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CHAPTER TWO

Assessment and Modeling of Soil Available Phosphorus in Sustainable Cropping Systems

Noura Ziadi[*], **Joann K. Whalen**[†], **Aimé J. Messiga**[*], **Christian Morel**[‡]
[*]Agriculture and Agri-Food Canada, Quebec, Canada
[†]Department of Natural Resource Sciences, Macdonald Campus of McGill University, Quebec, Canada
[‡]INRA, UMR 1220, TCEM (INRA-ENITAB), Villenave d'Ornon, France

Contents

Abstract

Phosphorus (P) is one of the most limiting essential nutrients for agricultural crop production. Diminishing global reserves of rock phosphate are expected to reduce supply and increase the cost of mineral P fertilizers, a major concern in regions where low soil available P levels constrain crop production. In other parts of the world, intensive livestock production and agricultural management have resulted in high soil available P concentrations, which contribute to environmental pollution and threaten water quality. The objective of this review was to examine the factors affecting soil available P in agroecosystems. Physicochemical and biological controls on the soil available P, in the context of P biogeochemical cycling, are presented. Agricultural management practices such as crop rotations, tillage, and P fertilizer sources influence the size of the soil available P pool, while environmental conditions such as freezing–thawing and

wetting–drying cycles control the temporal dynamics of this pool. Methods to evaluate soil available P in the laboratory and *in situ* are reviewed. Attention is given to the isotopic dilution method that quantifies fluxes of P ions between soil solid phase and soil solution, which can be combined with the Freundlich kinetic equation to describe diffusive soil P transfer, leading to the development of a process-based mass-balance model to assess soil available P. This model has potential to advance scientific understanding about soil available P dynamics for better decision making about P fertilization and agroenvironmental management in sustainable cropping systems.

1. INTRODUCTION

Phosphorus (P) is the second most essential nutrient for most crops and is required for optimal crop production in agroecosystems. Yet, there are questions about whether we have enough P to sustain future harvests. Forecasts up to 2050 indicate that the land area under crop production would have to increase by 20% to support the demand for food for global population and also assume an increase in P fertilizer consumption; however, the economically available reserves of rock phosphates might be exhausted under this scenario (Zapata and Roy, 2004). A conservative estimate, based on industry data, indicates that the peak in global P extraction could occur by 2033 (Cordell et al., 2009; Jasinski, 2011). "Peak P" is the point at which high quality, highly accessible reserves of rock phosphate are depleted. After this point, the lower quality and difficulty in accessing the remaining phosphate reserves make them uneconomical to mine and process. Given that demand for P fertilizers continues to grow and the supply of P fertilizer is constrained by finite resources, we must be proactive in developing technologies to maximize the fertilizer P use efficiency in agroecosystems of developed and developing countries.

The "4-R" approach (International Plant Nutrition Institute, 2012) and integrated soil fertility management framework (Sanginga and Woolmer, 2009) give excellent guidance on the selection of P fertilizer sources and appropriate agronomic rates, application methods, and timing for specific crops. For instance, sufficient P is required at the very early growth stages of maize (*Zea mays* L.) to maximize yield (Grant et al., 2001). Deficiencies in early P nutrition can affect maize leaf growth (Plénet et al., 2000), leaf emergence, and the number of adventitious nodal roots (Pellerin et al., 2000). Further, early deficiencies in P nutrition cannot be remedied by later P additions (Barry and Miller, 1989). Similar observations for other grain,

vegetable, and horticultural crops are reported in the scientific literature, conference proceedings, and agricultural extension bulletins. Yet, the fertilizer P use efficiency remains relatively low, less than 50% in annually cropped systems and around 20–30% in grasslands (Richardson et al., 2011). Since P fertilizers remain a relatively expensive input for farmers in developing countries, integrated soil fertility management approaches that combine P fertilizers with locally available organic materials can be helpful in improving crop P nutrition due to positive interactions between soil, biological, chemical, and physical properties (Sanginga and Woolmer, 2009). In addition, P-efficient plants can also improve the fertilizer P use efficiency in agroecosystems (Richardson et al., 2011).

The purpose of this review was to provide an overview of factors that influence soil available P, since it is essential that P be present in a plant-available form that can diffuse to roots and be absorbed by plants. For maximum P use efficiency, the soil available P supply would be synchronized with crop P requirements during the growing season. Yet, interactions with the soil physicochemical matrix and modification of soil reactions due to agricultural management and environmental conditions can reduce the size of the soil available P pool. Analytical methods to assess soil available P are described, and a process-based mass-balance model with potential to predict the evolution of soil available P in cultivated soils is presented.

2. PHOSPHORUS IN AGRICULTURAL SOILS

2.1. Importance of phosphorus in crop production

In crops, P is involved in energy metabolism and biosynthesis of nucleic acids and cell membranes and is required for energy transfer reactions, respiration, and photosynthesis. For optimal plant growth, plants require 0.3–0.5% P in dry matter during vegetative growth. There is a progressive concentration of P as it is absorbed from the soil solution (containing about 0.1 mg P l^{-1}) to the xylem sap (contains about 100 mg P l^{-1}) and accumulates in seeds (up to 4000 mg P kg^{-1}) (Marschner, 1995). Visually, P-deficient plants have less leaf expansion, reduced leaf surface area, and fewer leaves, which highlights the need for adequate P nutrition to sustain plant growth and functions.

Plant tissue P is present as nucleic acids and nucleotides, phosphorylated intermediates of energy metabolism, and membrane phospholipids. In seeds, P is stored as phytic acid, also known as phytate or phytin, with values between 0.5% and 5.0% (w/w) in cereals and legumes (Park et al., 2006).

Phytate accounts for 50–80% of total P in many seeds and is present as a mixed salt with cations such as potassium, magnesium, manganese, iron, and zinc. Phytate also acts as a reservoir of inositol phosphate and controls inorganic phosphate homeostasis in developing seeds and seedlings (Lott et al., 1995).

2.2. Phosphorus cycle in the plant–soil system

The P cycle in a cropped field is characterized by transformations among several P chemical forms. Pool sizes of these P forms vary by five to six orders of magnitude. Soil P compounds can be categorized as follows: (1) soluble inorganic and organic P in the soil solution; (2) weakly adsorbed (labile) inorganic and organic P; (3) insoluble P, which is associated with Ca in calcareous and alkaline soils or bound to Fe and Al in acidic soils; (4) P strongly adsorbed and/or occluded by hydrous oxides of Fe and Al; and (5) insoluble organic P in undecomposed plant, animal, and microbial residues within the soil organic matter (SOM) (Stevenson and Cole, 1999). In the plow layer of cropped soils, about 70% of the total P is present in inorganic forms, more than 20% is in organic forms, and only few percentages are in the soil microbial biomass (bacteria and fungi) (Grant et al., 2005).

A simplified P cycle is presented in Fig. 2.1, showing the major P pools in the soil–plant system, P exports and imports, and internal transformations under field crops in a developed country. On average, maize crops exported 30 kg P ha^{-1} year^{-1}, of which two-thirds are exported out of the field (20 kg P ha^{-1} year^{-1}) and the remainder are returned to the soil with crop residues (aerial parts $=$ 5 kg P ha^{-1} year^{-1} and roots $=$ 5 kg P ha^{-1} year^{-1}). Sources and amounts of P imported to typical field crops are mineral fertilizers (12 kg P ha^{-1} year^{-1}), animal manure (14 kg P ha^{-1} year^{-1}), urban sewage sludge (0.5 kg P ha^{-1} year^{-1}), urban composts (0.05 kg P ha^{-1} year^{-1}), P in seeds (0.1 kg P ha^{-1} year^{-1}), and atmospheric deposition (0–0.5 kg P ha^{-1} year^{-1}). Transport processes such as runoff and subsurface flow can account for the loss of 0.05–2.5 kg P ha^{-1} year^{-1}, while leaching and migration of sediments containing P toward the subsoil (0.5 kg P ha^{-1} year^{-1}) can also represent significant losses of P from the plough layer.

Agricultural producers rely on P imports from various sources to increase crop production, but the amounts required vary from field to field because of heterogeneity in the inherent P fertility of agricultural soils due to parent material, soil types, and agricultural practices. As a result, the concentration of P in the plow layer (0–20 cm depth) of a typical maize field may vary from
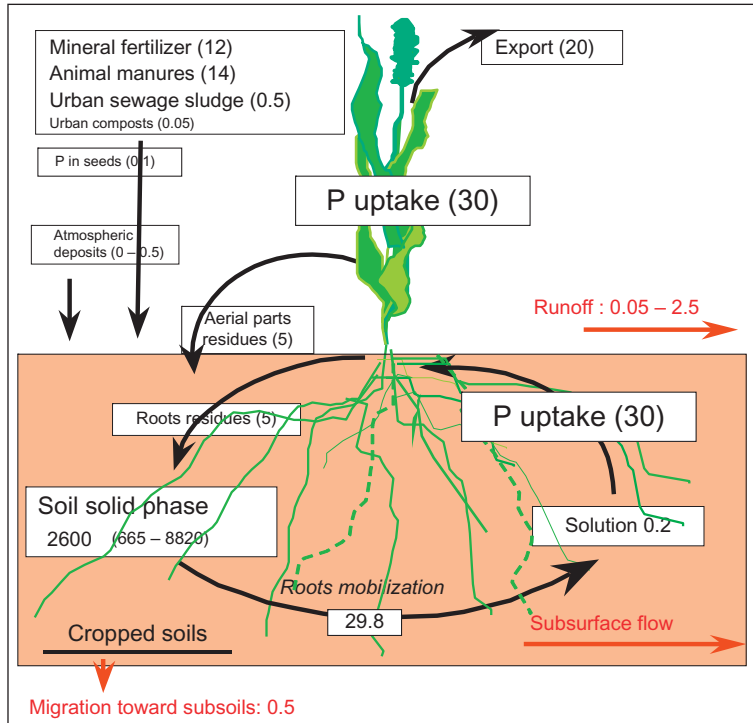
Figure 2.1 Annual flows and compartments of P involved in the P cycle in a temperate agroecosystem under maize (*Zea mays* L.) production. Data (in kg P ha^{-1}) are averages obtained from the scientific literature of fields that were conventionally tilled and fertilized with mineral P fertilizer in the long term (decades) in temperate climates. *Adapted from Morel (2002).*

100 to 2000 mg P kg^{-1} soil, representing about 665–8820 kg P ha^{-1} depending on the soil bulk density (Grant et al., 2005). Yet, the soil solution only contains about 0.2 mg P l^{-1}, meaning that most of the soluble P taken up by crops originates from the soil solid phase (Grant et al., 2005). On average, 29.8 kg P ha^{-1} year^{-1} is mobilized from the soil solid phase to replenish the soil solution as it is depleted by plant P uptake; this is supported by isotope dilution studies, showing that the isotopically exchangeable P ion is a good approximation of the soil available P pool (Morel and Fardeau, 1991; Morel and Plenchette, 1994; Zapata and Roy, 2004). Diffusion is the dominant mechanism whereby exchangeable P moves between the soil solid phase and the soil solution, across a

concentration gradient (Barber, 1995). Other possible reactions that mobilize P during the growing season are weathering, dissolution, desorption, and mineralization.

The P content is about 10 times greater in the plow layer than in the subsoil due to regular (generally annual) applications of P fertilizers and animal manure as well as the recycling of crop residues (aerial parts and roots). Phosphorus losses through runoff and leaching are relatively small, compared to the amount of P imported or recycled in the plow layer, in part, because soil minerals have strong P-binding capacity. Biological activity contributes to P solubilization through mineralization, weathering, and other physicochemical reactions so that the plow layer is the major source of soil available P for crops. However, the subsoil can also contribute soluble P for uptake by growing plants when P is translocated from the subsoil to the plow layer by roots and other microorganisms (Richardson et al., 2011; Watson and Matthews, 2008).

2.3. Definition of soil available phosphorus

Soil available P is the fraction of total P in soil that is readily available for absorption by plant roots. It is estimated in the laboratory using extracting solutions that rely on the dual contact time between the soil and the extracting solution (kinetic reaction) to capture inorganic P from the soil solution and the soil solid phase during a predetermined period of time (minutes to hours). The dominant inorganic P form extracted from soil is orthophosphate (HPO_4^{2-} and $H_2PO_4^-$ ions) that can be absorbed directly by plant and microbial cells. Polyphosphates (including pyrophosphate) are another form of inorganic P that may be present in soils, of biological origin, and generally in low concentrations relative to orthophosphate (Condron et al., 2005; Fardeau et al., 1988).

The definition of soil available P given above is accurate for P-rich soils (generally in developed countries) where years of inorganic P fertilizer applications result in large amounts of inorganic P associated with the soil solid phase and accounting for most of plant P nutrition. In regions of developed countries where intensive livestock production occurs, disposal of animal manure on a relatively small land base has led to massive accumulation of soil available P, as well as more SOM and a buildup of organic P compounds. The soil available P in such soils is probably a combination of inorganic P derived from the soil solid phase and P mineralized from the breakdown of soil organic P compounds. In the P-depleted soils of

developing countries where historical P fertilizer applications were limited, crop P nutrition relies more on other soil processes such as mineralization of SOM, weathering, and dissolution of P-bearing minerals to replenish the P ions in soil solution. The shortcomings of our definition of soil available P for heavily manured soils and soils in developing countries are demonstrated by the failure of models relying on sorption/desorption processes to characterize soil available P and predict crop P acquisition in P-poor soils (Hinsinger, 2001; Mollier et al., 2008). Further research is needed to account for the role of organic P (Achat et al., 2010; Oehl et al., 2001), other organic compounds (Giles et al., 2011; McDowell, 2003; McDowell et al., 2008; Turner et al., 2003, 2005), and interactions between the plant roots and the rhizosphere (Richardson et al., 2011) on the soil available P in such agroecosystems.

2.4. Factors affecting soil available phosphorus

The major constraint in achieving adequate P nutrition in crops arises from the fact that soil available P diffuses slowly through the soil solution toward roots, complicated by the fact that migrating P ions are susceptible to chemical fixation in most agricultural soils. These processes result in low-P use efficiency of mineral fertilizers applied to cultivated soils, where less than 50% of the fertilizer P is absorbed by crops during a growing season. This section describes how soil available P is affected by soil properties (chemical, physical, and biological), agricultural management practices, and environmental conditions.

2.4.1 Soil properties

Soil pH is the major factor affecting the speciation and availability of P ions in cultivated soils (Lindsay, 1979). At soil pH below 7.2, the dominant orthophosphate ion species in soil solution is $H_2PO_4^-$, while HPO_4^{2-} is the dominant ion in soil solution at pH greater than 7.2. The solubility of P ions in cultivated soils is affected by the presence of anions that compete for ligand-exchange reactions and metals (Ca, Fe, and Al) that coprecipitate P ions (Hinsinger, 2001). The binding affinity between P and other anions and metals in soil solution and on soil surfaces is also controlled by pH and affects the soil available P concentration.

Soil pH fluctuates when plants and other biota absorb ions from the soil solution. For example, the cation–anion uptake ratios alter soil pH in the rhizosphere because cation uptake results in H^+ released from the root

surface, whereas anion uptake is accompanied by release of OH^- to maintain electrical neutrality. Microbial reactions also generate H^+ ions. For example, ammonium N applied to agricultural soils is often transformed to nitrate by ammonia oxidizers and nitrifiers, which produces 2 mol of H^+ for every mole of nitrate (NO_3^-) released by the microbially mediated nitrification reaction. While NO_3^- absorption by plant roots is accompanied by the release of OH^- into the rhizosphere by root cells, which partially neutralizes excess acidity from nitrification, the net effect is soil acidification when more NO_3^- is produced than absorbed by plant roots or when NO_3^- is lost from the rhizosphere through leaching. One consequence of soil acidification is an increase in soluble Al and Fe ions that may precipitate with $H_2PO_4^-$ and HPO_4^{2-}, decreasing soil available P to plants (Arai and Sparks, 2007; Bolan et al., 2003; Stroia et al., 2011; Tran et al., 1988).

Parent material is important in the soil P cycle because the weathering of primary minerals contributes to the soil available P pool (Cross and Schlesinger, 1995). For example, in Aridisols with low SOM and high pH, weathering of calcium carbonate minerals is the primary geochemical reservoir of soil available P (Lindsay, 1979). In highly weathered and acidic Ultisols and Oxisols, the presence of sesquioxides results in greater chemical fixation of P and decreases soil available P (Sanchez et al., 1982; Sollins et al., 1988). In young and slightly weathered soils, hydroxyapatite is the major inorganic reservoir of soil available P, whereas in moderately weathered soils, soil available P is derived mostly from organic compounds or secondary clay minerals.

Soil available P is affected by soil physical properties such as texture. For soils with the same P saturation index, fine-textured (>300 g clay kg^{-1}) and gleyed soils tended to release more soil available P with water extraction than coarse-textured (≤300 g clay kg^{-1}) and podzolized soils (Pellerin et al., 2006). Soil available P is also influenced by soil structure due to interactions between soluble P and the soil solid phase associated with soil aggregates and SOM (Green et al., 2005, 2006; Messiga et al., 2011; Wright, 2009).

Biological controls on soil available P are evident in the rhizosphere, due to root-induced effects on soil physicochemical properties and interactions with soil microflora. Modification of root morphology and architecture to promote better exploration of the P-rich topsoil enhances P acquisition (Lynch and Brown, 2001). Such traits are found among maize, bean (*Phaseolus vulgaris* L.), wheat (*Triticum aestivum* L.), and soybean (*Glycine max* (L.) Merr) and, in many cases, resulted in a significant increase of P uptake (Bonser et al., 1996; Manske et al., 2000).

Chemicals released from the rhizosphere such as protons, carboxylates, phosphatases, and phytases are important in solubilizing P from sparingly available pools in soil (Marschner, 1995; Shen et al., 2011). The exudation of organic anions is closely linked with plant species that produce clusters of rootlets with abundant root hairs (Lambers et al., 2010). This root trait allows plants to effectively mine P from severely weathered soils where recycling of P from above-ground litter and below-ground root turnover was the sole P source and from highly weathered and strongly P-sorbing soils with low concentrations of soil available P (Lambers et al., 2006). Clustered roots are effective for capturing P ions mobilized when organic acids induce the dissolution of P ions from insoluble precipitates like $Ca_3(PO_4)_2$ or $AlPO_4$ (Zhang et al., 1997). Cluster roots are common in plants of the Proteaceae, Cyperaceae, and Restionaceae families, but there are some examples among agricultural crops. White lupin (*Lupinus albus*) in the family Fabaceae develops cluster roots when grown on young volcanic soils with low concentrations of soil available P, such as in Chile (Huyghe, 1997). The cluster root trait is generally inhibited as the soil available P concentration increases (Redell et al., 1997), and therefore, this trait has limited applicability to improve P fertilizer use efficiency, even on agricultural soils with high P-sorbing capacity (Simpson et al., 2011).

Mycorrhizal symbiosis produces a dense hyphal network and extends the absorptive surface of plant roots, effectively reducing the distance that P ions must diffuse to reach the rhizosphere. About 74% of angiosperms form symbiotic associations with arbuscular mycorrhizal fungi (Brundrett, 2009), and all agricultural crops are angiosperms. For most agricultural plants, mycorrhizal association is the rule rather than exception whereby water, P, and other nutrients are transferred through the mycorrhizal mycelium to plants and, in return, the fungi receives carbohydrates from the host plant. Isotopic dilution studies provide evidence that mycorrhizal and nonmycorrhizal plants rely on the same P source from soil (Bolan, 1991; Yao et al., 2001). However, some authors indicate that arbuscular mycorrhizal fungi enhance access to P compounds that normally would be sparingly soluble or insoluble to plants (Koide and Kabir, 2000; Tawaraya et al., 2006). The main difference between mycorrhizal and nonmycorrhizal plants is the larger soil volume explored by mycorrhizal plants permits greater P uptake through physical interception. Studies also showed that within the same genotype, plants with branched root systems, very fine roots, and long hairs tend to show relatively little improvement in growth when they are colonized by mycorrhizal fungi, even when soil available P is low

(Schweiger et al., 1995). In contrast, genotypes with constrained root systems exhibit greater P uptake with mycorrhiza, compared to non-mycorrhizal plants, especially in soils with low soil available P (Thomson, 1987). The beneficial effects of mycorrhizal symbiosis for crop P uptake can be very important for agricultural sustainability.

Soil microorganisms such as P-solubilizing bacteria and fungi also affect soil available P through direct solubilization of P from the soil solid phase (Richardson et al., 2009). The ability of these free-living microorganisms to mobilize P ions has mainly been studied in laboratories media with sparingly soluble Ca phosphate, rock phosphate containing hydroxy- and fluor-apatites, and Fe and Al phosphates such as strengite and variscite. Enhanced growth and P nutrition of plants inoculated with P-solubilizing microorganisms were observed in controlled studies (Whitelaw, 2000) but are more difficult to demonstrate cropped field soils (Wakelin et al., 2006; Whitelaw et al., 1997). The lack of consistent response to P-solubilizing microorganisms highlights a research gap regarding the mechanisms whereby free-living microorganisms influence soil available P. Isotopic dilution studies of P mobilization from sparingly soluble or insoluble soil P pools and the subsequent uptake by plant roots could prove helpful in understanding this phenomenon. Of course, these observations do not contradict the well–established role of microorganisms in degrading SOM and mineralizing P ions from organic compounds (Conyers and Moody, 2009; Cornish, 2009), a biochemically driven reaction that increases the soil available P concentration.

2.4.2 Agricultural management

Soil available P is affected by agricultural management practices like crop rotation, tillage, and fertilization. In this review, we examine these factors individually, while realizing that producers will develop a cropping system with specific crop rotations, tillage, and fertilizer sources according to their production goals and economic considerations. There is, however, relatively little information in the scientific literature where divergent cropping systems are compared since most agronomic trials are set up to evaluate the treatment effects separately, or in simple combinations. More complex agronomic trials or on-farm research experiments could be designed to validate the effect of agricultural management on soil available P.

Crops varying in root systems explore different layers of the soil profile. Residues from different crops vary in their mineralization rates and therefore contribute differently to the formation of SOM. Temporal and spatial

arrangements of crops in the rotation also affect soil available P (Karazawa and Tabeke, 2012). As discussed earlier, growing mycorrhizal plants in fields with low soil available P improves crop P nutrition. Another benefit of growing mycorrhizal host plants is the maintenance of a large population of indigenous mycorrhizal fungi, which facilitates the colonization of subsequent crops and their P nutrition. Greater P uptake and higher soil available P concentration in the plow layer of arable soils under a cereal–legume rotation system (Kabengi et al., 2003; Villamil et al., 2006) were attributed to maintaining the indigenous population of mycorrhizal fungi, since both crops were mycorrhizal host plants. Introducing nonhost plants in the rotation to break pest cycles associated with continuous cropping reduces the population of mycorrhizal fungi and can be detrimental for mycorrhizal colonization of subsequent crops and their P nutrition. An alternative is to intercrop mycorrhizal host plants with nonhost plants to increase indigenous mycorrhizal fungal populations, P uptake, and productivity of subsequent crops (Karazawa and Tabeke, 2012). Zheng et al. (2002) showed that inorganic and organic P-NaHCO$_3$ fractions, which are considered part of the soil available P pool, are increased by crop rotations. However, other studies showed a decrease in soil available P in cereal–legume rotations (Campbell et al., 1995; Riedel et al., 1998; Soon and Arshad, 1996). These results highlight the need for further research to fully understand how site-specific abiotic and biotic factors controlling soil available P are modified by choices of crops in a particular sequence.

Tillage involves plowing and harrowing, which mix P imported in amendments and P recycled from crop residues throughout the plow layer (typically the top 10–20 cm) of agricultural soils. When producers shift to conservation tillage or no-till systems, soil mixing and disturbance occur in discrete zones (e.g., in the tilled seedbed of a zone tillage system or in the planted row and fertilizer bands of a no-till system). Consequently, no-till systems are characterized by P stratification with depth, with high concentrations of soil available P in the top few centimeters of topsoil and decreasing concentrations lower in the soil profile (Cade-Menun et al., 2010; Messiga et al., 2012a). Phosphorus accumulation at the soil surface is the result of minimal mixing of surface-applied fertilizers and crop residues, limited vertical movement of P in most soils, and transfer of P from deep-soil layers to shallow layers through crop nutrient uptake, most of which becomes concentrated in residues left on the soil surface (Borges and Mallarino, 2000). Phosphorus stratification is of concern because lower soil available P concentrations at depth in the rooting zone may reduce crop

yields (Lupwayi et al., 2006), whereas high soil available P concentrations near the soil surface increase the risk of dissolved P loss in surface runoff (Sharpley and Smith, 1994).

Land under permanent grassland exhibits the same type of P stratification as no-till systems because fertilizers and crop residues are applied to the soil surface and there is limited mixing with topsoil (Blake et al., 1999; Malhi et al., 2003; Watson and Matthews, 2008). Soil available P accumulation was reported in a 10-year study of P balances on grazed grassland swards in Northern Ireland, where there was a gain of 17 mg P kg^{-1} $year^{-1}$ in the 0- to 5-cm soil layer and only 2 mg P kg^{-1} $year^{-1}$ in the 5- to 10 cm soil layer (Watson and Matthews, 2008). In a long-term grazed grassland in south-west England, the soil available P (Olsen P) concentration was 10-fold greater in the 0- to 2-cm soil layer than at depths below 45 cm (Haygarth et al., 1998). Fertilizer recommendations for grasslands in many European countries are based on the soil available P concentration in the 5- to 10-cm soil layer (Stroia et al., 2011), which should account for P accumulation at the soil surface for better protection of environmental quality.

Phosphorus fertilizer sources include mineral and organic fertilizers. Mineral P fertilizers are derived from rock phosphates, generally apatite. Morocco/Western Sahara possesses 70% of world reserves of apatite (estimated at 71,000 million metric tons), followed by Iraq (8%) and China (5%). Globally, the top producers of mined rock phosphates in 2011 were China (38%), United States (15%), Morocco (14%), and Russia (6%) (United States Geological Survey, 2012). Since rock phosphate is sparingly soluble, it is reacted with sulfuric acid to produce concentrated phosphoric acid for the formulation of water-soluble P fertilizer. Mineral P fertilizer sources include dry granulated fertilizers (simple superphosphate, triple super phosphate, diammonium phosphate, and monoammonium phosphate) and fluid fertilizers (superphosphoric acid, polyphosphates, ammonium polyphosphates, and suspensions). When applied to soil, mineral P fertilizers contribute orthophosphate ions directly to the soil solution, thereby increasing the soil available P concentration. Since the efficiency of mineral P fertilizer is fairly low (20–50% of the P applied is absorbed by crops during the growing season; Richardson et al., 2011) and most of the unused P is retained in the soil solid phase, repeated application of mineral P fertilizer increases the soil available P concentration.

Organic P fertilizers comprise a diverse array of organic materials that are fresh or composted before they are applied to soil. Farmyard manure, vegetable residue, and industrial by-products such as paper mill biosolids are potential sources of organic P fertilizer for agriculture. Fresh swine manure

contains more total P and soluble inorganic P on an equivalent mass basis than most other farmyard manures (Barnett, 1994; Peperzak et al., 1959). Liquid swine manure gave the greatest increase in soil available P (Mehlich–3 P) of the organic P fertilizers applied for silage maize production in eastern Canada (Gagnon et al., 2012). Another organic P fertilizer is paper mill bio-solids, the solid residues generated from pulp and paper mills that are rich in organic matter (cellulose, hemicellulose, and lignin). The effect of fresh paper biosolids application on soil available P is variable and affected by the amount applied, frequency of application, crops grown, and the chem-ical composition (total P and C:P ratio) of the biosolids (Gagnon and Ziadi, 2004; Gagnon et al., 2010, 2012). After 6 years of repeated paper mill bio-solids application, Fan et al. (2010) reported a significant linear increase of soil available P as measured by anionic exchange membranes. Simard et al. (1998) and Rato Nunes et al. (2008) also reported that the application of paper mill biosolids significantly increased soil available P, owing to the mineralization of organic P associated with the decomposition of the bio-solids. However, Vasconcelos and Cabral (1993) indicated that high appli-cations of combined primary/secondary paper mill biosolids did not have any effect on soil available P due to the high C:P ratio of the biosolids.

Composting is often employed to reduce the total mass and facilitate the handling of organic fertilizers, but it can also alter the chemical fractions of P within the organic material, thereby affecting the contribution to soil available P. Zvomuya et al. (2006) found that mature cattle manure compost contained lower percentages of labile P and higher percentages of nonlabile P (HCl–P) than the original fresh cattle manures. In composted solid urban waste, 30–50% of the total P was in inorganic P forms (extracted by water and $NaHCO_3$) and the remainder was bound in relatively insoluble com-pounds (Frossard et al., 2002). Although Miller et al. (2010) reported an increase of soil available P that exceeded the maximum agronomic limit of 60 mg P kg^{-1} for Alberta (western Canada) following land application of fresh and composted cattle manure, addition of composts with high C: P ratios can reduce soil available P for weeks or months (Cooperband et al., 2002; Frossard et al., 2002; Gagnon and Simard, 1999). This suggests that significant P immobilization may occur in compost–amended soil. Dur-ing a 13-week incubation study using 26 composts (23 on–farm and 6 indus-trial composts), Gagnon and Simard (2003) reported that P was strongly immobilized from week 1 to week 13 in the soils receiving partially com-posted cattle manure on wood bedding. Soil available P (Mehlich–3 P) was greatest with mature dairy manure composts. With time, the immobilized P was released into soil solution through microbial turnover, as there was

an increase in soil available P concentrations in soil amended with poultry litter, vegetable residue, and sheep manure composts after 13 weeks (Gagnon and Simard, 2003).

2.4.3 Environmental conditions

2.4.3.1 Effects of freezing and thawing cycles on soil available phosphorus

Seasonally snow-covered temperate soils are subject to freezing and thawing cycles (FTCs), particularly during years with little accumulated snowfall and during the late winter and early spring periods (Freppaz et al., 2007). The FTCs can stimulate soil mineralization and could therefore be one factor regulating the soil available P concentration in early spring. Lysis of plant cells releases soluble P from plant residue (Bechmann et al., 2005) and other organic compounds (Ron Vaz et al., 1994), with substantial amounts of soil available P (soluble-reactive P, dissolved P) released from alfalfa (Medicago sativa L.) and quackgrass (Agropyron repens L.) residues following an FTC (Roberson et al., 2007; Wendt and Corey, 1980). Timmons et al. (1970) reported that up to 80% of total plant P in bluegrass (Poa pratensis L.) residue was released in a water-soluble form after plant residue underwent various FTCs. Soil organic P is also susceptible to mineralization during FTCs, as intact cores of topsoil collected from no-till and conventional tillage systems released more soil available P (water-extractable P, Mehlich-3 P) with an increase in the number of FTCs (Messiga et al., 2010a). Given the projected increase in mean air temperatures for the coming decades, temperate and cold areas may experience an increasing number of FTCs due to reduced snow cover. This is expected to increase soil available P concentrations in early spring, but whether soluble P would benefit early season crop growth or be lost in runoff and drainage water during the spring thaw remains to be determined.

2.4.3.2 Effects of drying and rewetting cycles on soil available phosphorus

In most agroecosystems, soil water content changes rapidly following rainfall, particularly after high–intensity, short-duration events. The resulting drying and rewetting cycles affect the soil available P concentration. The increase in soil available P during the rewetting phase results from release of organic P from lysed cells of microbial biomass (Turner and Haygarth, 2001). In addition, occluded organic matter from disturbed soil aggregates also releases organic P compounds into soil solution. Mineralization of organic P to inorganic P can increase the soil available P concentration, but the effect may be transient due to chemical fixation or immobilization of P from soil solution. Soil rewetting is accompanied by rapid microbial

growth and respiration, presumably due to new microbial cells utilizing soluble substrates, including soluble organic P compounds that were released during the drying phase. Barrow and Shaw (1980) showed that the effects of a drying event (60 °C) on the soil available P concentration were short–lived, as the soluble P concentration returned to pretreatment levels after 1 day of soil rewetting. There is relatively little information published on how drying and rewetting cycle influences dynamics of soil P pools and the long-term impacts of climate change (more frequent drought or more intense rainfall events, depending on the region) on soil available P concentrations in agroecosystems.

3. SOIL AVAILABLE PHOSPHORUS MEASUREMENTS

The previous sections have defined and explained the factors that affect the soil available P, but how should it be measured? Ideally, agricultural producers would like to be able to predict soil available P throughout the growing season to ensure an adequate supply of P fertilizer, considering the soil properties, agronomic practices, and environmental conditions that control the soil available P concentration in their region. Practically, it is difficult to estimate soil available P during the growing season, but there are a number of laboratory and *in situ* methods giving measurements of soil available P that are well correlated with the P fertilizer requirements of various crops. These will be reviewed in the following sections.

3.1. Laboratory methods for assessing soil available phosphorus

3.1.1 Chemical extraction methods

Chemical extraction methods selectively remove P compounds (generally soluble and weakly adsorbed P compounds) from soil to estimate the P that is available for plants' uptake during a growing season, the soil available P concentration. Extracted P, or soil test P, is calibrated empirically against actual crop uptake or likelihood of response to fertilization (Heckman et al., 2006; Jokela et al., 1998; Maguire et al., 2005; McKenzie et al., 2003; Morel et al., 1992; Saarela, 2002; Simard et al., 1996). At the present time, there is little national or regional emphasis on soil test calibration research, partly because it is perceived academically as lacking originality and as low priority, and there are limited funds to do this work (Heckman et al., 2006). As a consequence, there are dozens of soil test P methods in use around the world (Tables 2.1 and 2.2). In Canada, up to four soil test P methods are used by university and private laboratories,

Table 2.1 Summary of soil test P methods used in Canada and the United States

Country	Province/state	Soil test P method	References
Canada	New Brunswick	Mehlich–3	Mehlich (1984)
	Nova Scotia		
	Prince Edward Island		
	Quebec		
	Manitoba	Olsen	Olsen et al. (1954)
	Ontario		
	Alberta	Kelowna	van Lierop (1988) and Ashworth and Mrazek (1995)
	British Columbia		
	Saskatchewan		
	Newfoundland & Labrador	Bray–2	Bray and Kurtz (1945)
United States	Delaware	Mehlich–3	Sims et al. (2002) and Sharpley et al. (2003)
	Maryland		
	New Hampshire		
	New Jersey		
	Pennsylvania		
	Massachusetts	Morgan	Ketterings et al. (2002)
	New York		
	Rhode Island		
	Connecticut	Modified Morgan	Jokela et al. (1998)
	Maine		
	Rhode Island		
	Vermont		
	Midwestern states	Bray–1	
	North Central states		
	Western states	Olsen	

Table 2.2 Summary of soil test P methods used around the world

Country	Soil test P method	References
Austria	Calcium ammonium acetate	Tunney et al. (2003)
	Double lactate	
	Water extraction	
Belgium	Ammonium lactate	Van Den Bossche et al. (2005)
	Calcium ammonium lactate	
Denmark	Olsen	
Finland	Acid ammonium acetate	Saarela (2002)
France	Dyer	Dyer (1894) and Joret and Hebert (1955)
	Joret Hebert	
	Olsen	
Germany	Calcium ammonium lactate	Tunney et al. (2003) and Vanderdeelen (2002)
	Double lactate	
	Water extraction	
Greece	Bray-2	
	Olsen	
Hungary	Ammonium acetate	
Italy	Olsen	
Ireland	Ammonium acetate	
Netherland	Ammonium acetate	Vanderdeelen (2002)
	Water extraction	
Norway	Ammonium acetate	
Poland	Double lactate	Vanderdeelen (2002)
Romania	Ammonium lactate	
Spain	Bray-2	
	Olsen	
Sweden	Ammonium lactate	

Table 2.2 Summary of soil test P methods used around the world—cont'd

Country	Soil test P method	References
Switzerland	Adapted method of Cottenie	Cottenie et al. (1982)
UK	Olsen	Olsen et al. (1954)
Latin America	Bray-1	Ghosh et al. (2001) and da Silva et al. (2010)
	Morgan	
	Olsen	
Asia	Bray-1	Song et al. (2011)
	Mehlich-3	
	Morgan	
	Olsen	
Africa	Bray-1	Buresh et al. (1997)
	Mehlich-3	
	Morgan	
	Olsen	
Australia	Colwell	Colwell (1963) and McIvor et al. (2011)
	Bray-2	
New Zealand	Bray-2	

including the Mehlich-3, Olsen, Kelowna, and Bray-2 methods. In the United States, five soil test P methods are common: Mehlich-3, Olsen, Bray-1, Morgan, and modified Morgan methods. Across Europe, up to 11 methods are used by analytical laboratories, while in Africa, Asia, and Latin America, the main methods used are Bray-1, Mehlich-3, and Olsen. In Australia and New Zealand, the Olsen, Colwell, and Bray-1 methods are the standard for measuring soil test P. Table 2.3 describes some characteristics of the most widely used soil test methods.

3.1.2 Water extraction methods

Chemical extractants are widely used to assess soil test P, but have certain drawbacks. Not only do chemical extractants remove P ions present in soil solution, but they also react and dissolve some P ions associated with the soil

Table 2.3 Selected characteristics of soil test P methods widely used in Canada, the United States, and around the world

Methods	Extractant	pH-extracting solution	Volume-to-mass ratio	Soil type	Soil pH	Minerals	Shaking time	Comments
Bray 1	0.5 N HCl+1 N NH$_4$F	3.0	7:1	Acidic; slightly acidic to slightly alkaline	<6.0; 6.0–7.2	Al-P, Fe-P, Mn-P, Mg-P, Ca-P	1 min	Extracts P only
Mehlich 1	0.05 N HCl+0.025 N H$_2$SO$_4$	1.2	4:1	Acidic; slightly acidic to slightly alkaline	<6.0; 6.0–7.2	Al-P, Fe-P, Mn-P, Mg-P, Ca-P	5 min	Multielement extracting solution
Mehlich 3	0.015 N NH$_4$F+0.025 N NH$_4$NO$_3$+0.2 N CH$_3$COOH+0.013 N HNO$_3$+0.001 N EDTA	2.3	10:1	Acidic; slightly acidic to slightly alkaline	<6.0; 6.0–7.2	Al-P, Fe-P, Mn-P, Mg-P, Ca-P	5 min	Multielement extracting solution
Olsen	0.5 M NaHCO$_3$	8.5	20:1	Slightly acidic to slightly alkaline; alkaline, calcareous	<6.0; 6.0–7.2; >7.2	Al-P, Fe-P, Mn-P, Mg-P, Ca-P	30 min	Extracts P only

Continued

Table 2.3 Selected characteristics of soil test P methods widely used in Canada, the United States, and around the world—cont'd

Methods	Extractant	pH-extracting solution	Volume-to-mass ratio	Soil type	Soil pH	Minerals	Shaking time	Comments
Ammonium acetate	1 N NH$_4$OAC	7	20:1	Alkaline; calcareous	<6.0; 6.0–7.2	Mg-P, Ca-P	30 min	Multielement extracting solution
Water		7	10:1; 60:1	Acidic; slightly acidic to slightly alkaline; alkaline; calcareous	<6.0; 6.0–7.2	Al-P, Fe-P, Mn-P, Mg-P, Ca-P	24 h	Extracts dissolved P only

solid phase, without differentiating between the two phases. In addition, chemical extractants can be either more acidic or more alkaline than the soil solution and, therefore, could extract P ions from the solid phase that are not likely to be available to plants under field conditions. These reactions mean that chemical extractions can overestimate soil available P. Distilled water as an extractant avoids these problems (Pote et al., 1995) since only P ions present in the soil solution or soluble in water are removed. Luscombe et al. (1979) described the method for using distilled water as an extractant to assess soil available P and reported a high correlation between the water-extractable P concentration and dry matter yield response in ryegrass. Water-extractable P was also significantly correlated with the cumulative P budget following 17 years of maize monoculture in France (Messiga et al., 2010b).

Water extraction methods rely on volume-to-mass ratios varying from 1-to-5 (Koopmans et al., 2001), 1-to-10 (Fardeau, 1996; Morel et al., 2000; Self-Davis et al., 2000), and 1-to-60 (Sissingh, 1971) and different shaking durations (between 1 and 72 h) to assess the soil P concentration. Since distilled water may dissolve P ions and organic P associated with organomineral colloids (Hens and Merckx, 2002; Sinaj et al., 1998), it can overestimate P ions present in the soil solution. Filtering soil suspensions through a 0.02-μm membrane to remove colloidal P is recommended in water extraction methods. Dry soil samples that are rewetted with distilled water for water extraction are likely to give more soil available P than fresh soil samples due to the release of P from the microbial biomass and lower reactivity of metal oxides (Haynes and Swift, 1985; Turner and Haygarth, 2001). McDowell and Sharpley (2003) used dilute $CaCl_2$ (0.01 M) to determine the soil solution P concentration because this method generally extracts less P than distilled water.

3.1.3 Phosphorus fractionation methods

The first attempts to characterize soil P fractions in the 1950s (Chang and Jackson, 1957) focused on inorganic P compounds in calcareous soils and sediments. The procedure was later modified by Fife (1962), Peterson and Corey (1966), and Smillie and Syers (1972) to improve the extractability of inorganic P fractions from soils and then adapted to describe the organic P fractions in cropped soils (Bowman and Cole, 1978). A significant modification of the method allowed the simultaneous determination of both inorganic and organic P fractions from a single soil sample (Hedley et al., 1982), and subsequent developments permit a fumigation step to quantify

the microbial P pool. Recently, Tiessen and Moir (2007) adapted the use of anion exchange resin to quantify the soil solution P.

Although P fractionation methods are widely used to understand the bio-geochemical cycle of soil P in natural ecosystems (Cross and Schlesinger, 1995), there is interest in understanding how these P fractions could be related to soil available P. In most studies of agricultural soils, inorganic and organic P fractions are grouped into available, nonavailable, and recalcitrant pools (Fan et al., 2010). Soil available P is assumed to comprise the resin-P, $NaHCO_3$-P, and NaOH–P pools. The nonavailable and recalcitrant P pools are HCl–P and residual–P. The P fractionation method is more descriptive than soil test P methods (chemical extractants and water extraction), but it takes several days to complete the fractionation procedure, which is too long for routine soil testing, and the recovery rates of various P fractions are more variable with this method than soil test P methods.

3.1.4 Optical measurements

3.1.4.1 Near-infrared reflectance spectroscopy

Near-infrared reflectance spectroscopy (NIRS) is an indirect analytical method based on the development of empirical models that predict the con-centration of a soil constituent from complex spectral data (Coûteaux et al., 2003). Near-infrared radiation is absorbed by different chemical bonds (e.g., C—H, O—H, N—H, C=O, S—H, CH_2, and C—C) found in soil constituents, and this absorption results in bending, twisting, stretching, or scissoring of the bonds (Ludwig and Khanna, 2000). Although soil P has no theoretical basis for NIRS prediction because it is not measured directly, Chang et al. (2001) noted that soil available P may be predicted by NIRS if it is related to primary properties such as SOM and texture. One of the advantages of NIRS is that it may predict soil P, several other elements, and chemical properties from a single spectrum (Viscarra Rossel et al., 2006). Moreover, the fact that NIRS requires a single piece of equipment, without chemical reagents, could make this method very attractive, consid-ering the large number of samples that can be analyzed prior to each growing season and even at the end of the season. Nduwamungu et al. (2009) per-formed NIRS on 150 air-dried samples collected from a 15-ha site domi-nated by Orthic Humic Gleysol and Gleyed Dystric Brunisol soils near Montreal, Canada. The spectra were poorly calibrated with soil available P (Mehlich-3 P) across all soil textures, probably due to the pH–dependent solubility of P extracted by the acidic Mehlich-3 solution.

More research is needed to assess the potential of NIRS for predicting soil available P, perhaps with neutral or alkaline chemical extractants (Abdi et al., 2012).

3.1.4.2 Electroultrafiltration

Electroultrafiltration (EUF) was introduced for routine soil analysis in late 1960s and early 1970s (Németh, 1985). At the time, the primary concern was to define the EUF fraction that was related to the P concentration in soil solution. Pot and field experiments demonstrated that soil available P released by extraction with EUF at 20 °C and 200 V for 30 min was related to P uptake during vegetative growth (Eifert et al., 1982; Grimme and Németh, 1982). Simard and Tran (1993) were the first researchers in North America to compare EUF with other extraction methods to predict soil available P and response to P fertilizer with oat (*Avena sativa* L.) and maize crops. They found that soil P desorbed by EUF after 30–55 min was comparable to the soil available P concentration measured by chemical extraction methods in soils from northeastern North America. Years later, EUF was used with other extraction methods to investigate the P-supplying power of the fine-textured soils from Abitibi-Temiscaming (Quebec, Canada) by Ziadi et al. (2001). The EUF results (75 min desorption period) revealed a sizeable pool of inorganic P in these soils, which explained the lack of response to P fertilizers of grass-based hayfields in this region. In Pakistan, Taha et al. (1982) used the EUF method to determine the P solubility and desorption rates at various soil depths throughout the cotton growing season and found an increase in soluble P concentration during the growing season, mostly associated with the slowly available P fraction (10–30 min desorption period). In Nigeria, Akinrinde et al. (2006) found that EUF was more useful in assessing soil available P than conventional soil test P methods. Although EUF has potential for describing soil available P, the major constraint to its adoption by analytical laboratories is the length of time (up to 75 min desorption per sample) needed to quantify soil available P by this method (Simard and Tran, 1993).

3.2. *In situ* measurements of soil available phosphorus

In situ measurements of soil available P are made with anion exchange membranes (AEMs) or resins. The first report of resins as a sink for P came from Amer et al. (1955). The assumptions in their study were that the rate of P sorption by resins depended solely on the rate of P desorption or

dissolution from the matrix and not on the properties of the resin itself. However, the first studies with resins proved inadequate for precise characterization of soil available P because they did not account for a phenomenon like diffusion (Abrams and Jarrell, 1992; Amer et al., 1955; Skogley et al., 1990).

Mixed-bed ion–exchange resin sink enclosed in spherical porous mesh bags was promoted as a way to use exchange resins as indicators of soil available P (Skogley et al., 1990). Sufficient resin was placed in the bag that it effectively represented an infinite sink for P adsorption throughout the experimental period. The porous bags could adsorb P for a long period of time with the principal mechanism of sorption being equilibrium anion exchange with a high–capacity exchanger. One constraint of these materials was the difficulty to accurately account for diffusion processes. Their three-dimensional spherical structure often resulted in two diffusion coefficients: surface diffusion and internal diffusion. If these diffusion coefficients differ, not all resin particles inside the bag interact with soil solution P (Vaidyanathan and Talibudeen, 1970). This is problematic when resin-exchangeable P is calculated on a per gram of resin basis or if resin bags are not left in contact with the soil long enough to overcome diffusion limitations (Bhadoria et al., 1991).

Stronger sinks for P were developed by Hsu and Rich (1960) and by Robarge and Corey (1979), who affixed hydroxyl–Al to exchange resin. Oxide-impregnated papers and synthetic resin membranes were also developed to measure soil available P and P ion supply (Sharpley, 1991; van der Zee et al., 1987). These materials constitute true sinks for P because the strong affinity between Al and Fe for P leads to the formation of essentially nonreversible ligand bonds between the metal and phosphate anions. As such, the P adsorbed on the membranes cannot return in the soil solution but can only be dissolved using strong acids. Abrams and Jarrell (1992) showed that resin-impregnated membranes bind a pool of P ions that is strongly correlated to soil available P. According to Cooperband and Logan (1994), resin-impregnated membranes hold promise for in situ measurements of P fluxes because they are not limited by diffusion constraints. The two-dimensional structure ensures greater contact with the soil and therefore more exchange sites for sorbing P ions. The planar surface of the resin–impregnated membranes also allows an easy calculation of the volume of soil with which they interact (Van Rees et al., 1990).

AEMs were tested for use in routine soil P testing on 135 soil samples, representing a range of soil types in western Canada (Qian et al., 1992). The

authors demonstrated that the soil available P concentration predicted by AEM was significantly correlated with that from conventional soil test P methods. The authors also demonstrated that P uptake by canola plants was more closely correlated with AEM-P than with Olsen-extractable soil P. These results are consistent with a study on 14 soils from Saskatchewan by Schoenau and Huang (1991), which also demonstrated that the coefficients of determination in equations predicting soil available P were nearly identical with AEM, water-extractable P, and Olsen P and were also highly correlated with P uptake by canola. Assessment of AEM-P- and Mehlich–3-extractable P in Humaquepts varying in clay content revealed that plant P uptake was more closely related to AEM-P than to Mehlich-3 P, suggesting AEM-P is a better indicator of soil available P in those soils (Zheng et al., 2003). Cooperband and Logan (1994) measured *in situ* changes in labile soil P with AEM and showed that the relationship was essentially linear when solutions contained 0–2 mg P l^{-1}, which was confirmed by a later study showing that AEM gives a good measure of soluble and readily desorbable P in low-P status soils and sediments (Cooperband et al., 1999). The AEM was compared with soil test P methods using 32 soils from Guatemala with widely varying physicochemical and mineralogical properties (Nuernberg et al., 1998). The study demonstrated that soil test P methods were not suitable for soils containing apatites, while AEM gave better predictions of soil available P regardless of the soil type. In addition to being well correlated with soil available P, AEM is cost-effective, simple, independent of soil type, and therefore superior to the other analytical methods for soil test P (Schoenau and Huang, 1991).

3.3. Isotopic dilution method to evaluate soil available phosphorus

The use of radio isotopes in assessing soil available P and P uptake by crops started in the early 1940s. The approach consists in labeling the orthophosphate ions of the soil solution with the radio isotopes ^{32}P or ^{33}P (Fardeau et al., 1985). It is assumed that the orthophosphate ions with the three isotopes of P (^{33}P, ^{32}P, and ^{31}P) have exactly the same behavior and are not affected by isotopic discrimination during chemical, physical, or biological reactions (Fardeau, 1993; Fardeau et al., 1985; Frossard et al., 2011).

The isotopic method provides quantitative data on P dynamics in the soil and soil–plant system (Fardeau, 1996). A full characterization of soil available P based on the determination of four factors in a single experiment can be made. The intensity factor quantifies the chemical potential of P ions in the

soil solution. The quantity factor estimates the quantity of P ions that are instantaneously exchangeable at 1 min. Two capacity factors, one "immediate" and the other "delayed," are also determined simultaneously. These four factors permit the application of a functional and dynamic model for soil available P (Fardeau, 1996). Comparing with routine analytical methods, chemical extractants used in soil test P analysis evaluate the quantity factor, whereas water extraction measures the intensity factor only. Although the isotopic dilution method allows quantification of intensity, quantity, and capacity factors, it is not recommended in routine soil analysis because of the radioactive nature of the ^{32}P or ^{33}P isotopes. However, the isotopic dilution method can be considered as the reference method for assessing the suitability of other soil test P for routine determination of soil available P.

Two experimental techniques were developed to simultaneously assess the intensity and the quantity factors in isotopic studies. These involve manipulation of soil suspensions, made by suspending a mass of soil with a volume of water and shaking the suspension for a known period until it reaches steady state (point at which sorption and desorption fluxes are equal). The first technique involves adding radio isotopes to steady–state soil suspensions followed by a dilution period (Fardeau, 1981, 1993; Fardeau et al., 1991). The second technique relies on adding P ions at increasing concentrations, followed by a contact period to reach the steady state, and then an isotopic dilution experiment similar to the first technique (Barrow, 1979; Chardon and Blaauw, 1998; Fardeau, 1981; Morel and Fardeau, 1991; Morel et al., 1994; Schneider et al., 2003). The methodology used for running the isotopic dilution experiment is presented in Fig. 2.2, and interpretation of results from isotopic dilution in the context of soil P modeling is described in Section 4.1.

4. MODELING SOIL AVAILABLE PHOSPHORUS

Modeling soil available P allows researchers and practitioners to describe P chemistry, transformations and removal from soil by plants, and through hydrological processes, which improves our understanding and management of P resources in agriculture and surrounding environments (Bar–Yosef, 2003). This section describes recent developments in modeling soil P availability to crops, focusing on the case of a process-based mass–balance model of soil available P in agroecosystems.
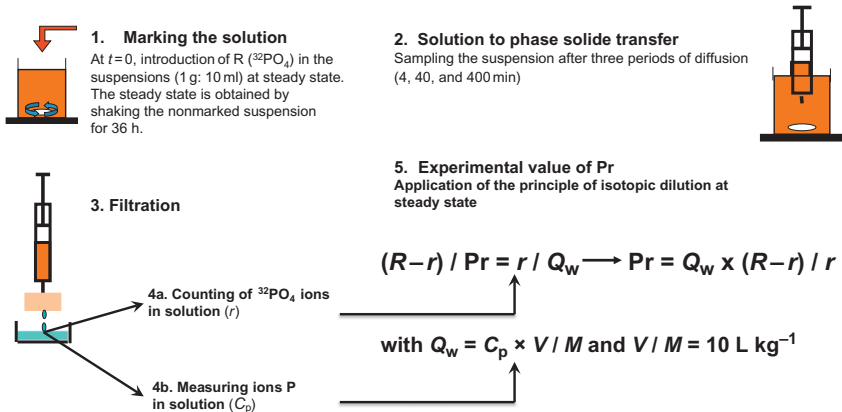
Figure 2.2 Flow chart of the isotopic dilution method to determine diffusive soil P transfers in the laboratory.

4.1. Case study: Development of a process-based mass-balance model to study soil available phosphorus in sustainable cropping systems

4.1.1 Assumptions

In field crops and permanent grassland, P ions (Pi) in the soil solution represent about 1% of P taken up annually by crops and the remaining 99% is derived from the soil solid phase (Grant et al., 2005). A simplified conceptual model describing the dynamics of soil available P in grassland (Fig. 2.3) was proposed by Messiga et al. (2012b). The model includes three P pools and two fluxes to explain the annual P budget. Two P pools contribute directly to the dynamic pool of soil available P: solution Pi and solid phase Pi. Variations in solution Pi match annual variations in the P budget.

While Pi in the soil solution can be measured with the water extraction method (Gallet et al., 2003; Messiga et al., 2010b; Morel et al., 2000; Sissingh, 1971), it is difficult to estimate the quantity of soil solid phase Pi because this Pi is desorbed and mixed with Pi already present in the soil solution. Calculating the flux of P transferred between the two phases permits estimation of solution and solid phase Pi pools. Three approaches are used to investigate the net or gross rates of Pi transferred between solid and solution phases: sorption/desorption, EUF, and isotopic dilution methods. For simplicity, we present a case that focuses on the isotopic exchange approach to determine the Pi flux. The isotopic dilution approach is similar to the conventional sorption/desorption approach because (1) diffusive Pi (Pr) is
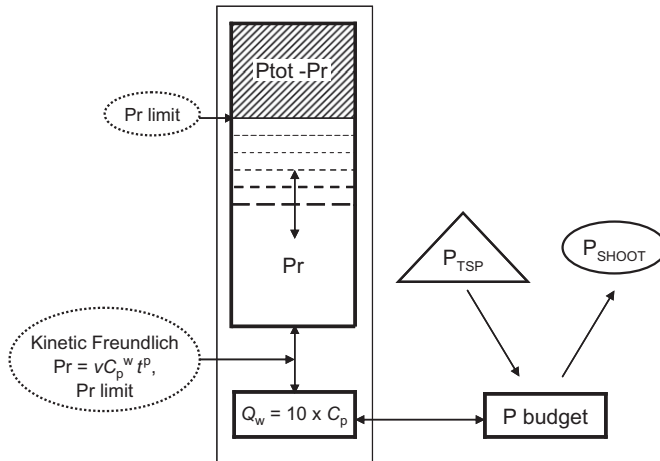
Figure 2.3 Structure of the P-cycling model describing the dynamics of plant-available soil P in grassland soils. The model includes three pools and two fluxes accounting for annual P balances. The three pools are the amount of P ions in solution, Q_w, calculated by multiplying the P ions concentration in solution (C_P) by the solution-to-soil ratio (10); the amount of soil diffusive P (Pr) that buffers P ions in solution with time; and the total soil P (P_{tot}). The transfer of P ions at the solid-to-solution interface is described by a Freundlich kinetic equation that accounts for solution P ions, slow and fast kinetic transfers. This equation controls the partitioning of P ions between soil solution and soil diffusive P. The two P fluxes are P input, P_{TSP} = amount of P added by fertilizer (triple super phosphate, 46% P_2O_5); P output, P_{SHOOT} = P removed in shoots at harvests. The P budget is the difference between annual P inputs and annual P outputs (Messiga et al., 2012b).

assessed as the quantity factor (Beckett and White, 1964), (2) the rate of Pr transfer is the capacity factor, and (3) the ^{32}P fraction remaining in solution and the change in desorption rate factors are described as a power function with time (Fardeau et al., 1985; Vadas et al., 2006).

4.1.2 Flux of Pi at the solid-to-solution interface

Several processes affect the flux of P at the solid–to–solution interface, including precipitation–dissolution, adsorption–desorption, and mineralization–immobilization (Frossard et al., 2000). The major process controlling Pi transfer between solution and solid phase is diffusion across a concentration gradient (Barber, 1995; Fardeau, 1981). The amount of P moving between the two phases is designated Pr (Stroia et al., 2007a), and it is in equilibrium with Pi in the soil solution (Vadas et al., 2006). The Pr acts as a reserve pool that replenishes the solution when Pi concentration is depleted, for instance, due to plant P uptake, or a sink for excess P when the concentration of Pi in the soil solution increases.

4.1.3 Estimation of the gross amount of diffusive soil phosphorus

The gross rate of Pr transferred between solid–to–solution interface is determined experimentally on soil suspensions under steady-state conditions (Fardeau et al., 1985; Frossard et al., 2011). Two experimental approaches may be used. The first is conducted in two steps by coupling a sorption experiment with isotopic dilution analysis and is appropriate for estimating Pr in soils with little variability in their P status (e.g., from natural ecosystems; Stroia et al., 2007a). The second approach relies on isotopic dilution analysis only to estimate Pr and is adapted for soils with variable P status, such as those with a history of P fertilizer applications. The latter approach was used by Messiga et al. (2012b) to model soil available P in grassland fertilized with N and P, and by Stroia et al. (2007b) to study the dynamics of Pr in two grassland experiments. The factor Pr is determined by applying the dilution principle to the isotopic composition (IC) of the different phases of the soil suspension using the following relationship (4.1):

$$IC = \frac{R - r}{Pr} = \frac{r}{10 C_P} \tag{4.1}$$

where 10 is the volume-to-mass ratio, C_P is the concentration of Pi in solution, R is the radioactivity introduced into the solution at time t_0, r is the radioactivity remaining in solution after elapsed time t, $R - r$ is the radioactivity transferred into the solid phase after elapsed time t, and Pr is the diffusive P. The experimental Pr values for all elapsed times during the isotopic dilution study are then calculated with Eq. (4.2):

$$Pr = 10 C_P \frac{R - r}{r} \tag{4.2}$$

4.1.4 Process-based modeling of diffusive P ion transfer at the solid-to-solution interface

According to Eqs. (4.1) and (4.2), for any elapsed time in the isotopic dilution study, Pr and C_P can be determined simultaneously in the same soil suspension. The gross rate of Pr transfer is therefore a function of C_P and time, two important factors affecting the dynamics of P in the rhizosphere of cultivated soils (Morel et al., 2000). Dynamics of Pr transfer at the solid-to-solution interface is described mathematically using a deterministic modeling approach, which combines different values of C_P and isotopic dilution kinetics (Fardeau et al., 1985; Frossard et al., 2011). The dynamics of Pr transfer is accurately described by a Freundlich kinetic equation (4.3):

$$\text{Pr} = v \times C_P^{w} \times t^{p}, \quad \text{with Pr} < \text{Pr}_{\text{LIMIT}} \tag{4.3}$$

where Pr (mg P kg^{-1}) is the gross amount of diffusive P; C_P (mg P l^{-1}) is the concentration of P ion in solution; t (min) is the time of transfer; and v, w, and p are fitted parameters. The v-parameter is the Pr value at time $t = 1$ min and for $C_P = 1$ mg P l^{-1}, the w-parameter describes the nonlinear increase in Pr with C_P, and p-parameter describes the nonlinear increase in Pr with time. The Pr value can be calculated at any time during the isotopic dilution study, but it is limited by an unknown value, the Pr$_{\text{LIMIT}}$, which is lower than the total inorganic P concentration in soil (Frossard et al., 2011).

This mathematical function has been tested under various experimental conditions, and the parameterized Freundlich kinetic function is used to extrapolate the gross amount of Pr from short-term isotopic dilution studies to longer periods, months to years (Achat et al., 2010; Fardeau et al., 1985; Frossard et al., 1994; Messiga, 2010; Messiga et al., 2012b; Morel et al., 1994; Némery et al., 2004; Stroia et al., 2007a,b). It is desirable to have an estimate of Pr for longer period of time because this accounts for both the rapid and slow reactions of Pi between solid and solution phases for better understanding of soil P dynamics.

4.1.4.1 Influence of soil properties on the kinetics of diffusive soil P transfer

Soil properties vary at relatively small spatial scales, and this affects estimates of diffusive soil P transfers. Consequently, Stroia et al. (2007a) recommended parameterizing the kinetic Freundlich function for soil samples on a plot-by-plot basis to better characterize the immediate and slow Pi reactions and account for variability among experimental plots. Stroia et al. (2011) also demonstrated that N fertilization significantly changes the dynamics of Pr in the 0- to 5-cm soil layer of grassland in the French Pyrenees following 6 years of cultivation. In a timothy grassland in eastern Canada, Messiga et al. (2012b) showed that Pr dynamics were not affected by N fertilization after 9 years of cultivation, based on soil samples collected from the 0- to 15-cm soil layer. These contrasting results may be due to a dilution effect caused by choice of soil depth, but illustrates the need for additional studies to evaluate how soil properties affect the kinetics of Pr transfer.

4.1.5 Assessment of soil available phosphorus using a process-based mass-balance model

The principle supporting field-scale mass-balance models is that soil available P increases if the P budget (difference between P imported and P exported) is positive, decreases if the P budget is negative, and remains constant if the P budget is zero. Several long-term studies in field crops and grasslands show

a linear relationship between soil available P and P budgets (Boniface and Trocmé, 1988; Ciampitti et al., 2011; Messiga et al., 2010b, 2012b). Most of these studies relied on soil test P as an indicator of soil available P, which does not differentiate between solution Pi and Pr. Field-scale mass-balance models often rely on soil P indices (Meals et al., 2008; Vadas et al., 2008) or P sorption coefficients (Vadas and Sims, 2002; Vadas et al., 2006) that are derived from sorption–desorption experiments. Thus, they do not consider the continuum of Pi forms in the soil solution that are immediately available and Pr that serves as a reserve pool that is described with kinetic functions (Lookman et al., 1995). This shortcoming can be overcome by integrating the parameterized Freundlich kinetic equation in the P budget. This process-based approach considers Pi in the solution, Pr of the solid phase, and the rate of transfer between the two phases which is triggered by fluctuations in the P budget. The development of a process-based mass-balance model permits researchers to simulate the solution Pi dynamics throughout the cultivation period, thereby advancing our understanding of P-cycling in managed agroecosystems.

The process-based mass-balance model was first presented by Gallet et al. (2003), who demonstrated that for six arable trials (>9 years in duration), the isotopic exchange kinetics parameters and P exchangeable within 1 min could be estimated from the values measured at the beginning of the trial and the cumulative P budget. In a long-term maize monoculture of 17 years in southern France, this model was successfully used to simulate the solution Pi values on a yearly basis for several P fertilizer treatments (Messiga, 2010). Model simulations were affected by the diffusive P transfer period, which varies between 1 and 5 years. Soil available P (Pi and Pr) dynamics in a long-term grassland in eastern Canada were modeled successfully with diffusive P transfer periods of 2–3 months (Messiga et al., 2012b). A similar approach to describe soil available P in Podzols from five Maritime pine stands in the forest range of the "Landes de Gascogne" in southwestern France showed that Pr values were between 1.4% and 4.4% of total inorganic P in soil, considering a diffusive P transfer period of 1 year (Achat et al., 2010). Messiga et al. (2012b) stressed the importance of knowing the fraction of total inorganic P in soil, which enables a more reasonable estimate of Pr and sets the length of the transfer period used in the Freundlich kinetic equation.

5. CONCLUSIONS AND FUTURE WORK

Soil available P is the principal pool that supplies crop P requirements and is susceptible to transport in the environment through hydrological

pathways (runoff and leaching). Agronomists can rely on soil test P values to calculate fertilizer P recommendations for a particular region. However, these simple measures do not provide much information about the size and dynamics of the soil available P pool, which can vary within and between agricultural fields due to site-specific soil properties such as pH and interactions between soil microbiota and crops, current and historical agricultural management practices, and environmental conditions. If soil test P values are to be incorporated in watershed- and landscape-scale hydrological models for environmental protection, those measurements should reflect the actual dynamics of the soil available P pool for the best possible predictions. These considerations support the integration of process-based kinetic measurements into P budget models, and examples of integrated process-based mass-balance models were described in this review.

Selection of an appropriate method for determining soil available P is another topic that deserves further research. Most routine methods used by analytical laboratories assume that Pi associated with the soil solid phase is the major reserve pool that enters the soil solution and select chemical extractants that desorb this Pi pool. This is probably a good assumption for soils with a history of mineral P fertilization but remains to be validated for temperate soils that have received organic P fertilizer over the longer term (e.g., from manure and other organic materials) as well as tropical soils that rely on weathering and mineralization of organic materials as sources of soil available P. The isotopic dilution method could directly measure Pr derived from primary minerals, secondary minerals, and organic matter, thereby alleviating the shortcomings of traditional soil test P methods, but would require modifications of the Freundlich kinetic equation or a mixing model to partition the Pr among various sources. Further research on this topic is suggested to develop models of soil available P that consider the contribution of both inorganic and organic P compounds to crop nutrition, for sustainable cropping systems around the world.

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