertaken in relation to the soil and fertilizer nutrient uptake by various crops. For example, Inkson (1964) found no toxic effects of P if applied at more than its optimum level, while toxic effects of N and K were observed at higher rates of application. These toxic effects of over-fertilization can result in a non-asymptotic response, which is not consistent with the Mitscherlich-Bray model. A specially constructed quadratic function (Inkson, 1964) proved to be a popular model for the analysis of such cases. Nelder's inverse polynomials were also used as they facilitate improved curve fitting at data end-points (Nelder, 1966).

Baseline soil nutrients are insufficient for agriculture and that necessitates supplementation by the use of fertilizers (e.g., N, P, K or their mix) to optimize crop yield. The N_r needed for crop production is much greater than that available in the soil nutrient pool (as indicated by observed yield from the control plots in crop growth studies). Bray (1945) developed protocols for balanced fertilizer use through tests for soil fertility. Following this research, Bray and his associates proposed a nutrient mobility concept after modifying that developed by Mitscherlich, Baule and Spillman. Bray's concept states that "As the mobility of a nutrient in the soil decreases, the amount of that nutrient needed in the soil to produce a maximum yield increases from a variable net value, determined principally by the magnitude of the yield and the optimum percentage composition of the crop, to an amount whose value tends to be a constant." The magnitude of this constant is independent of the amount of crop yield, provided that the kind of plant, planting pattern and rate, and fertility pattern remain constant and that similar soil and seasonal conditions prevail (Gowariker et al., 2009). Combination of N fertilizer (plus P and K as well) and suitable crop varieties, has revolutionized food production. However, the downsides of this practice are the polluting consequences. Losses of nutrients to watercourses via surface runoff and leaching, and emissions to air, e.g., nitrous oxide (N_2O) emission, are major concerns. Like crop growth, N_2O emission is a function of nutrients in soil and the applied N.

The primary purpose of this article is to revisit fertilizer response models of Mitscherlich, Baule and others, using UK datasets covering a period of over 40 years, and apply them to quantify N_2O-N emission as related to relevant N-forms in the soil and the applied N resource.

2. Overview and data

2.1 Crop response to nutrient application

2.1.1 Mitscherlich and Baule models

Response curve methodology in relation to soil fertility and growth factor application (e.g., N fertilizer) was developed from the end of 19th century. von Liebig (1855), for example, used a single node linear curve (maximum A) with a plateau ending at nutrient input x_A:

$$y = y_0 + mx, x \leq x_A; y = A, x > x_A \tag{1}$$

where y is yield, m is slope (rate of yield increase with respect to nutrient application, x, in a given soil and environment) and y_0 is the y-axis intercept corresponding to $x = 0$, i.e., the "control" yield.

Following on from the work of Liebig and his peers, Mitscherlich (1909, 1928) proposed a mathematical function for crop growth in response to the added growth factor.

(i) Mitscherlich's law of physiological relationships: Yield can be increased by each single factor even when it is not present in the minimum as long as it is not present in the optimum.

(ii) Mitscherlich's growth law: Increase in yield of a crop as a result of increasing a single growth factor is proportional to the decrement from the maximum yield obtainable by decreasing the particular growth factor.

His response function related crop growth to nutrients. When plants were supplied with all nutrients except one limiting factor, growth was found to be proportional to the amount of this limiting or efficiency factor, c, when added to the soil. His function was:

$$\frac{dy}{dx} = (A - y)c \tag{2}$$

where A is the asymptotic value (maximum) of y. After integration this equation on the log-scale becomes:

$$\ln(A - y) = \ln(A) - cx \tag{3}$$

This can be written in y-axis intercept and asymptote form:

$$y = y_0 + (A - y_0)(1 - e^{-cx}); \quad y = y_0 \text{ when } x = 0 \tag{4}$$

However, it is often rewritten in the form proposed by Baule (1918):

$$y = A\left(1 - e^{-c(x+d)}\right); \quad d = \ln[A/(A - y_0)]/c \tag{5}$$

The parameter d is the soil nutrient applied (for further details see Schneeberger, 2009a, 2010). Once the estimate of d is known, the right-angled triangle of nutrient and yield formed by the 3 points with coordinates $\{x = -d, y = 0\}$; $\{x = 0, y = 0\}$; $\{x = 0, y = y_0\}$ may be used to calculate the linear slope of production response from soil nutrient d.

To study the response to added nutrient alone, Schneeberger (2009a) partitioned the Mitscherlich (Eq. 4) into two parts (y_{01} and y_{02}):

$$y = A(1 - e^{-cx}) + y_0 e^{-cx} = y_{01} + y_{02} \tag{6}$$

Here y is the yield, A is the asymptote (ideal maximum yield), in the absence of any toxic effects if nutrient is added at more than the optimum level (Inkson, 1964), and c the efficiency of utilizing added nutrient. If adding to a low N-status soil, the yield growth profile may vary. The Mitscherlich-Baule model is summarized in Fig. 1.

2.1.2 Bray modification

Starting with the Mitscherlich (Eq. 3), Bray (1945) studied soil fertility using soil tests and protocols he had developed. He replaced fertilizer x with the amount available in the soil (b_1) as indicated by the soil test, i.e.,

$$\ln(A - y) = \ln(A) - c_1 b_1 \tag{7}$$

where c_1 is the efficiency of soil nutrient uptake. Using experimental estimates of A, y and b_1 he was able to obtain estimates of c_1 for various soils

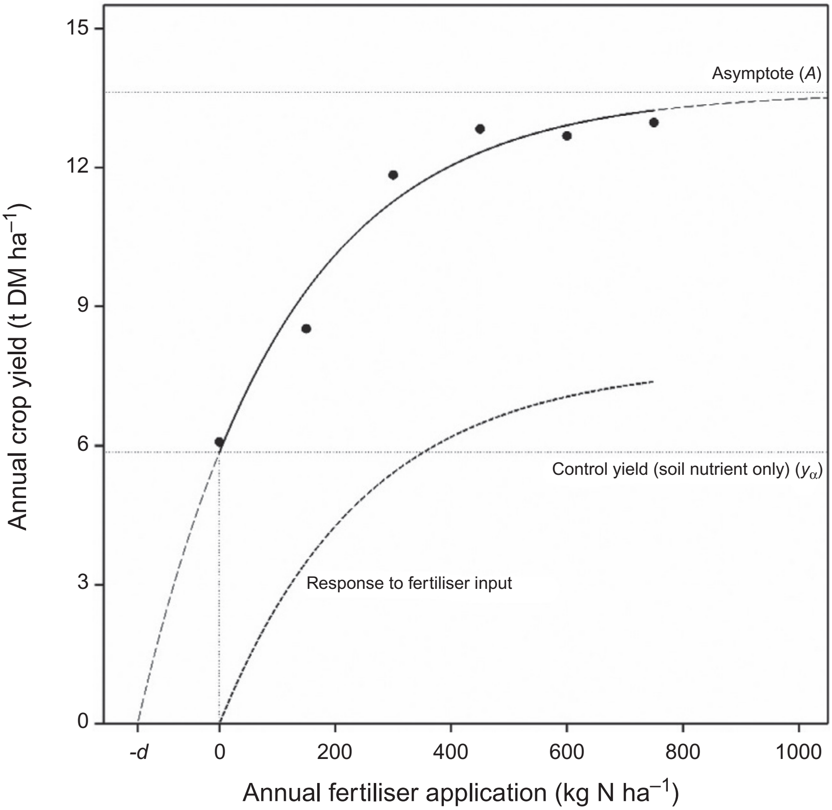

Fig. 1 Features of the Mitscherlich-Baule response model. (A) fitted curve (solid line) to Combo site data (dots), (B) control plot yield from soil nutrient only (horizontal dotted line), (C) soil nutrient level *d* (at the intersection of dashed line and the negative side of *x*-axis, i.e., at zero crop yield), (D) response to fertilizer input (increasing close dash curve starting from the origin (net of control yield)).

and crops. In order to link his equation to applied nutrient, the Mitscherlich-Bray equation was developed:

$$\ln(A - y) = \ln(A) - c_1 b_1 - cx \text{ or } y = A\left(1 - e^{-c_1 b_1 - cx}\right) \tag{8}$$

Using these equations, Bray (1945) developed balanced fertilizer protocols for various soils, crop and environment combinations.

Balba and Bray (1956, 1957) further extended this equation to accommodate more than one soil nutrient, viz.

$$y = A\left(1 - e^{-c_1 b_1 - c_2 b_2 - cx}\right) \tag{9}$$

They also proposed the formula $\frac{cx}{c_1b_1+cx}$ to calculate contribution of fertilizer to nutrient content of the plant. Among many innovations they expanded this formula to calculate the proportion of nutrient in plant supplied from

(i) The fertilizer
$$\frac{cx}{c_1b_1+c_2b_2+cx} \tag{10}$$

(ii) The absorbed form
$$\frac{c_1b_1}{c_1b_1+c_2b_2+cx} \tag{11}$$

(iii) The easily acid soluble form
$$\frac{c_2b_2}{c_1b_1+c_2b_2+cx} \tag{12}$$

More details can be found in Balba and Bray (1957).

2.1.3 Non-asymptotic response due to toxic effects of over-fertilization

Inkson (1964) found toxic effects of N and K when applied in excess of their optimum levels. In such cases, the Mitscherlich equation will not be applicable. Inkson (1964) proposed a specially constructed quadratic function:

$$y = a_0 + a_1(x+B) + a_2(x+B)^2 \tag{13}$$

where y is yield, x is the added nutrient and B is nutrient in the soil.

Another applicable option is using inverse polynomials (also known as rational functions) as proposed by Nelder (1966):

$$\frac{1}{y} = \frac{b_0}{x+B} + b_1 + b_2(x+B) \tag{14}$$

Here b_0 is associated with the rising part of a curve and b_2 with the declining part. A biphasic Mitscherlich function can also be used (Schneeberger, 2009b). If the declining part of the response curve is short and nearly linear then "Mitscherlich + linear" may be a simpler option (Powell et al., 2020; Dhanoa et al., 2021).

2.1.4 Incomplete study due to resource limitation and/or environmental vagaries

It may happen that the maximum yield cannot be estimated experimentally due to unforeseen and uncontrollable factors. In such a situation Dickson (1942) described a method of prediction of the maximum yield. In order to do this, experimental yield (y_1, y_2 and y_3) corresponding to three equal interval nutrient applications (x_1, x_2 and x_3) is needed with the condition that $x_2 - x_1 = x_3 - x_2$. Substituting these in the Mitscherlich equation (Eq. 3) and solving the resulting three simultaneous equations, we can estimate maximum yield A as:

$$A = \frac{y_2{}^2 - y_1 y_3}{2y_2 - y_1 - y_3} \tag{15}$$

Dickson (1942) also estimated the efficiency of applied nutrient (activity constant c in Eq. 3), viz.

$$c = \frac{\ln(A - y_1) - \ln(A - y_2)}{x_2 - x_1} \tag{16}$$

Given estimates of A and c, an estimate of b_1 can now be obtained from the Mitscherlich-Bray equation (Eq. 8) as:

$$b_1 = \frac{\ln(A) - \ln(A - y_0)}{c} \tag{17}$$

2.1.5 Possible mitigation of over-fertilization effects

Over-fertilization effects kick in when fertilizer N in excess of the optimum is applied. Crop responses below the optimum N application are largely unaffected. This should allow us to predict the asymptote (see above), assuming there are no toxic effects. Replacing crop response data beyond the optimum (empirically corresponding to the maximum yield) with the predicted asymptote we obtain a response profile that will be consistent with the Mitscherlich response model. This allows the apparent over-fertilization effects to be quantified.

2.1.6 Baule's fertilizer units

In order to study nutrient application, Baule developed the idea of units such that the first Baule unit moves a crop response to 50% of the asymptotic value and the second Baule unit moves the response to a point half-way from the 50% to the asymptote, i.e., 75% (= 50% + 25%), and so on. The formula for these proportions (ρ_n) being:

$$\rho_n = 1 - \left(\frac{1}{2}\right)^n \tag{18}$$

where n (= 1, 2, 3, …) is the number of Baule units. After the 1st Baule unit, 2nd, 3rd, 4th units will take us to 75% (= 50% + 25%), 87.5% (= 50% + 25% + 12.5%) and 93.75% (= 50% + 25% + 12.5% + 6.25%), respectively, of the asymptote. Nutrient input corresponding to these response points (which will vary with soil fertility, crop and the environment) can be used to compare and contrast different environments at various geo-positions. In the case of two limiting nutrients (e.g., N and P), if soil has 2 Baule units of N and 3 Baule units of P then yield achieved will only be 66% (= 75% × 87.5%) of the maximum yield possible. Note that Baule units (X_n, kg applied nutrient ha^{-1}) are net of absolute soil nutrient; substituting $\rho_n \times A$ for y in Eq. (5) gives the nth Baule unit:

$$X_n = c^{-1} n \ln 2 - d \tag{19}$$

where d (control soil nutrient) plus X_n (nutrient applied) make up absolute total nutrient. The estimate of d is on the negative part of the added nutrient axis (Fig. 2).

2.1.7 Baule's sufficiency ratio

Percentage sufficiency is defined by Baule (1918) as the ratio of control yield to maximum attainable yield at a chosen site:

$$\text{Percentage sufficiency} = 100 \times (y_0/A) \tag{20}$$

where y_0 is the control yield and A the asymptotic yield. The complement of this is:

$$v = 100 \times (1 - y_0/A) \tag{21}$$

which is the percentage deficiency and it is equal to $100 \times e^{-c_1 b_1}$ as stated in Eq. (8).

2.1.8 Baule-Mitscherlich limiting factor equation

While working with Mitscherlich, Baule generalized Mitscherlich's equation to study a system with 2, 3 or more limiting-factors (Inkson, 1964; Verduin, 1953):

$$E = E_{\max}\left(1 - b_1 r_1^{x_1}\right)\left(1 - b_2 r_2^{x_2}\right)\left(1 - b_3 r_3^{x_3}\right)\ldots \tag{22}$$

where E is the rate of a process, $E_{\max}$ is the rate if factors (x_1, x_2, x_3, …) are present in abundance, and the b and the r are constants introduced to facilitate fitting the equation.

Verduin (1988) evaluated this equation for freshwater lakes sampled in the USEPA National Eutrophication Survey (1972–76). He applied it to determine chlorophyll concentration using four limiting factors N, P, carbon and light. The equations listed above have been applied widely, e.g., Harmsen (2000) modified the Mitscherlich equation for rain-fed crop production in semi-arid areas.

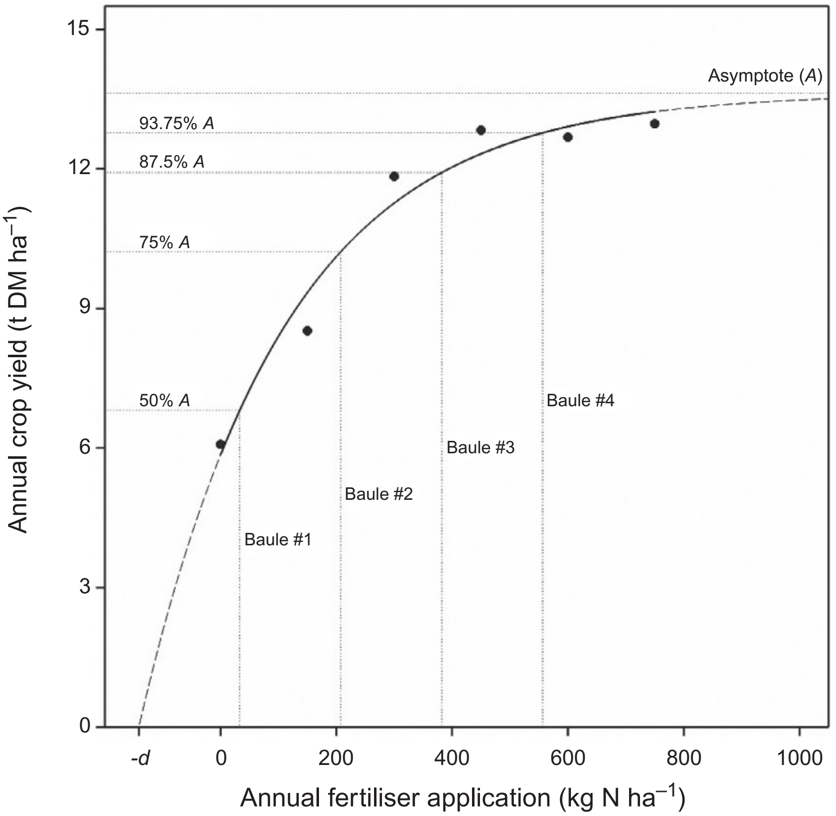

Fig. 2 Baule's fertilizer units in relation to the fitted Mitscherlich-Baule response equation such that the first Baule unit increases the response to 50% of the asymptote and the second Baule unit moves it to a point half-way between the 50% and the asymptotic value, i.e., 75%, and so on. The figure also shows the intersection of the dashed part of the fitted curve at the negative side of the *x*-axis which gives soil nutrient level.

2.1.9 Type II linear regression

As the model parameters (fitted or predicted) carry errors, an ordinary least squares regression model is not wholly appropriate, and a Type II model is needed to avoid slope attenuation (Dhanoa et al., 2010). For this purpose, two special cases of the general maximum likelihood solution, i.e., major axis (MA) and reduced major axis (RMA), are sufficient. Quoting Dhanoa et al. (2010), the general maximum likelihood (ML) estimates the slope as:

$$\hat{\beta}_{\mathrm{ML}} = \frac{\hat{\sigma}_y^2 - \lambda_{\mathrm{ML}}\hat{\sigma}_x^2 + \sqrt{\left(\hat{\sigma}_y^2 - \lambda_{\mathrm{ML}}\hat{\sigma}_x^2\right)^2 + 4\lambda_{\mathrm{ML}}\hat{\sigma}_{xy}^2}}{2\hat{\sigma}_{xy}} \tag{23}$$

Here $\lambda_{\mathrm{ML}} = \hat{\sigma}_\varepsilon^2/\hat{\sigma}_\delta^2$ where $\hat{\sigma}_\varepsilon^2$ is the estimator of the error variance of a single y-value while $\hat{\sigma}_\delta^2$ is the estimator of the error variance of a single x-value with the assumption that both $\hat{\sigma}_\varepsilon^2$ and $\hat{\sigma}_\delta^2$ are constant over the range of the data. The variances of x and y sample values are denoted by $\hat{\sigma}_x^2$ and $\hat{\sigma}_y^2$ respectively and $\hat{\sigma}_{xy}$ is the sample covariance. An alternative form of Eq. (23) is the Deming formula (Cornbleet and Gochman, 1979; Deming, 2003):

$$\hat{\beta}_{\mathrm{Deming}:y.x} = U + \sqrt{U^2 + \left(1/\lambda_{\mathrm{Deming}}\right)} \tag{24}$$

where

$$U = \left[\hat{\sigma}_y^2 - \left(\frac{1}{\lambda_{\mathrm{Deming}}}\right)\hat{\sigma}_x^2\right] / \left[2r_{yx}\hat{\sigma}_x\hat{\sigma}_y\right] \tag{25}$$

and $\hat{\sigma}_{yx} = r_{yx}\hat{\sigma}_x\hat{\sigma}_y$ with correlation r_{yx}. Here $\lambda_{\mathrm{Deming}}$ is the reciprocal of λ_{ML}, i.e., $\lambda_{\mathrm{Deming}} = \hat{\sigma}_\delta^2/\hat{\sigma}_\varepsilon^2$.

If we can justifiably assume that $\hat{\sigma}_\varepsilon^2$ and $\hat{\sigma}_\delta^2$ are equal (i.e., $\lambda_{\mathrm{ML}} = 1$) then the MA regression model may be used. For MA, the solution reduces to:

$$\hat{\beta}_{\mathrm{ML}} = \frac{\hat{\sigma}_y^2 - \hat{\sigma}_x^2 + \sqrt{\left(\hat{\sigma}_y^2 - \lambda_{\mathrm{ML}}\hat{\sigma}_x^2\right)^2 + 4\lambda_{\mathrm{ML}}\hat{\sigma}_{xy}^2}}{2\hat{\sigma}_{xy}} \tag{26}$$

Similarly the RMA (or geometric mean functional relationship) regression model may be appropriate when $\hat{\sigma}_\varepsilon^2$ and $\hat{\sigma}_\delta^2$ are assumed to be proportional to $\hat{\sigma}_y^2$ and $\hat{\sigma}_x^2$, respectively, giving $\lambda_{\mathrm{ML}} = \hat{\sigma}_y^2/\hat{\sigma}_x^2$ and Eq. (23) reduces to $\pm\hat{\sigma}_y/\hat{\sigma}_x$.

2.2 Experimental data

2.2.1 First experimental data collection

The National Grassland Manuring (GM) series of trials were conducted by ADAS (a major UK agricultural consultancy) and the former Grassland Research Institute, at Hurley, UK. Multi-site experiments were carried out between 1971 and 1984 (Final report, MAFF project code BD 1438).

The objectives were (a) to assess the response of grassland to fertilizer N, and (b) to examine contribution of white clover and its interaction with fertilizer N and slurry/excreta. For the purposes of this study, we analyzed the grassland response to N-fertilizer data from the GM20 series of experiments conducted at 21 sites (see Table 1 for locations) over the period 1970–74 (Morrison et al., 1980).

Table 1 Parameter values[a] obtained by fitting the Mitscherlich-Baule response model (Eq. 27) to annual perennial ryegrass yield (t DM ha^{-1}) vs annual fertilizer application (kg N ha^{-1}) at each of 21 sites from the GM20 series of trials.

Site	***R***	***B***	***A***	**S.E. *R***	**S.E. *B***	**S.E. *A***
Cambo	0.9960	−7.77	13.62	0.00135	0.987	0.883
Harewood	0.9948	−9.19	13.52	0.00074	0.492	0.362
Drayton (1)	0.9968	−10.87	12.30	0.00037	0.487	0.488
Morley	0.9940	−8.69	12.66	0.00142	0.776	0.517
Gleadthorpe	0.9955	−10.86	11.29	0.00137	1.226	0.998
Cambridge	0.9950	−5.26	6.50	0.00136	0.540	0.411
Bridgets	0.9951	−8.58	10.42	0.00109	0.712	0.547
Oxford	0.9966	−11.80	14.63	0.00093	1.246	1.219
Rowsham	0.9963	−9.54	13.29	0.00088	0.848	0.791
Hurley (1)	0.9969	−10.42	11.99	0.00082	1.075	1.089
Wye	0.9955	−8.02	10.65	0.00082	0.550	0.454
Pluckley	0.9971	−12.91	13.64	0.00025	0.453	0.468
Cannington	0.9955	−9.03	10.50	0.00083	0.620	0.507
High Mowthorpe	0.9938	−6.67	8.14	0.00091	0.442	0.232
Hurley (2)	0.9962	−8.26	9.43	0.00056	0.450	0.435
Jealotts Hill	0.9968	−9.27	12.70	0.00037	0.410	0.422
Drayton (2)	0.9978	−10.76	12.43	0.00062	1.435	1.541
North Wyke	0.9951	−5.17	10.71	0.00186	0.800	0.614
Pant-y-dwr	0.9956	−6.30	10.16	0.00161	0.953	0.770
Ponterwyd	0.9964	−7.54	10.67	0.00116	1.006	0.891
Selborne	0.9969	−8.18	12.84	0.00106	1.177	1.119

[a] S.E. denotes standard error.

2.2.2 Second experimental data collection

Data used in this study come from two different sites where crop yield and greenhouse gases (GHG) were measured, viz. Hereford, UK (Williams et al., 2017) and Bedford, UK (Cardenas et al., 2017). We used these data to investigate N_2O emission response to added N fertilization.

2.2.3 Third experimental data collection

The third data collection comprises 20 experiments under 4 projects conducted over 7 years at 14 UK sites (Chadwick et al., 2016). We used these data to address the question: do different types of the same nutrient applied affect N_2O emission?

3. Application and discussion

3.1 Using the first experimental data collection

In this section, we explore application of the Mitscherlich-Baule response model. This has different functional forms, e.g.,

$$y = A\left(1 - \mathrm{e}^{-c(x+d)}\right) = A\left(1 - \mathrm{e}^{-cx}\mathrm{e}^{-cd}\right) = A + BR^{x} \qquad (27)$$

where $B = -\mathrm{e}^{-cd}$, $R = \mathrm{e}^{-c}$, $c = -\ln R$.

Statistical package Genstat (VSN International, 2015) uses the form $y = A + BR^{x}$ as the initial estimate of parameter R must lie in the interval $[0.0 \rightarrow 1.0]$ for an asymptotic response. From the fit of the full Mitscherlich-Baule model one can derive the following important information that will characterize a specific site or geo-position regarding:

(i) Efficiency of utilizing the added nutrient (N in this example) and other parameters

(ii) Yield from the nutrient pool in the soil alone (Eq. 3)

(iii) Maximum derivable yield A at the particular geo-position (including the control yield)

(iv) Baule's nutrient units at the selected sites (for 50% A, 75% A, …) (Eq. 18)

(v) Baule's sufficiency ratio (Eq. 20) regarding control yield and asymptote yield

(vi) Most of these curves have well defined asymptotes, so our data sets are suitable for testing the Dickson formula (Eq. 15) for asymptote prediction

(vii) Dickson (1942).also proposed the formula to predict the Mitscherlich efficiency (c) of applied nutrient utilization, and the efficiency of the same nutrient from the soil (Bray's b_1, kg ha^{-1}).

All these site characteristics are specific to the soil potential at that site, both from the relevant nutrient available from the soil, and also that which can be activated in response to the same nutrient when added to the soil. These characterizing features can be used to compare, contrast and classify the chosen sites. The differences can be displayed (Fig. 3) for all 21 sites; and show the y-axis yield response, when no fertilizer is added ($x = 0.0$). The Fig. 3 data profiles were quantified using Eq. (27).

The parameter estimates R, B, A for each of the 21 sites are listed in Table 1. The individual curves may differ in terms of the values of both the linear and non-linear parameters. For this purpose, parallel curve

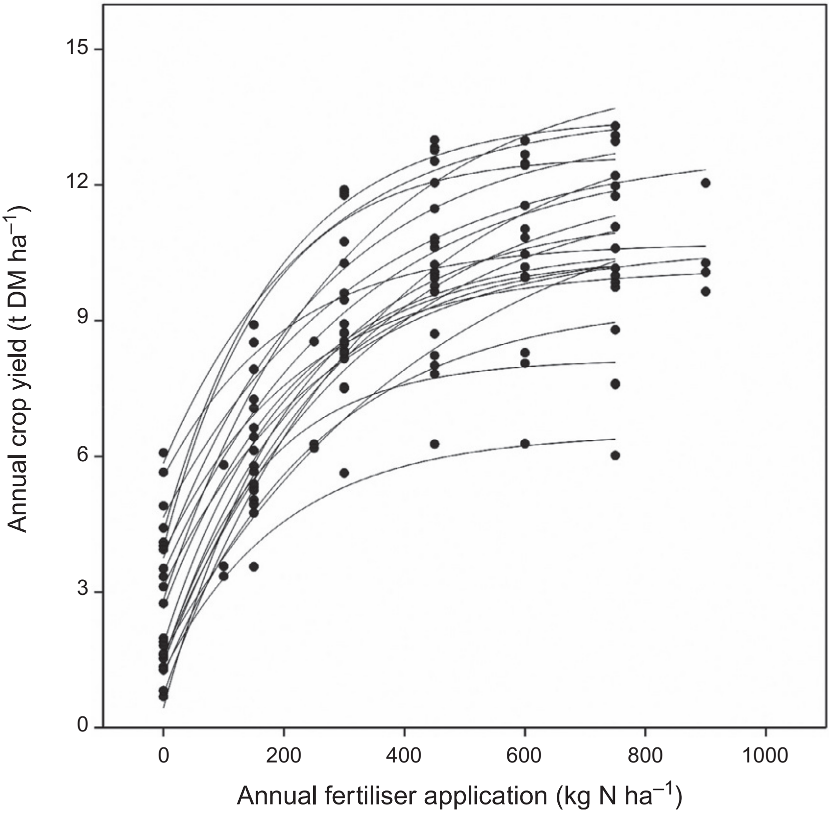

Fig. 3 The GM 20 series data as collected from the 21 selected sites. When no nutrients were added the control yield (y-axis intercept) varies considerably. These control yield differences contribute to the major differences among the fitted asymptotes.

analysis, i.e., nonlinear regression ANOVA (Heitjan, 1989), was carried out by separating variance accounted for by the model parameters, and subjecting these components to a variance ratio test (F test). Linear parameters (y-intercept and asymptote) were shown to differ ($P < 0.05$) among the 21 sites but the shape parameter, R, (efficiency of use of added nutrient) was similar ($P > 0.05$) across all sites. Further output and other meaningful quantities are listed in Table 2, viz. adjusted R^2, control (unfertilized) yield, added nutrient asymptote (i.e., net asymptote), Baule's sufficiency ratio, relevant nutrient from the soil (i.e., absolute numerical value of the x-axis intercept), efficiency of added nutrient utilization and magnitude of the Baule unit at each site. The dendrogram showing a hierarchical clustering analysis for site similarity (Earle and Hurley, 2015) is shown in Fig. 4.

In order to apply the Dickson formula for asymptote prediction (Eq. 15), three equal interval nutrient inputs (x_1, x_2, x_3) and their corresponding yields (y_1, y_2, y_3) were required. Here we demonstrate applications of N input at 150, 300 and 450 kg ha^{-1} and at 300, 450 and 600 kg ha^{-1}. To cover the earlier part of the response curve, applications $y_1 = 150$, $y_2 = 300$, $y_3 = 450$ were used and the estimated asymptote values at each site calculated as pA_1. Likewise, to cover the later part of the curve, applications $y_1 = 300$, $y_2 = 450$, $y_3 = 600$ were chosen and the estimated asymptotes at each site calculated as pA_2. These results together with the fitted asymptote A are shown in Table 3. To check the reproducibility of these estimates (pA_1, pA_2), Lin's concordance correlation coefficient (CCC) was used relative to the estimate from the response model (Lin, 1989; Dhanoa et al., 1999). Results for the 14 sites where both pA_1 and pA_2 were estimated give CCC = 0.9618 (slope with respect to the reference value, $C_b = 0.9950$) and CCC = 0.9344 ($C_b = 0.9679$), respectively; results which suggest using applications covering the earlier (steeper) part of the response curve are preferable to those covering the later (flatter) part when using the Dickson formula. Dickson asymptote prediction is illustrated in Fig. 5 where the fitted lines were obtained using four types of regression analysis (y on x, x on y, MA and RMA). Best prediction was obtained using Type II linear regression (MA and RMA). Fig. 5 clearly shows that inclusion of 3 of the 4 additional sites (i.e., North Wyke, Pant-y-dwr, Selborne) majorly distorts prediction of pA_1.

3.2 Using the second experimental data collection

As with control crop yield, control N_2O emission is also related to the innate nutrient in the soil. Likewise as applied to crop yield, the Mitscherlich-Baule model can be used to obtain information on a set of soils in order to study

Table 2 Derived parameter and other values associated with nutrient uptake and yield obtained by fitting the Mitscherlich-Baule response model (Eq. 27) to annual perennial ryegrass yield (t DM ha^{-1}) vs annual fertilizer application (kg N ha^{-1}) at each of 21 sites from the GM20 series of trials.

Site	Adj. R^2	y_0 (t DM ha^{-1})	Net A (t DM ha^{-1})	Baule's sufficiency (%)[a]	Soil N (d) (kg N ha^{-1})	c (kg^{-1})	Baule unit (kg N ha^{-1})
Cambo	0.942	5.85	7.77	43.0	141.2	0.00398	174.3
Harewood	0.987	4.32	9.20	32.0	73.8	0.00522	132.7
Drayton (1)	0.994	1.43	10.87	11.6	38.4	0.00321	215.6
Morley	0.963	3.97	8.69	31.4	62.6	0.00601	115.4
Gleadthorpe	0.948	0.44	10.85	3.9	8.7	0.00456	152.1
Cambridge	0.954	1.24	5.26	19.0	42.4	0.00499	139.0
Bridgets	0.970	1.84	8.58	17.6	39.4	0.00493	140.6
Oxford	0.967	2.83	11.80	19.4	63.5	0.00339	204.7
Rowsham	0.973	3.75	9.54	28.2	89.5	0.00371	186.9
Hurley (1)	0.973	1.58	10.41	13.1	45.2	0.00311	222.6
Wye	0.981	2.63	8.02	24.7	63.4	0.00447	155.0
Pluckley	0.997	0.73	12.91	5.4	18.9	0.00290	238.6
Cannington	0.980	1.47	9.03	14.0	33.3	0.00453	153.0
High Mowthorpe	0.958	1.47	6.67	18.1	32.2	0.00619	112.0
Hurley (2)	0.992	1.17	8.26	12.4	34.4	0.00383	180.8
Jealotts Hill	0.996	3.43	9.27	27.0	97.4	0.00323	214.8
Drayton (2)	0.985	1.66	10.76	13.4	66.1	0.00217	318.9
North Wyke	0.919	5.54	5.17	51.8	147.2	0.00495	140.0
Pant-y-dwr	0.924	3.86	6.30	38.0	108.1	0.00443	156.6
Ponterwyd	0.946	3.13	7.54	29.3	95.6	0.00363	191.0
Selborne	0.945	4.66	8.18	36.3	145.8	0.00309	224.2

[a] Baule sufficiency ratio for each site is given by y_0 divided by gross A (shown in Table 1).

their capacity to emit N_2O. N_2O data were not collected along with the crop yield data for the 21 sites of the first data collection. For the purpose of illustration, we use the second data collection from different UK sites (Hereford and Bedford; Williams et al., 2017 and Cardenas et al., 2017 respectively),

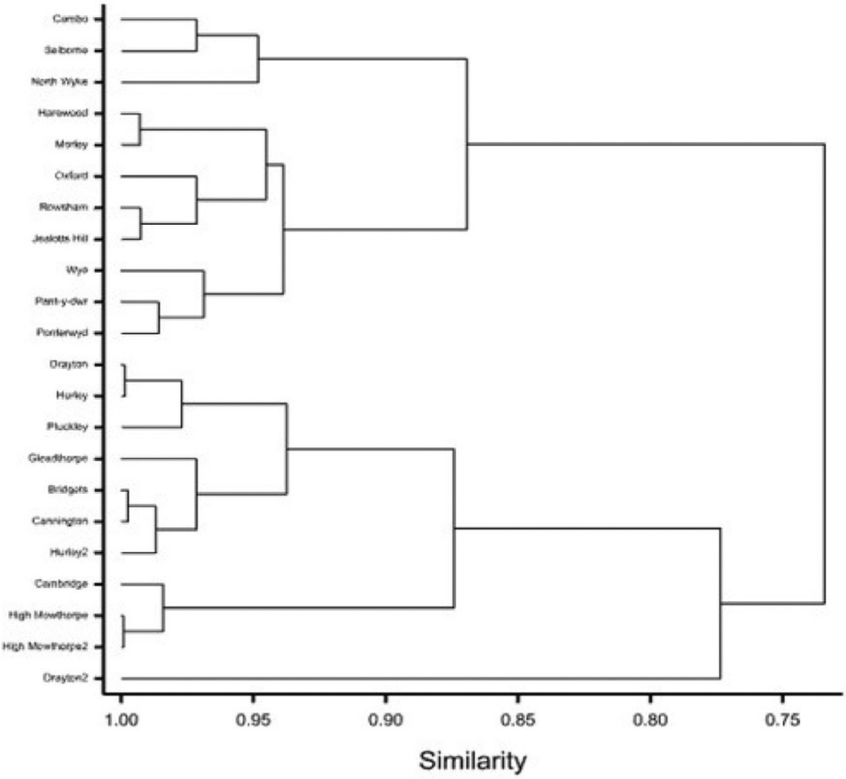

Fig. 4 Dendrogram showing a hierarchical clustering analysis for site similarity. Similarity is a dimensionless quantity ranging between unity and zero. *After Morrison, J., Jackson, M.V., Sparrow, P.E., 1980. The response of perennial ryegrass to fertilizer nitrogen in relation to climate and soil. Report of the joint ADAS/GRI Grassland Manuring Trial- GM20. GRI Technical Report No. 27.*

where winter wheat yield and GHG were measured. We have found that N_2O emission is not always consistent with the Mitscherlich-Baule model, as is the case with crop yield data in situations of over-fertilization, but if for example soil moisture content is low the N_2O flux will most likely plateau at a low level (Cardenas et al., 2010). Herein we just focus on the asymptotic shape of N_2O profiles. Any attributes of a GHG producing source can be helpful in designing mitigating protocols, hence the inspiration to conduct this study with the use of the long established Mitscherlich-Baule model.

The fits obtained with the Mitscherlich-Baule response model are shown in Fig. 6 and the associated parameter estimates given in Table 4. Though not the case with this example, soil nutrient estimates in relation to N_2O are

Table 3 Predicted asymptotes[a] from the Dickson formula (Eq. 15), pA_1 using N applications 150, 300 and 450 kg ha^{-1}, pA_2 using N applications 300, 450 and 600 kg ha^{-1} and the fitted asymptote A, estimated from the model $y = A + BR^x$.

Sites	pA_1	pA_2	A
Cambo	13.25	12.70	13.62
Harewood	13.64	12.99	13.52
Drayton (1)	13.55	11.49	12.30
Morley	12.75	12.48	12.66
Gleadthorpe	11.86	11.16	11.29
Cambridge	6.56	6.28	6.50
Bridgets	11.26	9.99	10.42
Oxford	14.71	13.00	14.63
Rowsham	14.63	12.55	13.29
Hurley (1)	11.88	10.69	11.99
Wye	11.03	10.24	10.65
Pluckley	12.88	14.41	13.64
Cannington	10.21	10.07	10.50
High Mowthorpe	7.87	6.82	8.14
Hurley (2)	–	–	9.43
Jealotts Hill	–	–	12.70
Drayton (2)	–	–	12.43
North Wyke	21.76	–	10.71
Pant-y-dwr	14.55	–	10.16
Ponterwyd	11.75	–	10.67
Selborne	16.62	–	12.84

[a] Missing values (–) not available, i.e., selected fertilizer levels were not applied at those sites.

generally lower when compared to the corresponding estimates from crop yield modeling. However, the crop yield incorporates effects related to root functionality and plant growth, and these are related factors that are not part of the measured N_2O flux, which is the product of chemical reactions and other factors in the soil ecosystem.

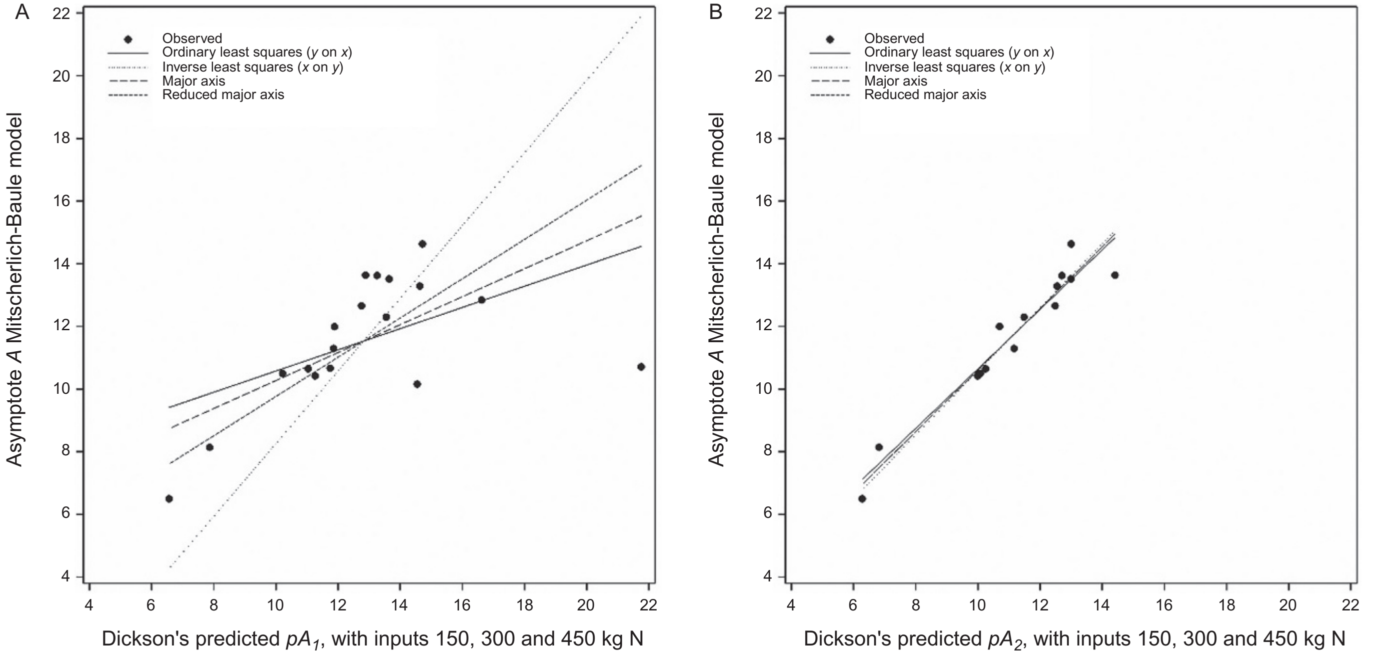

Fig. 5 Dickson asymptote prediction with annual inputs (A) 150, 300 and 450 (using estimates from 18 sites) and (B) 300, 450 and 600 kg N ha^{-1} (estimates from 14 sites).

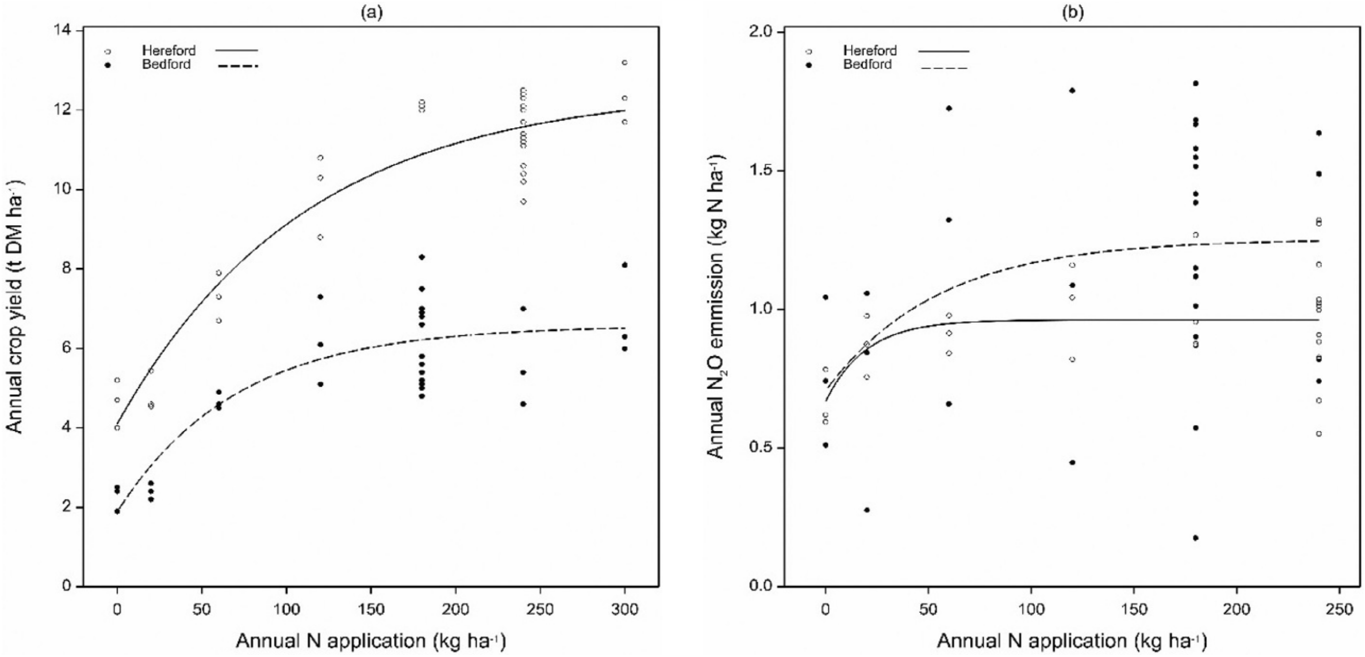

Fig. 6 Mitscherlich-Baule response model fitted to (A) winter wheat yield and applied N and (B) N_2O emission and applied N (Hereford and Bedford data).

Table 4 Estimates of parameters obtained fitting the model $y = A + BR^x$ to the Hereford and Bedford, crop yield and N_2O emission data.

	Hereford		Bedford	
Parameter	**Estimate**	**Standard error**	**Estimate**	**Standard error**
R	0.9910	0.00221	0.9845	0.00682
B (t DM ha^{-1})	−8.45	0.625	−4.58	0.596
A (t DM ha^{-1})	12.55	0.650	6.44	0.471
Soil N (d; kg N ha^{-1})	43.85	–	21.79	–
Baule unit (kg N ha^{-1})	76.85	–	44.45	–
R	0.9552	0.0413	0.9818	0.0270
B (kg N ha^{-1})	−0.302	0.107	−0.547	0.254
A (kg N ha^{-1})	0.973	0.0357	1.254	0.162
Soil N (d; kg N ha^{-1})	25.49	–	45.22	–
Baule unit (kg N ha^{-1})	15.11	–	37.78	–

3.3 Using the third experimental data collection

In addition to spatial and temporal variability, nutrients input to soil can cause further variability. So it is necessary to look if different sources and types of added nutrients affect soil nutrient status, leading to some impact on N_2O emission flux to the same extent, or different, across geo-positions. For this purpose, data are required for the same soil with the added nutrients coming from different sources (for example using N fertilization from various sources). The data we use here comes from 20 experiments under 4 projects conducted over a period of 7 years at 14 sites (Chadwick et al., 2016). Added N nutrients were of 22 types across 11 arable and grassland crops. The response variable was N_2O flux with soil attributes pH, crop yield, soil organic carbon percentage, bulk density and clay percentage. This collection of data from individual sites is not entirely suitable for fitting the Mitscherlich-Baule model. However, site-to-site variability can be illustrated by the overall fit of the model to annual N_2O flux data (Fig. 7). The average control emission of N_2O flux from this fit works out to be 0.359 kg N ha^{-1} per year.

Boxplots of N_2O emission by site and by N type are shown in Fig. 8. The vertical differences in Fig. 8A are due to site totals that were caused by all relevant factors. N_2O flux was lowest in Oxfordshire and next lowest in County Down, Devon and Midlothian. Data skewness and a large range

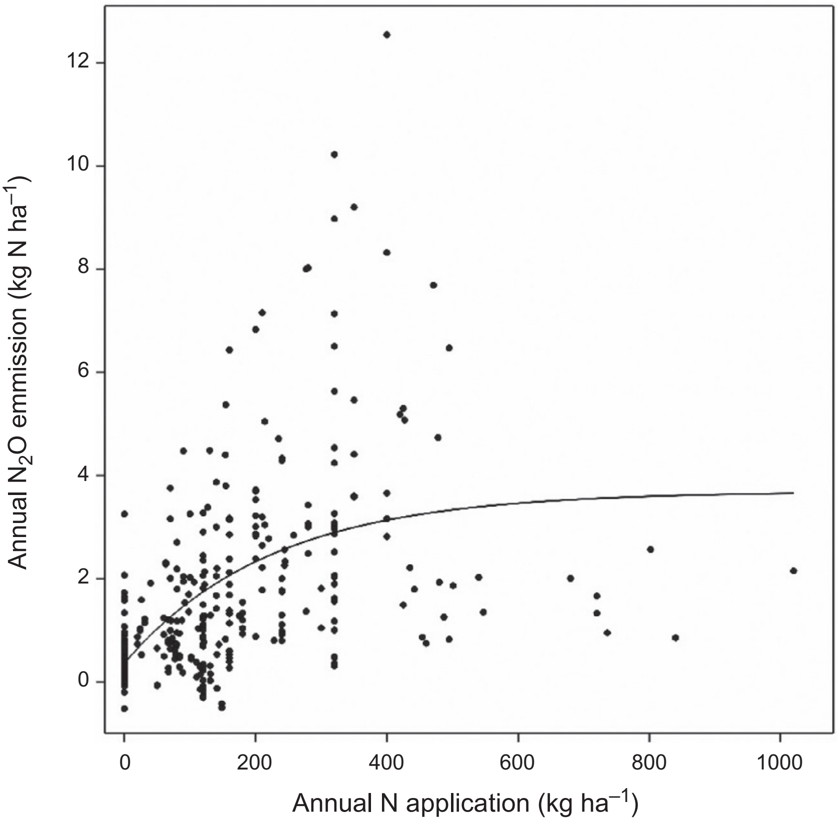

Fig. 7 The Mitscherlich-Baule model fitted to N_2O emission and various N types (UK county data).

are apparent at several sites. Similar patterns can be seen by inspecting the boxplot by N type (Fig. 8B).

Although crop yield data were tested for fitting with the Mitscherlich-Baule model, they only followed the model loosely and produced a variable spread of yield, as it is not wholly appropriate to compare crops of different grass, clover and cereal types incorporating a wide range of yields. Fig. 9 shows the site variation in yield and soil pH. Crop yield in Midlothian is the lowest but others are similar or skewed. Soil pH tends to be variable across geo-position both naturally and by management practice. The value is highest for Cambridgeshire and lowest for Devon, Ceredigion and Dumfries. In such a diverse collection of data with many factors and covariates, some missing combinations are not a surprise, though that rules out standard multivariate analyses such as principal components analysis and cluster analysis. To look at more than two factors or covariates together we suggest using a regression tree modeling approach (Breiman et al., 1984).

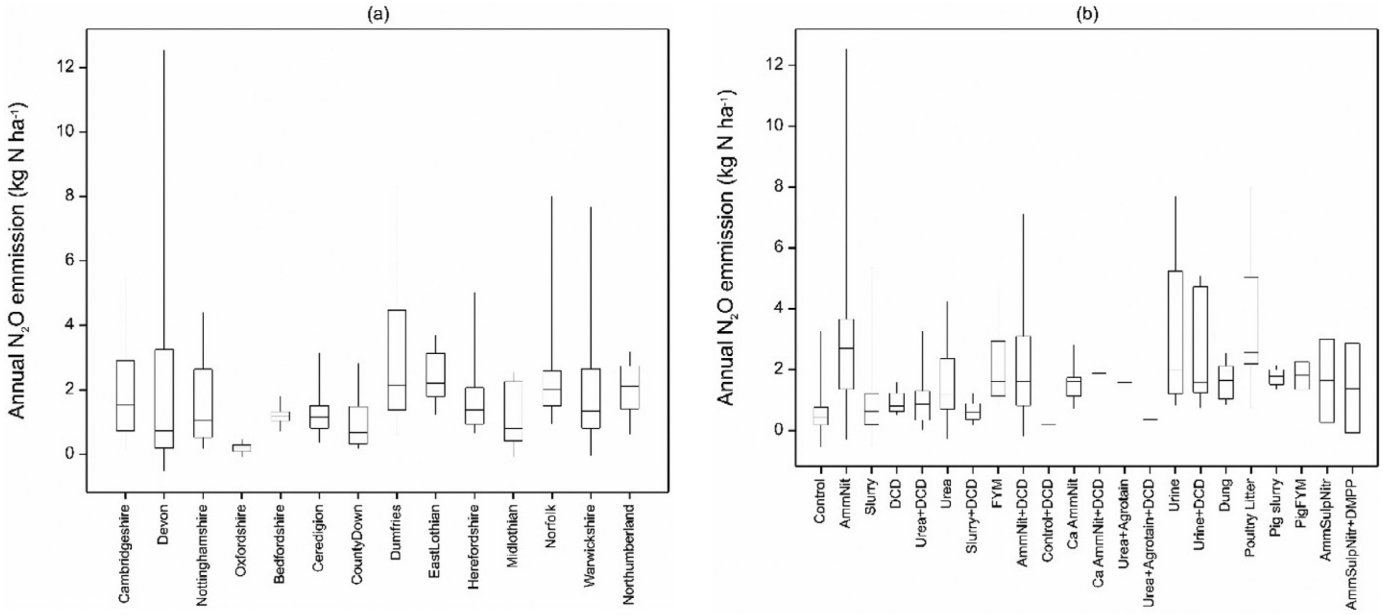

Fig. 8 Boxplots of annual N_2O flux (kg N ha^{-1}) (A) by site and (B) by N type (using UK county data). Boxes and horizontal lines indicate inter-quartile range and median, whiskers indicate range of data.

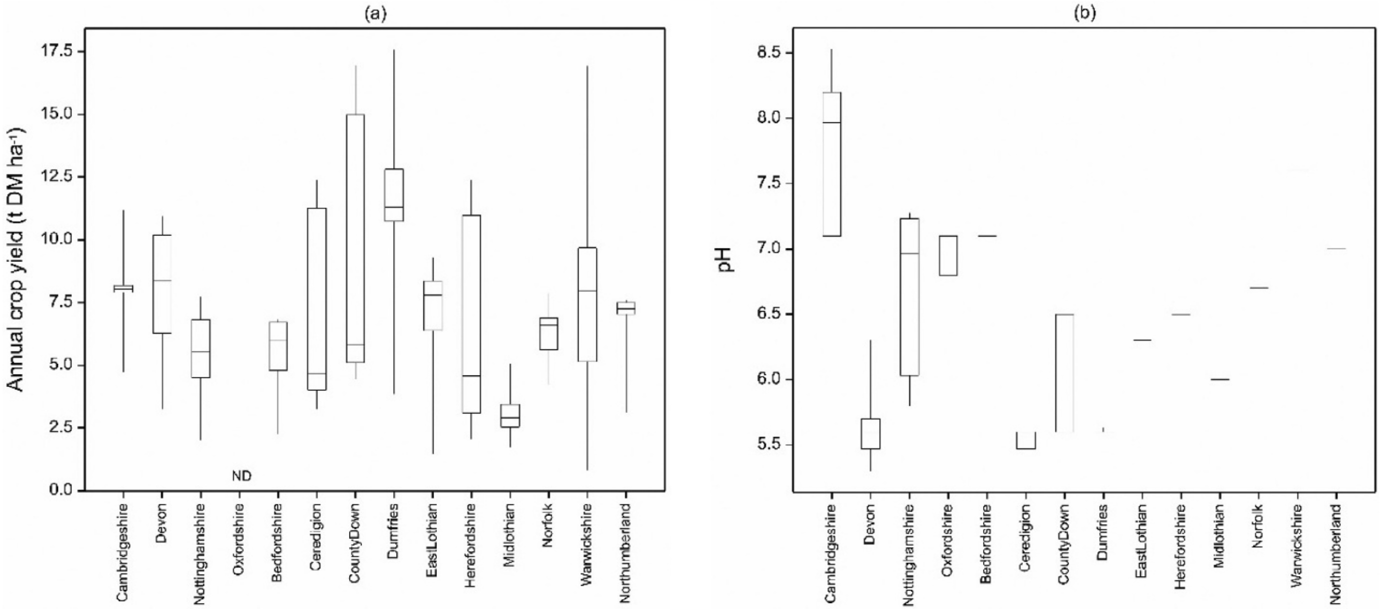

Fig. 9 Boxplots of site variation in (A) annual crop yield (t DM/ha) and (B) annual pH (using UK county data). Boxes and horizontal lines indicate interquartile range and median, whiskers indicate range of data. ND = not determined.

4. Conclusions

Application of the Mitscherlich-Baule model results in valuable site treatment specific information that enables geo-positions and their relevant ecosystems to be compared and contrasted. The nutrient estimate in the soil is the result of local environment and local soil type and composition that determine the control plot yield and potential for further yield in response to added growth factors. Baule units may be used to quantify this input for the required percentage of estimated local asymptotic yield. Information on N_2O emission potential of a given soil can help design mitigation strategies.

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