

SPECIAL ISSUE ARTICLE

Cycling of reduced phosphorus compounds in soil and potential impacts of climate change

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Funding information

Elemental digest systems Limited; Soils to
nutrition (S2N); STARS CDT

Abstract

Soil phosphorus (P) remains an ever-increasing topic of importance, notably for its key role as a nutrient for driving food production but with parallel concerns over damaging water quality, all against a backdrop of uncertainty of long-term rock phosphate supplies. Soil is a key interface that holds P and regulates its onward flow to plants or leakage to waters. Often overlooked are a ubiquitous group of P compounds that exist in alternative oxidation states to that of phosphate (+5). Redox cycling, and the behaviour that chemically reduced P compounds exhibit in soils, introduces alternative routes of cycling P that may become more important as the soil system itself alters, especially due to the external pressures of climate change, bringing about critical dynamics in rainfall and runoff and also wetting and drying. All of these factors are known to affect soil redox potential and consequently the oxidation state of soil P. This review considers the chemically reduced species in the P cycle, exploring their sources and sinks, while considering their importance within the primary global biogeochemical cycling of P and how this may be impacted by climate change in the temperate climate of the northern hemisphere.

Highlights

- This paper addresses how climate change will affect soil phosphorus cycling.
- This review is novel as it considers the reduced phosphorus forms when discussing P transfer in soils.
- Climate change is likely to increase prevalence of reduced P and free phosphate in northern hemisphere temperate soils.
- Phosphorus cycling relies partly on redox P processes. Their importance will increase as climate alters soils.

KEYWORDS

climate change, cycling, phosphorus, redox, soil

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1 | INTRODUCTION

Climate change is predicted to change patterns of annual rainfall globally, with temperate parts of the northern hemisphere expected to experience increases in the occurrence of flash flooding in autumn/winter months and prolonged dry spells in spring/summer months (Masson-Delmotte et al., 2018). As a result, the soil system will experience noticeable changes in hydrologic dynamics (Green et al., 2019; Borrelli

et al., 2020). In the UK, for example, it is predicted that soil water saturation levels will not only increase during winter, but the period for which they remain saturated will also increase (Ockenden et al., 2017). It has been estimated that the Earth will experience an increase of between 16 and 24% of heavy precipitation events by the year 2100 and will see an average of 20% less rainfall during periods of drought (Fischer, Sedlacek, Hawkins, & Knutti, 2014). These climate predictions are expected to result in soil available phosphorus

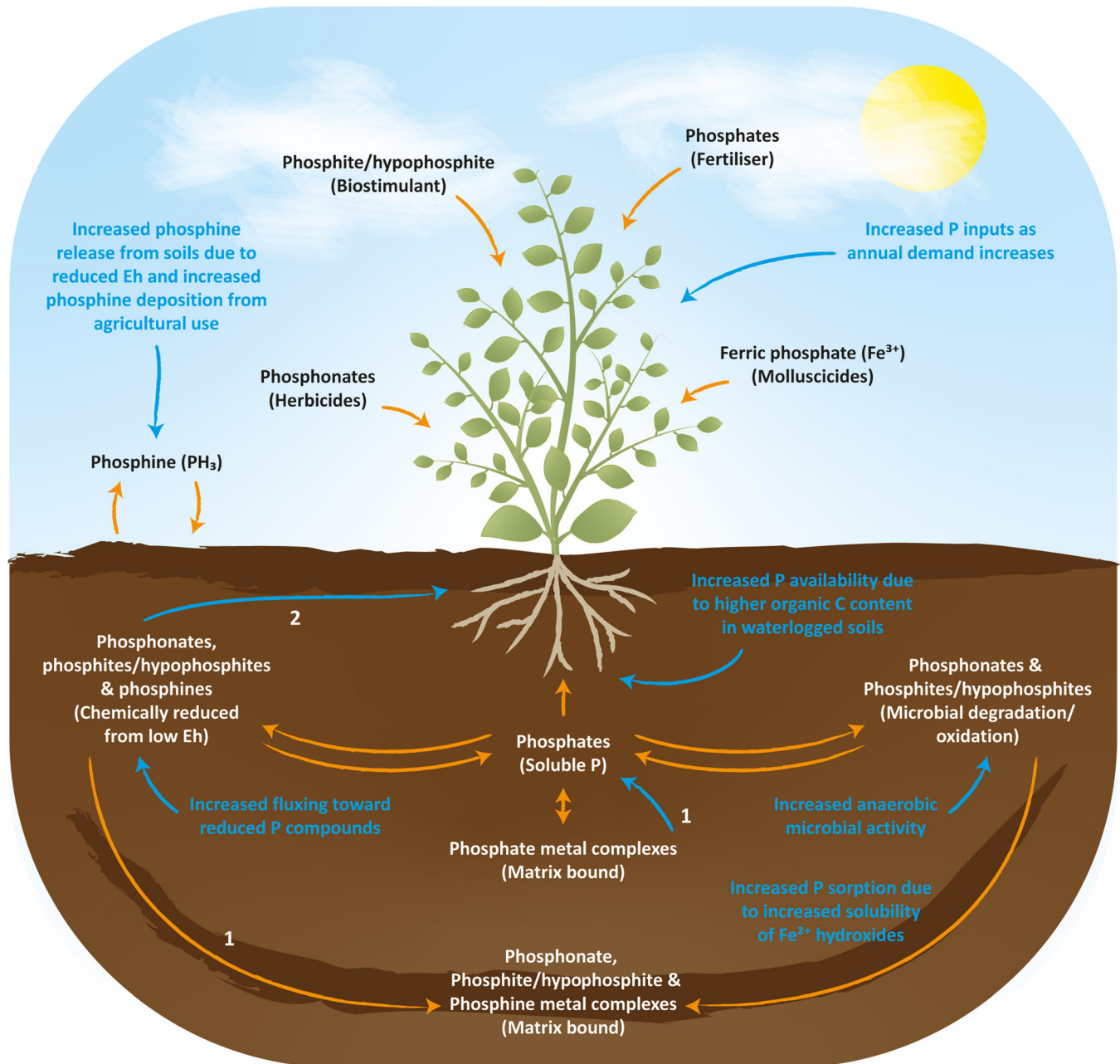


FIGURE 1 Climate change and consequent predicted changes in soil redox condition, demonstrating the suggested changes to the reduced P cycle. Process 1: Increased mobility of P forms due to reduction of Fe-hydroxides (Fe³⁺ to Fe²⁺). Process 2: Uptake of reduced P forms, with phosphites/hypophosphites benefiting the plant and other reduced P acting negatively on plant life [Color figure can be viewed at wileyonlinelibrary.com]

(P) concentrations significantly decreasing with increasing mean annual temperature and precipitation (Hou et al., 2018).

During intense precipitation events, an increase in saturated soil conditions will promote reductions in soil redox (Eh) values due to lower oxygen concentrations associated with greater saturation. With the Earth's temperature rising on average 0.18°C per decade (NOAA, 2019) and the average soil temperature rising 0.47°C per decade (Fang, Luo, & Lyu, 2019), autumn/winter soil microbial activity is also likely to increase, assisting in driving down the Eh of many temperate European and North American soils (Vaughan, Rabenhorst, & Needelman, 2009) (Zhang, Wang, Chen, Zheng, & Zeng, 2014). Increases in soil moisture will also assist with heat transfer to soils, with moisture increasing heat dissipation down the soil profile (Ochsner et al., 2001). It has also been demonstrated that although soil microbial enzymatic activity generally decreases during colder winter periods, the activity of some fungal species increases (Isobe et al., 2018; Wang Hai et al., 2018). In such circumstances, anaerobic microorganisms use oxidized compounds in soils as electron acceptors for respiration, thus converting them to reduced chemical forms and lowering the overall Eh value of the soil (Pezeshki & Delaune, 2012). This introduces redox processes into soil P biogeochemical cycling. There is considerable knowledge on redox processes associated with the primary biogeochemical cycles of nitrogen (N) and carbon (C), for example denitrification and methanogenesis (Andalib, Nakhla, McIntee, & Zhu, 2011), but the impact of redox processes on P cycling in soils has been studied to a much lesser extent, with P usually discussed as the stable oxidized P compound phosphate (+5). However, P also exists as multiple reduced compounds made up of the phosphonates (+3), phosphites (+3), hypophosphites (+1) and phosphines (−3) (Pasek, Sampson, & Atlas, 2014), that are actively involved in P cycling and are also thought to assist with other biogeochemical soil processes such as methanogenesis (Cao, M, N, & Smith, 2017; Redfield, 1958; Vaughan & Malcolm, 1985). These forms currently attract much less attention, but as discussed here, may well become more important as climate change shifts the water saturation and redox equilibrium in many soils (Figure 1).

1.1 | The introduction of phosphorus to the soil system

In agricultural systems the largest inputs of P to soils are primarily from fertilizer applications (Bhattacharya, 2019). Fertilizers are applied commonly in both organic (composed of natural ingredients of plant or animal origin) and

inorganic forms (mined from mineral deposits or manufactured from synthetic compounds) (Milne, 2018). Typical soil concentrations of phosphate (in the form of orthophosphate, PO_4^{3-}) in a managed soil system range between 500 and 800 mg/kg of dry soil (Mengel, Kirkby, Kosegarten, & Appel, 2001). Mineral phosphate fertilizers added to soils are readily available to plants because they are soluble. This is why mineral P fertilizer is the most popular choice of fertilizer over organic fertilizer worldwide (Morgan & Connolly, 2013).

The majority of soil P remains in phosphate form, usually accounting for up to 70% of total P in soils (Harrison, 1987). However, it is thought that, as soils are increasingly affected by extreme rainfall events predicted under climate change, saturated soil systems will result in further increases in P availability with regard to phosphate forms (Wright, Lockaby, & Walbridge, 2001). In recently flooded dried soils, soil solution phosphate concentrations increased drastically, leading to an initial boost in P availability, which has been shown to assist crop growth in areas that are P fertilizer deficient. The phenomenon of phosphate release can be explained through enhancement of the concentration gradient, which increases the rate of diffusion of P to plant root systems (Turner & Gilliam, 1976). In this instance, the oxidized forms of Fe(III) and Mn(IV) are reduced, allowing them to become the major electron acceptors for anaerobic microbes. This process releases iron and manganese-bound phosphates into solution through reductive dissolution (Gotoh & Patrick, 1974). If the climate continues to change in a way in which flooding events are seasonally followed by droughts, then it is predicted that this may positively affect crop growth and ease the need for P fertilizer dependency in P-deficient soils, subject to availability of sufficient water (Brodlin, Kaiser, Kessler, & Hagedom, 2019).

1.2 | Scope of review

Soil P transport models typically only consider direct phosphate impacts on environmental health (Das, Huth, Probert, Condrón, & Schmidt, 2019; Shiri et al., 2020; Ziadi, Whalen, Messiga, & Morel, 2013), with very little or no account of reduced P species and their influence on global P cycling. Table 1 shows common reduced P compounds from a variety of everyday sources, demonstrating how easily they can find their way into the environment for subsequent cycling. As the climate changes, specifically focusing on changes to the European temperate climate, we predict P redox cycling to become an increasingly important part of the global P cycle within the time frames of the climate changes predicted by the IPCC (Masson-Delmotte et al., 2018). The mechanisms

TABLE 1 A summary table showing commonly found reduced phosphorus (P) compounds in soils, showing their production, sources and sinks

Reduced P compound group	Presence in the environment	External sources of input to the environment	Processes of formation	Processes of degradation	References
Phosphonates (C – PO(OR) ₂)	2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)	Industry use as: metal complexing agents, textile and paper production, bleaching agents for cosmetics, industrial cooling water	NA	Through adsorption onto activated sludge, biodegradation and removal in wastewater treatment plants	Rott, Steinmetz, and Metzger (2018) Gledhill & Fejitel, (1992) Jaworska, Van Genderen-Takken, Hanstveit, van de Plassehe, and Fejitel (2002)
	1-hydroxyethane 1,1-diphosphonic acid (HEDP)	Industry use as: laundry detergent and cleaning products, medical use (bone disease), metal complexing agent, textile and paper production, bleaching agents for cosmetics, industrial cooling water	Reaction of phosphorous acid and acetic anhydride	Through adsorption onto activated sludge, biodegradation and removal in wastewater treatment plants	Jaworska et al. (2002) Metcalf & van der Donk (2009) Svara and Hofmann (2008) Rott et al. (2018) Gledhill and Fejitel (1992))
	Nitrioltris (methylene phosphonic acid) (NTMP)	Industry use as: laundry detergent and cleaning products, metal complexing agents, textile and paper production, bleaching agents for cosmetics, industrial cooling water	From the reaction of phosphonic acid, ammonia and formaldehyde	Through adsorption onto activated sludge, biodegradation and removal in wastewater treatment plants	Rott et al. (2018) Gledhill & Fejitel (1992) Savignac and Iorga (2003)
	Ethylenediamine tetra (methylene phosphonic acid) (EDTMP)	Industry use as: laundry detergent and cleaning products, medical use (bone disease), metal complexing agents, textile and paper production, bleaching agents for cosmetics, industrial cooling water	Structural rearrangement of aminopolycarboxylate	Through adsorption onto activated sludge, biodegradation and removal in wastewater treatment plants	Leonard et al. (2016) Jaworska et al. (2002) Rott et al. (2018) Gledhill and Fejitel (1992)
	Diethylenetriamine penta (methylene phosphonic acid) (DTPMP)	Industry use as: laundry detergent and cleaning products, metal complexing agents, textile and paper production, bleaching agents for cosmetics, industrial cooling water	Structural rearrangement of aminopolycarboxylate	Through adsorption onto activated sludge, biodegradation and removal in wastewater treatment plants	Satani et al. 2016) Jaworska et al. (2002) Rott et al. (2018) Gledhill and Fejitel (1992)
	Aminotrimethylene-phosphonic acid (ATMP)	Industry use as: laundry detergent and cleaning products, metal complexing agents, textile and paper production, bleaching agents for cosmetics, industrial cooling water	Reaction of ethanamine, formaldehyde and phosphorus acid	Through adsorption onto activated sludge, biodegradation and removal in wastewater treatment plants	Kelland (2014) Rott et al. (2018) Gledhill and Fejitel (1992) Jaworska et al. (2002)

TABLE 1 (Continued)

Reduced P compound group	Presence in the environment	External sources of input to the environment	Processes of formation	Processes of degradation	References
2-aminoethylphosphonate (AEP)	Biogenic synthesis	Biogenic synthesis	Intramolecular rearrangement of phosphomutase enzyme (PEP). Produced in <i>Tetrahymena pyriformis</i> and <i>Bacteroides fragilis</i>	Biodegradation/oxidation	Roberts, Simonsen, Horiguchi, and Kittredge (1968) Metcalf and van der Donk (2009)
2-hydroxyethyl phosphonate (HEP)	Biogenic synthesis	Biogenic synthesis	Intramolecular rearrangement of PEP in the production of fosfomycin	Biodegradation/oxidation	Hidaka et al. (1995) Metcalf and van der Donk (2009)
Phosphonoalanine (P-ala)	Biogenic synthesis	Biogenic synthesis	Transamination of phosphonopyruvate by <i>Tetrahymena</i>	Biodegradation/oxidation	Roberts et al. (1968) Metcalf and van der Donk (2009)
(1R,2S)-Epoxypropylphosphonic acid (fosfomycin)	Biogenic synthesis	Biogenic synthesis	Intramolecular rearrangement of PEP produced by <i>Streptomyces fradiae</i> , <i>S. wedmorensis</i> , <i>S. viridochromogenes</i> and <i>Pseudomonas syringae</i> and <i>Pseudomonas viridiflava</i>	Biodegradation/oxidation	Hendlin et al. (1969) Shoji et al. (1986) Katayama, Tsubotani, Nozaki, Harada, and Ono (1990)
Alendronate (osteoporosis treatment, medicinal)	Man-made	Man-made	Reaction of γ -aminobutyric acid by treatment with P trichloride and phosphoric acid in chlorobenzene followed by quenching with water	Biodegradation/oxidation	Ananchenko and Tikhomirova (2013) Metcalf and van der Donk (2009)
Amino-methyl phosphonic acid	Man-made	Man-made	Glyphosate (herbicide) breakdown	Biodegradation/oxidation	Grandcoin, Piel, and Baures (2017)
Dehydrophos (antibiotic)	Biogenic synthesis	Biogenic synthesis	Intramolecular rearrangement of PEP produced by <i>Streptomyces luridus</i>	Biodegradation/oxidation	Hunt and Elzey (1988)
Plumbemycin (antibiotic)	Biogenic synthesis	Biogenic synthesis	antimetabolites from <i>Streptomyces plumbeus</i> and <i>Bacillus subtilis</i> ATCC 6633	Biodegradation/oxidation	Park, Hirota, and Sakai (1977) Gahungu et al. (2013)

(Continues)

TABLE 1 (Continued)

Reduced P compound group	Presence in the environment	External sources of input to the environment	Processes of formation	Processes of degradation	References
Phosphites (R_2HPO_3)	Phosphinothricin tripeptide (PTT) (herbicide)		Intramolecular rearrangement of PEP produced by <i>S. hygrosopicus</i> and <i>S. Vitidochromogenes</i>	Biodegradation/oxidation	Schwartz et al. (2004) Blodgett, Zhang, and Metcalf (2005)
	Phosphonothrixin (herbicide)	Biogenic synthesis	Intramolecular rearrangement of PEP. Produced by actinobacteria	Biodegradation/oxidation	Seto and Kuzuyama (1999) Metcalf and van der Donk (2009)
	FR900098 (antimalarial)	Biogenic synthesis	Produced by <i>streptomyces rubellomurinus</i> , <i>Streptomyces lavendulae</i> and <i>Streptomyces lividans</i>	Biodegradation/oxidation	Iguchi, Okuhara, Kohsaka, Aoki, and Imanaka (1980) Okuhara et al. (1980) Metcalf and van der Donk (2009)
	Fosmidomycin (antimalarial)	Biogenic synthesis	Produced by <i>Plasmodium falciparum</i> , <i>rubellomurinus</i> and <i>Streptomyces lavendulae</i>	Biodegradation/oxidation	Wiesner, Borrmann, and Jomaa (2003) Kuemmerle, Murakawa, and De Santis (1987)
Phosphites (R_2HPO_3)	Potassium phosphite	Industrial fertiliser	Produced by mixing a solution of potassium hydroxide with phosphorus acid	Oxidised by phosphite oxidoreductase/phosphite dehydrogenase through assimilatory phosphite oxidation or dissimilarly phosphite oxidation Chemical oxidation to phosphonates	Bisson et al. (2017) Griffith, Davis, and Grant (1992)
	Calcium phosphite	Industrial fertiliser	Produced by mixing a solution of calcium hydroxide with phosphorus acid	Oxidised by phosphite oxidoreductase/phosphite dehydrogenase through assimilatory phosphite oxidation or dissimilarly phosphite oxidation Chemical oxidation to phosphonates	Bisson et al. (2017) Griffith et al. (1992)
	Magnesium phosphite	Industrial fertiliser	Produced by mixing a solution of magnesium hydroxide with phosphorus acid	Oxidised by phosphite oxidoreductase/phosphite dehydrogenase through assimilatory phosphite oxidation or dissimilarly phosphite oxidation Chemical oxidation to phosphonates	Bisson et al. (2017) Griffith et al. (1992)

TABLE 1 (Continued)

<i>Reduced P compound group</i>	<i>Presence in the environment</i>	<i>External sources of input to the environment</i>	<i>Processes of formation</i>	<i>Processes of degradation</i>	<i>References</i>
	Sodium phosphite	Chemical reducing agent	Sodium hydroxide with phosphorous acid	Oxidised by phosphite oxidoreductase/phosphite dehydrogenase through assimilatory phosphite oxidation or dissimilarly phosphite oxidation	Bisson et al. (2017) Griffith et al. (1992)
	Basic lead phosphite	Stabilizer in PVC and related chlorinated polymers	Produced with lead monoxide, lead acetate and phosphorous acid	Biodegradation/oxidation	Betterman, Krause, Riess, and Hofmann (2005)
Hypophosphites (RPO ₂ H ₂ ·H ₂ O)	Sodium hypophosphite	Electroless nickel plating	Produced by heating white phosphorus in sodium hydroxide solution	When heated, produces phosphine gas and sodium phosphite. Oxidised biologically by hypophosphite/2-oxoglutarate dioxygenase	Abrantes and Correia (1994)
	Potassium hypophosphite	Electroless nickel plating	By reaction of hypophosphorous acid and potassium carbonate solution, and/or by reaction of potassium hydroxide solution and phosphorus on heating	When heated produces phosphine gas and potassium phosphite	Abrantes and Correia (1994)
Phosphines (R ₃ P)	Gallium phosphide	Industrial use as semi-conductors	Gallium oxide in a P rich atmosphere	At temperatures above 900 °C, gallium phosphide dissociates and P escapes as a gas	Betterman et al. (2005) Haynes (2016) Tang, Fan, de la Chapelle, Dang, and Li (2000)
	Indium phosphide	Industrial use as semi-conductors	A reaction of white phosphorus and indium iodide.	NA	Betterman et al. (2005)
	Pure phosphine gas	Industrial use as agricultural fumigant	In agriculture when aluminium, calcium or zinc phosphide tablets come in contact with moisture phosphine gas is released	Phosphine gas release to the atmosphere, where environmental degradation and oxidation occurs	Pohanish (2014) Pasek et al. (2014)

and drivers for the cycling of these compounds are not fully understood and characterized (Roels & Verstraete, 2001; White & Metcalf, 2007), but research is recognizing some of the critical biochemical pathways that are almost entirely driven through the action of reduced P species in the environment (MetCalf & Van der Donk, 2009; Pasek et al., 2014; White & MetCalf, 2007). Here we describe in detail the chemistry, sources and cycling of the reduced P groups in order of their degree of reduction and how an altering soil climate will have an impact on them. Following this, their analytical limitations will be discussed in order to shed light on the difficulties encountered that have prevented this area of science from progressing at pace.

2 | SOIL PHOSPHONATES

Phosphonates are a broad family of organic molecules that are characterized by a functional group, which consists of two hydroxyl moieties, a double bonded P=O bond and a single bonded C-P bond (Figure 2) (Demmer, Krogsgaard-Larsen, & Bunch, 2011). It is the characteristic stable covalent C-P bond that sets the phosphonates apart from other P compounds (Glindemann, Eismann, Bergmann, Kuschik, & Stottmeister, 1998) and in soils most phosphonates are found as long chain phosphonic acids (Sevrain, Berchel, Couthon, & Jaffres, 2017) that, within microbially driven systems, have the primary metabolic functions of cell signalling, metabolism and synthesis of natural antibiotics (McGrath, Chin, & Quinn, 2013).

2.1 | Formation and inputs of the phosphonates to the soil system

There are two entry routes for phosphonates into the soil system: through biogenic processes within the soil or through external anthropogenic inputs. There is now a general underpinning knowledge of the pathways involved for nearly all biogenic phosphonate compounds, which involves intramolecular rearrangement of the intermediary metabolite phosphoenolpyruvate, a phosphate bonded ester molecule, into phosphonopyruvate, a carboxylic acid that contains the C-P bond (Figure 3) (Metcalf & Van der Donk, 2009). This rearrangement is known to be synthesized by the phosphomutase enzyme (PEP) (Bowman, McQueney, Barry, & Dunawaymariano, 1988; Metcalf & Van der Donk, 2009). Certain phosphonate-utilizing genes are required to access P from a C-P bond, with the specific *pepM* gene associated with microbial phosphonate production. Around 5% of microbes present in global soils contain this gene (Yu et al., 2013). In soils, phosphonates are found as side groups, typically on

exopolysaccharides and glycoproteins and additionally in the polar head groups of membrane phosphonolipids. This is suspected to provide structural rigidity for certain molecules, as the covalent C-P bond is strong enough to resist the action of phosphatases in soil systems, resulting in immunity to enzymatic degradation (Hilderbrand & Henderson, 1983).

Phosphonate-utilizing microorganisms typically reside in anaerobic environments, such as wetlands or deep in unsaturated soils where redox values are lower (Schowanek & Verstraete, 1990). The cycle of seasonal soil saturation and drying may promote the release of phosphates temporarily, but in the long term, as these cycles become exacerbated, we propose phosphonate formation will increase. This is because, although P availability is enhanced in this cycle, as time progresses, anaerobic processes will dominate. When a dry soil experiences the initial release of P upon flooding, it also experiences an increase in bacterial activity. With increased productivity and no oxygen replenishment, eventually the onset of anoxia will occur and consequently, an increase in anoxic microbial processes (Baldwin & Mitchell, 2000). Based on the formation processes involved in phosphonate C-P bond production, it is likely that during the predicted increases in frequency and duration of saturated soil conditions in autumn/winter seasons, an increase in concentrations of phosphonates will occur (Wu et al., 2005). During soil saturation, it is shown that soil moisture positively affects microbial biomass (Iovieno & Bååth, 2008). Extended periods of soil saturation, for example over 3 months, are expected to increase expression of the proteins within anaerobic bacteria that control metabolism (Wu et al., 2005). Often, in anaerobic soil systems, there is an increase in diversity and abundance of phosphonate biosynthetic genes that are required to process the reduced P forms (Yu et al., 2013).

Anthropogenic sources of phosphonates for the soil system originate largely from the agricultural industry, through application of herbicide treatments. Most widely applied is the compound *N*-(phosphonomethyl) glycine, known more commonly as glyphosate (Benbrook, 2016). Through enzymatic degradation of this compound by *Arthrobacter atrocyaneus* ATCC 13752 (Pipke & Amrhein, 1988), the metabolite aminomethyl phosphonic acid (AMPA) is formed (Figure 4), which is a simple chain phosphonate (Botta et al., 2009; Forlani, Mangiagalli, Nielsen, & Suardi, 1999). Glyphosate usage in soils is common, with usage having increased 14.6-fold in the space of just 20 years as weed resistance increases (Benbrook, 2016). Since 1974, 8.6 billion kg of this compound have been applied to soils globally, leaving a multitude of phosphonate breakdown products in soils (Benbrook, 2016). Given the predicted increase in soil moisture and consequent reduced redox potential of most soils under climate change, these compounds are more likely to persist. However, pressure is

increasing to ban this phosphonate compound globally, with expectations that it will no longer be in circulation by 2024 (European Commission, 2020).

2.2 | Degradation and fate of phosphonate compounds in the soil system

Phosphonates frequently undergo adsorption in soils (Held, 1989), as they have a strong tendency to adsorb onto mineral surfaces at a pH of around 6.5–8.5 (Stone, Knight, & Nowack, 2002). Certain surfaces favourable for phosphonate bonding include calcium carbonates (Xyla, Mikroyannidis, & Koutsoukos, 1992), barium sulphates (Black et al., 1991), zinc oxides (Nowack & Stone, 1999a), iron oxides (Nowack & Stone, 1999b) and clays (Fischer, 1992). Adsorption of a phosphonate will impact its ability to degrade in a soil system, with formation of metal complexes commonly known to decrease biodegradability. This phenomenon has been demonstrated on the phosphonate nitrilotriacetate by the bacteria *Chelatobacter heintzii*, where rate of degradation slowed but did not completely stop under the influence of metal complex surface adsorption (Bolton & Girvin, 1996). Additionally, it is theorized that phosphonates with a higher adsorption affinity will be more slowly degraded in a heterogenous soil system than in a homogenous system, which has been found to be true for glyphosate (Zaranyika & Nyandoro, 1993). Degradation can occur via biodegradation, chemical degradation and oxidative degradation (Nowack, 2003).

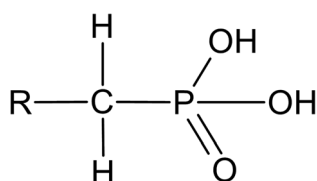


FIGURE 2 Phosphonate structure demonstrating the arrangement of single and double bonds to the P element (Svara and Hofmann (2008))

2.3 | Biodegradation

Biodegradation occurs via the enzymatic degradation of the C-P bond by adaptive microorganisms, which metabolize phosphonates as nutrient sources for growth (McMullan & Quinn, 1993). Phosphonate degradation and utilization is common among prokaryotes, eubacteria and fungi (Wanner, 1994). Certain bacterial strains, including *Arthrobacter*, were found to degrade amino polyphosphonates from a variety of soils (Schowanek & Verstraete, 1990). Phosphonobutane tricarboxylic acid has also been shown to degrade under microbial action when P scarcity occurs, with rapid degradation by *Pseudomonas* (Raschke, Rast, Kleinstuck, Sicius, & Wischer, 1994). It is useful to note, however, that it is possible for simultaneous utilization of phosphonates and phosphate to occur, with *Pseudomonas paucimobilis* strain MMM101a demonstrating this (Schowanek & Verstraete, 1990). The predominant route for microbial utilization and therefore breakdown of phosphonates is through the C-P lyase enzymatic pathway (Ternan, McMullan, & Quinn, 1998). The broad specificity of the C-P lyase multienzyme complex is not fully characterized (Hove-Jensen, McSorley, & Zechel, 2011). However, research conducted on *Escherichia coli* is beginning to shed some light on the catalytic machinery for the C-P lyase reaction (Chen, Ye, Zhu, Wanner, & Walsh, 1990; Yakovleva, Kim, & Wanner, 1998). C-P lyase activity is only inducible under conditions of phosphate limitation (Chin, McGrath, & Quinn, 2016). This enzyme is capable of dephosphonation of a wide range of structurally diverse phosphonates (Chin et al., 2016). These polypeptides catalyze C-P bond cleavage, in which alkylphosphonates are converted to the corresponding alkanes and inorganic phosphate (Wackett, Shames, Venditti, & Walsh, 1987).

With a known abundance of phosphonate-utilizing microbes located in anaerobic environments compared to aerobic systems (van der Wal, de Boer, Lubbers, & van Veen, 2007), it is our conjecture that biodegradation of phosphonate compounds is likely to increase under climate change as a result of increases in the occurrence and duration of seasonally saturated soil systems. With a

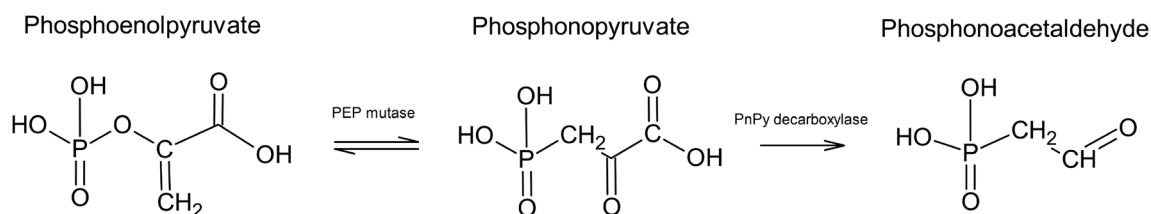


FIGURE 3 Pathway for the formation of C-P compounds through the rearrangement of phosphoenolpyruvate to phosphonopyruvate by the phosphomutase enzyme (PEP) mutase enzyme (White & Metcalf, 2007)

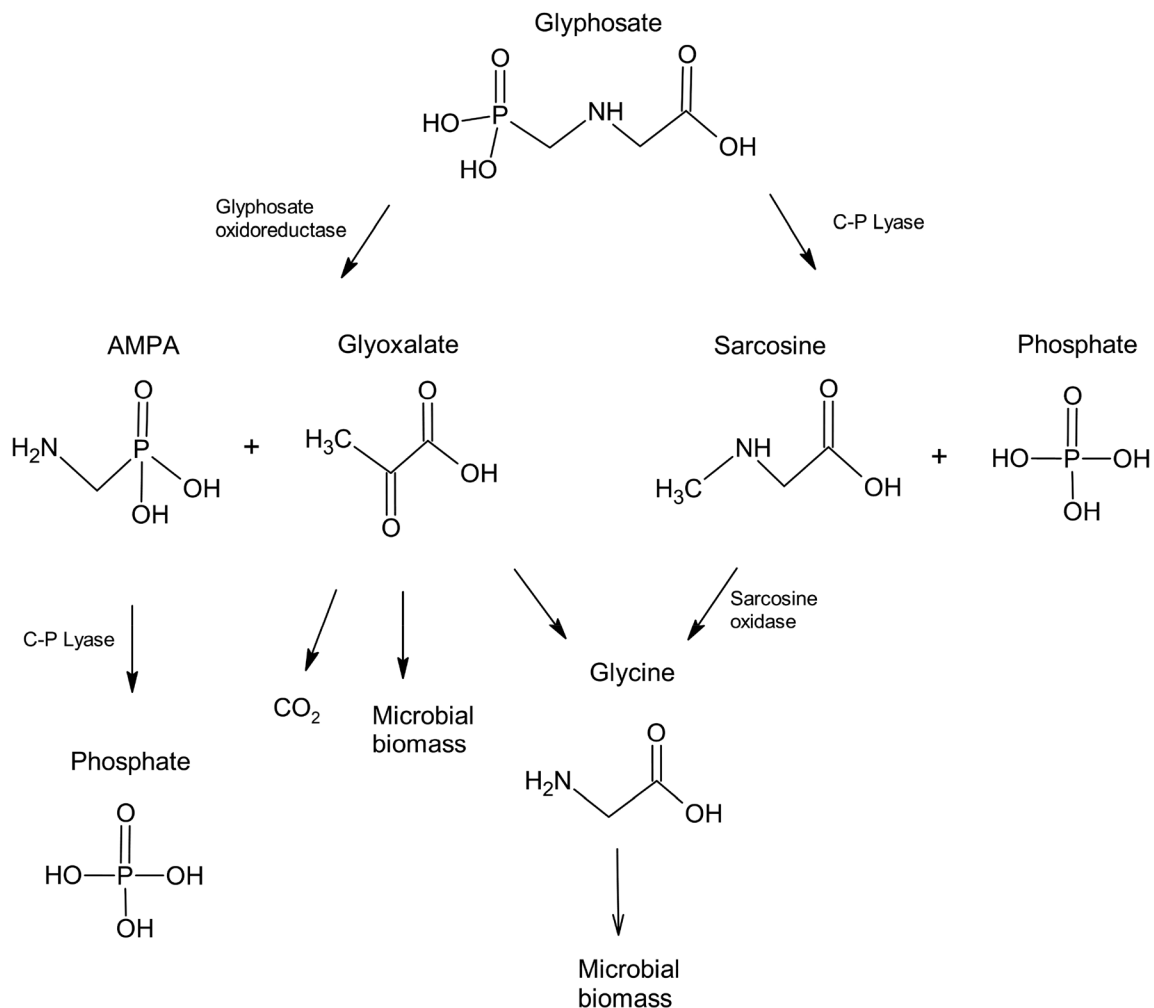


FIGURE 4 The breakdown products of glyphosate via the enzymatic action of microorganisms (Grandcoin et al., 2017)

predicted increase of anaerobic C-P bond-breaking microorganisms in saturated soils, reduced P cycling will increase as phosphonate compounds in the soil system will be utilized in a higher capacity. It is likely that the process of methanogenesis will also be affected by an increase in phosphonate bond-breaking processes (Pasek et al., 2014). During more intensive dry seasons, generally predicted under climate change, there is likely to be a negative impact on the biodegradative processes that are involved in C-P bond cleavage. Lower microbial growth rates are observed on air-dried soils (Iovieno & Bååth, 2008) and in extreme drying events microbial mortality is common (Baldwin & Mitchell, 2000). In instances of extreme drought, the death of microbes will increase mineralization of P (Baldwin & Mitchell, 2000).

2.4 | Chemical degradation

The strength of the covalent C-P bond in phosphonate compounds requires long timescales for its breakdown,

along with extreme chemical conditions (Kononova & Nesmeyanova, 2002). It has been proven, however, that chemical degradation does occur naturally in the environment. In one study, the phosphonate EDTMP (ethylenediaminetetra (methylene phosphonic acid)) was left at room temperature and at a pH range of 6.5–8.5, and hydrolysis resulted in the formation of phosphate, phosphite, and a simpler chain phosphonate (Tschabunin, Schwedt, & Fischer, 1989). It is suspected that the metal that a phosphonate is bound to has a large impact on its ability to chemically degrade (Nowack, 2003).

Under saturated autumn/winter soil conditions, the diffusion of atmospheric oxygen into the soil is reduced. Anaerobic microbes flourish under these conditions and due to their microbial activity, CO₂ accumulation will occur. This will cause the soil solution pH to drop in calcareous alkaline soils specifically (Fageria, Carvalho, Santos, Ferreira, & Knupp, 2011; Nikolić & Pavlović, 2018). In these soils, the lowering of soil pH is likely to result in a reduction in the chemical degradation of phosphonates (Lesueur, Pfeffer, & Fuerhacker, 2005). Soil saturation will

have the additional effect of reducing Fe(III) to Fe(II) (Pezeshki & DeLaune, 2012), which in turn will facilitate the chemical conversion of phosphonates to phosphates in metal-phosphonate complexes (Nowack, 2003). Despite this, degradation is negligible for Fe(II)-phosphonate complexes in saturated systems despite the reaction being hydrolysis (Steber & Wierich, 1987). In a circumstance where the seasonal change from saturated soil conditions to dry soil conditions is occurring much more rapidly, chemical degradation of phosphonates is likely to increase. This is because, as waterlogging encourages formation of Fe(II)-phosphonate complexes, and as seasonal change occurs, subsequent rapid soil drying will result in the rapid introduction of oxygen to the soil. This will result in a proportion of the residual Fe(II)-phosphonate complexes degrading before converting to Fe(III)-phosphonate complexes. The overall effect of this is that during rapid seasonal changes a decrease in soil phosphonate concentrations is likely to occur.

2.5 | Oxidative degradation

Oxidative degradation of phosphonates occurs in soils when metal oxides are abundant. A study conducted by Barrett and McBride (2005) demonstrated an accumulation of orthophosphate in common soils from the short chain phosphonate AMPA (aminomethylphosphonic acid) with the addition of an oxide. Abiotic degradation is the process responsible for this, with manganese (Mn) in particular, driving C-P bond cleavage at the metal oxide surface. As with all other phosphonate degradation processes, the metal itself plays the largest part in whether a phosphonate compound remains bound to soils or is released and degraded. Cu^{2+} appears to inhibit degradation, with the metal-phosphonate complex formation favoured, thus limiting the transition of the phosphonate to reactive oxidation sites (Barrett & McBride, 2005).

The oxidative degradation of metal-phosphonate complexes does not appear to be connected to whether a soil environment is oxic or anoxic and for this reason is unlikely to be affected by the climatic changes predicted by the IPCC (Barrett & McBride, 2005; Masson-Delmotte et al., 2018). However, with more oxygen sites available to bond for non-metal phosphonate complexes during periods of extreme soil drought in many northern-hemisphere temperate spring/summer seasons, there is likely to be an increased conversion of phosphonate to phosphate (Yu et al., 2013). Oxidative processes, however, will not affect soil phosphonate transformation and cycling during flooding events (Pasek et al., 2014).

3 | SOIL (HYPO)PHOSPHITES

Phosphites (+3) are compounds that contain the phosphite ion $(\text{HPO}_3)^{2-}$ and are the salts of phosphorous acid. Despite phosphites being a group of highly soluble compounds, they are kinetically stable in the soil environment and can account for between 10 and 30% of all P compounds on the planet (Figuerola & Coates, 2017). This group of compounds is bio-accessible and although this fact has been known since the 1950s, its role in biogeochemistry is frequently overlooked (Adams & Conrad, 1953). Hypophosphites (+1) are the next reduced P group along from phosphonates in the P reduction chain (Rhodehamel, Pierson, & Leifer, 1990).

3.1 | Formation and inputs of the (hypo) phosphites to the soil system

Whether microorganisms can biogenically produce phosphite compounds is poorly understood; theories exist that suggest the reduction of phosphonates as the primary pathway for (hypo)phosphite biogenic formation (Metcalf & Wanner, 1991; Pasek et al., 2014; White & Metcalf, 2007). Phosphonate degradation has been shown to produce methane and inorganic phosphate upon the breakdown of the C-P bond (Karl et al., 2008). Through this process, via the action of the C-P lyase enzyme, a phosphate radical intermediate is formed (Buckel, 2013) and under a reduced redox environment, such as a saturated soil, the facilitation of phosphate radical rearrangement into phosphite occurs (Pasek, 2008; Pasek et al., 2014). Additionally, phosphonates that contain hydroxyl or carbonyl groups tend to favour formation of phosphites over phosphates during C-P bond cleavage (Freeman, Irwin, & Schwalbe, 1991).

In a changing soil climate, the process of phosphite formation is likely to increase through the formation of anoxic conditions and subsequent increase in phosphonate bond-breaking processes (Bains, Petkowski, Sousa-Silva, & Seager, 2019; Pasek, 2008). With an increase in soil anoxia, along with a chemically induced increase in soil phosphite concentration, the concentration of phosphite-utilizing microbes will also increase. This will amplify the rate at which phosphite is consumed within soils (Bisson et al., 2017). The counter effect is likely to be periods when soils start to dry and there is an increase in oxygen concentration as the increased presence of phosphate may inhibit the uptake of phosphite by microorganisms that otherwise would have been capable of utilizing phosphite for growth, with phosphate being favoured as a substrate (Foster, Winans, & Helms, 1978).

Anthropogenic inputs of phosphite to the environment are well documented, with the agricultural industry annually introducing phosphite products marketed as biostimulators into the soil system (Gomez-Merino & Trejo-Tellez, 2015). Typically, they are applied as potassium phosphite to soils, which has the benefit over phosphate of its fast P release capability, due to the high mobility of phosphite molecules to plant root systems. This occurs because phosphite has one less oxygen molecule than phosphate, resulting in higher solubility (Gomez-Merino & Trejo-Tellez, 2015; Lovett & Mikkelsen, 2006). In many regions of expected increased winter rainfall, predicted climate change will result in increased phosphite concentrations through chemical reduction of phosphate in saturated soils, resulting from decreases in Eh (Pasek et al., 2014). This means there will be an increase in free phosphite ions that can easily be taken up through plant root systems (Gomez-Merino & Trejo-Tellez, 2015). As discussed above, phosphite is more readily available for plant uptake than phosphate, and therefore is likely to have a positive effect on plant growth throughout periods of extended soil saturation (Lovett & Mikkelsen, 2006).

3.2 | Degradation and fate of (hypo) phosphite compounds in the soil system

The pathways for phosphite and hypophosphite oxidation are relatively well studied for assimilatory phosphite oxidation (APO) (Figueroa & Coates, 2017), alongside dissimilatory phosphite oxidation (DPO) (Schink & Friedrich, 2000). Assimilatory phosphite oxidation is the process in which P from phosphite sources is converted into phosphate, whereas DPO is the biological process by which phosphite acts as an electron donor and energy source for growth and C fixation (Schink & Friedrich, 2000). Both phosphite and hypophosphites have been identified as sole P sources for some common soil microorganisms, such as *E. coli*, *Bacillus sp.*, *Pseudomonas fluorescens*, *Klebsiella aerogenes* and *Erwinia sp.* (Foster et al., 1978; Lauwers & Heinen, 1977; Metcalf & Wanner, 1991). Utilization is preferable under P scarcity, with phosphite and hypophosphite metabolization often linked together in their mechanisms of degradation. Research suggests that hypophosphite oxidation occurs through a phosphite intermediate as the genes involved in phosphite oxidation are the same as those used for growth when hypophosphite is utilized (Metcalf & Wolfe, 1998). With phosphite being up to 1,000 times more soluble than phosphate and the phosphate/phosphite redox potential being low, utilization of phosphite and

hypophosphite is completed efficiently (Pasek, 2008; Roels & Verstraete, 2001; White & Metcalf, 2007).

The microbial process of APO occurs in around 20 microbial isolates (Figueroa & Coates, 2017) and, unlike the phosphonates, a multitude of enzymes are capable of completing the oxidation process through bond breaking and oxygen acquisition (White & MetCalf, 2007). This includes some C-P lyases, but not all, which are known to be the only group of enzymes so far identified for phosphonate breakdown, implying that specific microbes have the ability to utilize multiple forms of reduced P species to access P (Metcalf & Wanner, 1991). It is theorized from the knowledge of the workings of C-P lyase-driven degradation, that the P-H bond undergoes radical cleavage (Kamat, Williams, Dangott, Chakrabarti, & Raushel, 2013).

The process of DPO works by conserving energy through coupling with the reduction of sulphate (SO_4^{2-}), carbon dioxide (CO_2) or nitrate (NO_3^-), which produces energy to drive ATP formation. Dissimilatory phosphite oxidation uses phosphite as its sole electron donor to build up a source of phosphate in the medium (Poehlein, Daniel, Schink, & Simeonova, 2013). The process requires a higher concentration of phosphite than APO and is the likely reason that APO is more commonly used as a method of P accumulation from phosphite/hypophosphite compounds. The DPO process, however, produces more phosphate than APO and is perhaps why areas of phosphite enrichment, such as marine sediments, would prefer DPO pathways to access P (Figueroa & Coates, 2017).

With both APO and DPO occurring under redox conditions only (Sosa, 2018), the conversion of phosphite to phosphate will require highly saturated conditions with low redox, which is unlike the other reduced P compounds, which require oxic environments to push the transformation of reduced P to the fully oxidized phosphate form. In saturated soil systems, it is likely that phosphite will become depleted (Figueroa & Coates, 2017), even though its biogenic existence is dependent on the very same soil conditions.

4 | PHOSPHINES AND THE SOIL SYSTEM

Although considered negligible in the environment, it is suggested that up to 10% of the global P flux is attributed to phosphine release into the atmosphere (Morton & Edwards, 2005). The lowest P valence state compounds are known as the phosphines, with a P oxidation state of -3 . Phosphines are primarily volatile compounds that are released under biogenic conditions where an environment is highly reducing (Niu et al., 2013), such as

waterlogged soil systems. Phosphine (PH_3) can also be matrix-bound within soils and sediments, typically increasing in concentration with depth due to increasing anaerobiosis and lowered redox (Ding et al., 2005; Gassmann, 1994; Yu & Song, 2003; Han et al., 2011b). Pure phosphine gas is odourless and colourless, but when produced biogenically in the natural environment it has a garlic-like odour (Lyubimov & Garry, 2010). It is toxic to most living things (Latimer, 1952); however, concentrations detected in our environment are significantly lower than in the human health risk concentration of 1 mg/m^3 (WHO, 1988), with typical trophospheric concentrations at around 1 ng/m^3 (Glindemann, Bergmann, Stottmeister, & Gassmann, 1996).

4.1 | The formation and inputs of phosphine to the soil system

The occurrence of phosphine in the natural environment, as well as its role in the biogeochemical cycling of P, has been in dispute for over half a century due to the poor characterization of its origin (Cao, Liu, Zhuang, & Glindemann, 2000; Mackey and Paytan, 2009). It is understood that phosphine gas is formed through the breakdown of alkali metal or alkali earth metal phosphides in soil systems with the addition of water, which comprises several chemical reactions (Mackey and Paytan, 2009). Phosphine gas release is focused around areas of organic P abundance, such as wetlands, slurries and marshlands, and around decaying matter (Eismann, Glindemann, Bergmann, & Kuschik, 1997; Han et al., 2010). Reducing conditions are a key factor for natural phosphine release from soils, as it is likely to be formed through the reduction of phosphate upon acceptance of electrons from donor species, such as glucose, starch, methanol and sodium acetate (Cao et al., 2017). This explains why anaerobic soils and other environments with these conditions have been identified as areas of high phosphine gas release (Devai & Delaune, 1995; Glindemann et al., 1996).

Matrix-bound phosphine is present in soils at increasing concentration with depth (Gassmann, 1994). It has been reported that matrix-bound phosphine is promoted at low pH; this is likely to be a result of acidic bio-corrosion of metal particles or of metal phosphides (Ding et al., 2005). Research conducted by Yu and Song (2003) demonstrated a strong correlation (r^2 0.82) between organic P and matrix-bound phosphine concentrations. Preliminary investigations have indicated that phosphine content is positively correlated with total anaerobic microorganisms, organic phosphate compound-dissolving bacteria, denitrifying bacteria, and the activities of alkaline phosphatase and dehydrogenase. An example is

manure fermentation processes, such as those induced by anaerobic microbial metabolism, which produces measurable phosphine release (Eismann et al., 1997). The strong correlation between highly anaerobic conditions and phosphine gas production (Glindemann et al., 1996; Han et al., 2010) suggests that as soils become increasingly waterlogged under climate change, phosphine production is likely to increase.

The agricultural industry is the largest producer of anthropogenically produced phosphine globally, with 9,800 t of phosphine fumigant products per year being manufactured (Degesch America, Inc., personal communication, 2002). Its primary use is as an agricultural fumigant, widely used for its effective disinfestation of stored grains (Tyler, Taylor, & Rees, 1983), often in the form of magnesium, aluminum or zinc phosphide pellets, which release phosphine upon contact with atmospheric moisture. Alternatively, the fumigant can be applied directly as phosphine gas to crops (Gurusinghe, 2014). This market is expected to grow rapidly due to climate change, with increases in insect pest populations expected. A compound annual growth rate in sales of 5.31% is expected to occur up until the year 2025 (Verified Market Research, 2020).

With the consumption of phosphine in the agricultural industry growing, the predicted IPCC increase in annual rainfall is likely to bring with it an increased deposition of phosphine-derived phosphate from the atmosphere as phosphine gas has a relatively short half-life. Depending on the type of fumigant used, a fumigant that has not had time to convert to other P forms may have implications for phosphine fluxes to saturated soils from the atmosphere. Eismann et al. (1997) reported that soils act as sinks to phosphine gas when in the presence of the oxidized Fe(III) form, but not in the presence of Fe(II). However, flux rates remain unchanged in both aerobic and anaerobic sites, implying that climate change will not directly affect the ability of soils to act as phosphine sinks. With phosphine concentrations likely to increase over the coming years due to increased use in agriculture, alongside a suspected sharp rise in Fe(III) soil concentrations in summer months as Fe(II) is easily oxidized, it is likely that dry soils will act as a successful sink of phosphine gas, thus leading to a general increase in soil/matrix-bound phosphine concentration.

4.2 | Degradation and fate of phosphine compounds in the soil system

Unlike other reduced P compounds, phosphine is not biologically accessible and is toxic to both microorganisms and plants (Glindemann, Edwards, & Morgenstern, 2005). Matrix-bound phosphine is liberated into the toxic gaseous form through either acid (typically H_2SO_4 or

HCl) or alkaline (typically NaOH) digestion, as proven in laboratory experiments (Han et al., 2010). Alternatively, the acid or alkaline digestion will hydrolyze non-volatile solid phosphides located readily in soils as phosphine gas (Glindemann et al., 2005).

Gaseous phosphine release from rice paddy fields is higher during the evening, when compared to concentration fluxes measured during the daytime (Gassmann and Glindemann, 1993); this is explained purely by the autoxidation of phosphine in the atmosphere. During evening/night-time hours UV levels are reduced, thus PH_3 is not autoxidable and can accumulate and disperse. During the daytime the UV light induces cleavage of PH_3 through the reaction $\text{PH}_3 \rightarrow \text{H} + \text{PH}_2$, with the oxidation of these radicals into soluble phosphate (Gassmann and Glindemann, 1993). Due to phosphine's high vapour pressure and high Henry's Law Constant, phosphine near the soil surface diffuses into the atmosphere, where it degrades (Frank & Rippen, 1987).

Autoxidation is rapid and phosphine gas does not persist in the atmosphere for long (Mackey and Paytan, 2009). As a highly reactive compound, it reacts with hydroxyl radicals in the air at the rapid rate of $1.5 \times 10^{-11} \text{ cm}^3/\text{mol}/\text{sec}$, meaning that in conditions with a typical concentration of hydroxyl radicals, the half-life of phosphine is 28 h (Gurusinghe, 2008). The eventual oxidation products from this process are P oxyacids and inorganic phosphate, which are then deposited back into the soil system through rainfall, closing the reduced P cycle (Gurusinghe, 2008). Within the atmosphere, upon exiting the soil system, phosphine also can compete with other greenhouse gases such as CO_2 and CH_4 for the acceptance of the hydroxyl radicals, consequently having a coupled greenhouse effect and indirectly contributing to the deterioration of the ozone layer (Han, Zhuang, Liu, & Glindemann, 2000).

Based on the knowledge that autoxidation is common for phosphine that persists in the atmosphere, if it is unable to find a sink then it is likely that soils will see an increase in phosphate deposition as mean rainfall increases for the autumn/winter months. This is demonstrated within the N cycle, where heavy rainfall increases the deposition of N from previously gaseous forms (Hornung & Langan, 1999). Further to this, wetland soils are known to be a common source of phosphine gas (Eismann et al., 1997; Han et al., 2010, Han et al., 2011a), thus an increase in phosphine production is likely to follow. With an increase of phosphine production, a proportion will be fixed in the soil, creating an increase of soil phosphine flux from the soil to the atmosphere (Eismann et al., 1997). Positive phosphine emission flux is also increased with the addition of phosphate to a system (Devai & Delaune, 1995), so there is an expectation that as soil phosphate levels increase as a result

of climate change, residual soil phosphate will further encourage phosphine emission under extreme saturated soil conditions.

5 | ANALYTICAL METHODS AND LIMITATIONS

The limited range of literature about the reduced P compounds is almost entirely due to the analytical limitations that exist for their accurate quantification. Reduced P compounds, although ubiquitous, appear in trace levels within the natural environment. Although only existing in low concentrations, different forms may be significant pathways, but due to their transient nature, we do not appreciate their importance. In addition, much of the natural environment is highly oxidizing and a sample removed from its low redox formative environment may have a tendency to oxidize if unstable. Currently, a range of instrumental techniques exist which allow analysis of these compounds with a high level of accuracy able to quantify typical environmental concentrations. However, these techniques are expensive and specialist, often requiring multiple preparation steps to complete an analysis. Due to the distinctive nature of each of the reduced P forms, each has a different preferred and suitable method for its analysis. It is often the case that a specific form of reduced P is analysed differently depending on the type of environmental sample in which it occurs.

5.1 | Phosphonates

Phosphonates are by far the simplest to analyse and quantify and currently three methods exist for their measurement. The most commonly used method is ^{31}P -NMR, which is well suited to the analysis of environmental samples as the samples are treated in a way that preserves their condition close to collection. ^{31}P -NMR itself has a low detection limit, typically down to 0.8 mg/L (Oromi-Farrus, Minguell, & Canela-Garayoa, 2013), with a chemical shift range of -20 to $+5$ for phosphonates. Recent developments mean that it is now known how to use this method and it is widely accepted as the best method available (Kühl, 2008).

5.2 | (Hypo)phosphites

Ion chromatography followed by inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometry (ICP-OES) analysis are the preferred methods for analysis and quantification of phosphite and hypophosphite compounds (Borza et al., 2014; McDowell et al., 2004).

5.3 | Phosphines

The development of phosphine analytical techniques has continued over many years, with a universally agreed robust methodology using gas chromatography with the addition of a nitrogen-phosphorus detection unit (NPD) (Glindemann et al., 1996, 1998, 2005; Morton, Glindemann, & Edwards, 2003). The NPD add on can detect concentrations as low as picomolar concentrations, which are vital for such a trace gas. The standard method of environmental sampling is through a closed chamber system placed directly over a soil or sediment sample, to prevent gas escaping and allow for a concentration build up prior to analysis. The chambers are always opaque as photodegradation occurs rapidly for phosphine compounds. The sample is collected from the closed chamber with a polypropylene syringe and then passed through a drying tube for the removal of H₂O, CO₂ and H₂S. This sample is inserted into a gas chromatography system (GC), where cryotrap cool the samples to -110°C before entering the injection port. The thermo-ionic NPD is capable of detecting phosphine at concentrations as low as 0.1 ng/m³ (Han et al., 2000; Glindemann and Gassman, 1993).

When considering matrix-bound phosphines, they need to be released from the soil profile prior to GC-NPD analysis, through acid digestion using sulphuric acid (Nowicki, 1978). The soil sample must be extracted under an N atmosphere to preserve its integrity and extraction is carried out at 100°C. The released phosphine is collected directly into a polypropylene syringe ready for GC analysis (Han et al., 2000). This is regarded as the only accurate method for phosphine measurement that currently exists.

6 | GAPS IN KNOWLEDGE AND OPPORTUNITIES FOR FUTURE RESEARCH

A basic understanding exists of the processes that govern the cycling of reduced P compounds, but major gaps exist in our understanding of the biogenic redox processes that transform and cycle P. However, with developments in the methods of reduced P analysis, the difficulties associated with the study of reduced P are being overcome and their relevance is beginning to be recognized. Studies reveal that reduced P is in fact an important source of nutrients for some microorganisms that rely on phosphonate and (hypo)phosphite to complete biological processes (Figuerola & Coates, 2017; Nowack, 2003; Raschke et al., 1994; White & MetCalf, 2007). Despite the knowledge that cycling of reduced P compounds occurs and is important in some ecosystems, there is still a lack of knowledge on how P redox biochemistry impacts P cycling in soils.

The cycling of chemically reduced forms of P, has the potential to influence a large amount of soil processes, especially in a changing soil environment. Although chemically reduced P compounds are often found only in small concentrations, this is likely in part to be due to the difficulties in measuring and quantifying them as outlined above, but also due to their often transient nature, and in many cases their overall rates of production and role in the P cycle in soils could be much higher than currently considered. Climate change poses many questions about the future of our soils globally, with changes to P cycling undoubtedly a huge cause for concern (Ockenden et al., 2017). The predicted increase in patterns of drought followed by flooding in many regions may promote phosphate release that would otherwise be trapped in soils, aiding plant growth in some low-P soils (Bunemann et al., 2013; Forber et al., 2017), but in other soils these weather patterns may have more negative impacts (Bunemann et al., 2013). The processes involved in the cycling of reduced P compounds are not usually taken into account when theorizing how climate change will impact our soils, but their behaviour under different soil conditions provides sources and sinks of P that are not accounted for.

In summary, in regions where climate change results in increases in soil saturation levels, reduced P compounds will have an impact not only on an increased release of phosphate to soils, but also on the plant ecosystems associated with those soils through mineralization processes and P availability (Table 2). During periods of drought, the impacts of reduced P forms are predicted to be negligible, but the soil biochemical changes that occur during periods of flooding will have a secondary impact on soils during periods of drought. External influences will impact heavily on this as agricultural consumer markets develop. The quantity of chemically reduced P compounds entering soils will drive microbial processes to cycle some synthetic compounds through the biogenic P utilization methods described throughout this review.

Although we review changes that might be observed through the effects of climate change within Europe and

TABLE 2 Predictions of the changes in reduced P prevalence in soils under the changing climate conditions of prolonged drought and saturation.

Phosphorus group	Predicted prevalence in soils under saturated conditions	Predicted prevalence in soils under drought conditions
Phosphate	Increased	Increased
Phosphonate	Increased	Decreased
(Hypo)phosphite	Increased	Decreased
Phosphine	Increased	Decreased

other temperate northern hemisphere climates, a full quantification of chemically reduced P within soils has not been conducted due to lack of data and difficulties in measurement and it is therefore difficult to predict how much of an impact reduced P cycling will have on soil health. However, the world's soils are changing, and with a prediction that heavy precipitation events will increase by up to 24% and decrease by 20% during droughts (Fischer et al., 2014), soil environment alterations are expected to be drastic (Green et al., 2019). With so many issues surrounding the future of P in soils, it is important to focus on the developments in the reduced P sector, not only regarding alternative ways of cycling P through microorganisms and plant systems, but also to account for the chemical changes the available forms of phosphate are likely to undergo. This will allow for improved accuracy in modelling the true impact climate change will have on P in soils.

ACKNOWLEDGEMENTS

This work was supported by the BBSRC and NERC [grant number NE-M009106-1] through the Soils Training and Research Studentships (STARS) Centre for Doctoral Training, Elemental digest systems Limited and the UK Biotechnology and Biological Sciences Research Council (BBS/E/C/000I0310 and BBS/E/C/000I0320).

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

AUTHOR CONTRIBUTIONS

Anchen Kehler: Investigation; writing-original draft. **Philip Haygarth:** Conceptualization; funding acquisition; project administration; supervision; writing-review & editing. **Federica Tamburini:** Conceptualization; project administration; supervision; writing-review & editing. **Martin Blackwell:** Conceptualization; project administration; supervision; writing-review & editing.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in [repository name e.g. “figshare”] at <http://doi.org/10.1111/ejss.13121>, reference number [reference number].

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How to cite this article: Kehler A, Haygarth P, Tamburini F, Blackwell M. Cycling of reduced phosphorus compounds in soil and potential impacts of climate change. *Eur J Soil Sci*. 2021; 1–21. <https://doi.org/10.1111/ejss.13121>