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Use of Phosphorus Isotopes for Improving Phosphorus Management in Agricultural Systems

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USE OF PHOSPHORUS ISOTOPES FOR IMPROVING PHOSPHORUS MANAGEMENT IN AGRICULTURAL SYSTEMS

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PREPARED BY THE
JOINT FAO/IAEA DIVISION OF NUCLEAR TECHNIQUES IN FOOD AND AGRICULTURE

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FOREWORD

Phosphorus (P) is an essential element in plant, human and animal nutrition. Soils with low levels of P are widespread in many regions of the world, and their P deficiency limits plant growth and reduces crop production and food quality. External P inputs such as manufactured P fertilizers, organic P sources (crop residues and animal manures) and rock phosphates can be applied to ameliorate this low soil P availability to plants. However, the extent of their availability is governed by complex physicochemical processes such as P adsorption to/desorption from colloidal soil particles; biological processes driven by soil microorganisms that influence the decomposition of soil organic matter and added animal manures; and other processes occurring in the root–soil interface (rhizosphere) that determine P acquisition by plants. Thus, it is of great importance to understand the various cycling processes that determine P fluxes and dynamics in soil–plant systems and ultimately influence the extent of P availability to plants. Isotopes can be used to unravel the main factors that influence these fluxes so that appropriate soil, plant and fertilizer management practices can be put in place to enhance the efficient use of soil P and added external P inputs. On the other hand, in intensively cultivated areas the continuous use of external P inputs can lead to its accumulation in the topsoil, and to increased pollution risks and eutrophication of water bodies if such accumulated P finds its way into streams and rivers. In these cases, these science based management practices would also help to minimize the adverse effects of surplus P and potential losses to the environment.

The purpose of this publication is to provide comprehensive and up to date information on several topics related to P in soil–plant systems, in agricultural systems and in the environment. It presents the theoretical background as well as practical information on how to use nuclear and radioisotope tracer techniques in both laboratory and greenhouse experiments to assess soil P forms and plant-available soil P pools, and to understand P cycling processes in soil–plant systems. The publication focuses on practical applications of radiotracer techniques and can serve as a resource for research projects on improving sustainable P management in agricultural systems and as practical guidance on the use of phosphate isotopes in soil–plant research.

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SUMMARY

Recognizing the urgent need to address the soil P constraints for a sustainable intensification of agricultural production in developing regions of the world to ensure food security of the ever growing population, the Soil and Water Management and Crop Nutrition Section of the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture decided to produce this publication "Use of Phosphorus Isotopes for Improving Phosphorus Management in Agricultural Systems" as a training and reference publication for agronomists, crop and soil scientists, plant physiologists, and other end users in developing Member States.

The publication comprises four papers. The first paper is an extensive review of several topics related to P in the soil plant system, and also in agricultural systems and the environment. This chapter describes key processes influencing soil P dynamics, P acquisition mechanisms by plants and P cycling in soil-plant systems. Selection and management of organic and inorganic P fertilizers, including farm effluents, bio solids (sewage sludge) as well as the prospects for the utilization of rock phosphate (PR) products for direct application in agriculture to help build the soil P capital are discussed. The need for sustainable P management strategies in agroecosystems, research activities to address P constraints in soils using P isotopes conducted by the Joint FAO/IAEA Programme and environmental issues related to soil P surplus are highlighted.

The second paper deals with a range of conventional (chemical) and nuclear and isotopic techniques for investigating soil P forms and estimating P availability, fluxes and balances. Interpretations of soil P testing results for providing appropriate fertilizer recommendations are also discussed.

Paper 3 describes the use of P isotope tracer techniques for measuring the P uptake from applied P fertilizers and thus determining fertilizer P utilization efficiency, the P contribution from other P sources such as rock phosphates and crop residues and the assessment of plant available soil P pools including procedures and calculations. It provides also an insight into Radiation Protection and Safety issues in handling phosphorus radioisotopes. The measurement of the activities of P radioisotopes using liquid scintillation counters/analysers is briefly covered. Three case studies are presented in the Appendix.

AN OVERVIEW OF PHOSPHORUS IN THE SOIL PLANT SYSTEM, AGROECOSYSTEMS AND THE ENVIROMENT

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Abstract

Phosphorus (P) is an important nutrient and a strategic resource to plants. A better and holistic understanding of P dynamics in the soil/rhizosphere-plant-animal continuum is vital to guide integrated P management strategies associated with the manipulation of soil and rhizosphere processes, development of P efficient crops, and improving P recycling efficiency. However, some aspects of overall P dynamics in the soil/rhizosphere-plant-animal continuum are not thoroughly understood. These include the regulation of P acquisition and P-starvation mechanisms in plants, P sources (organic and inorganic forms) and its adverse effects on human health and environmental quality. The paper summarizes the key processes influencing soil P dynamics, soil P cycling processes and its availability and P acquisition mechanisms by plants. Selection and management of organic and inorganic P fertilizers, including farm effluents, bio solids (sewage sludge) as well as the prospects for the utilization of rock phosphate (PR) products for direct application in agriculture are discussed. Environmental issues related to the use of P sources such as heavy metals contamination and P losses and water quality are described. Management strategies for sustainable phosphorus management in agroecosystems are also examined.

1. INTRODUCTION

The name phosphorus (P) is derived from the Greek word *phos*, which means “light” and *phorus* which means “bringing”. Phosphorus, after nitrogen (N), is the most important essential nutrient element for plant growth and agricultural production in most parts of the world. A shortage of P limits crop yield on 30–40 % of the world’s arable land [1]. Correcting P deficiency by fertilizer applications is not possible for the mostly resource-poor farmers in the tropics and subtropics, especially in soils (e.g. Ultisols, Oxisols) with high P fixing capacity [2]

1.1 Phosphorus in the soil-plant system

Phosphorus (P) is an element that is widely distributed in nature and occurs, together with nitrogen (N) and potassium (K), as a primary constituent of plant and animal life. P is one of the essential nutrients required for plant growth and development and plays a series of key functions in the plant metabolism, i.e. structural component of several macromolecules such as nucleic acids, sugar phosphates, nucleotides, coenzymes, phospholipids, inositol-phosphates and also of energy transfer in metabolic pathways of biosynthesis and degradation. Unlike nitrate and sulphate, phosphate is not reduced in plants but remains in its highest oxidized form [3].

P is absorbed mainly during the vegetative growth and, thereafter, most of the absorbed P is re-translocated into fruits and seeds during reproductive stages. At early stages it promotes the growth of a vigorous root system. P deficient plants exhibit retarded growth (reduced cell and leaf expansion, respiration and photosynthesis), and often a dark green colour (higher chlorophyll concentration) and reddish coloration (enhanced anthocyanin formation). It has been reported that the level of P supply during reproductive stages regulates the partitioning of photosynthates between the source aerial organs and the sinks reproductive organs, this effect being essential for N-fixing grain legumes [3]. Healthy animals and human beings also require adequate amounts of P in their food for normal metabolic processes. Calcium phosphate is the major constituents of the skeletal bones and teeth and contains 85% of the body's total phosphorus [4].

Although the total P content in soils range from 0.035 to 5.3 g kg^{-1} and the mean content in the earth's crust is 1 g kg^{-1} [5], P availability is declining in many agroecosystems because of soil degradation, which has affected over half of global agricultural land and 75% of agricultural land in Africa. With increasing demand for agricultural production as the peak of global production will occur in the next decades, the need for integrated and sustainable P management strategies involving manipulation of soil and rhizosphere process, development of P-efficient crops and improve P-recycling efficiency in future [6]. According to [7] approximately 15–80% of total P occurs in organic forms that comprise a range of compounds such as inositol-phosphates (2–50% of total organic P), phospholipids (1–5%), nucleic acids (0.2–2.5%), sugar phosphates and metabolic phosphates (trace) and other unknown components (>50%). Mineralization and immobilization of organic P compounds are relevant processes for P cycling in soils containing significant amounts of organic matter [8].

The concentration of P ions present in soil solution is normally small. Such low P concentration is usually adequate for normal plant growth. However, for plants to absorb the total amounts of P required to produce good yields, such low P concentration of the soil solution in contact with the roots requires continuous renewal during the growth cycle. This nutrient is absorbed by plants from the soil solution as monovalent (H_2PO_4) and divalent (HPO_4) orthophosphate anions, each representing 50 per cent of total P at a nearly neutral pH (pH 6–7). At pH 4–6, H_2PO4 is about 100 per cent of total P in solution. At pH 8, H_2PO_4 represents 20 per cent and HPO_4 80 per cent of total P. Phosphorus dynamics in soil, rhizosphere, uptake and utilization by plants, and strategies for optimizing P management to improve P use efficiency in crop production has been extensively reviewed [6].

A number of conventional (chemical methods) have been developed to determine the soil P availability to plants. Conventional soil P testing are either methods based on chemical extraction such as Bray I & II, Truog, Mehlich, Olsen P, Colwell, etc. or ion sink methods based on P sorption processes (anion exchange resin and Pi strip). No single chemical extraction method is suitable for all soils and fertilizers [9]. Under continuous cultivation, external P inputs, in particular water soluble phosphate (WSP) fertilizers must be added to agricultural soils to either maintain the soil P status of fertile soils or increase that of soils with inherent low P fertility. It is reported that P fertilizer recovery efficiencies commonly range from 5 to 20 % (sometimes are as low as 1% in high P fixing soils) for the first crop and thereafter 1–5% for the subsequent crops indicating there is scope for improving P utilization by crops [10]. Transformation processes responsible for the release of Pi from Al–, Fe– and Ca–bound P and for the incorporation of fertilizer P in soils have been studied extensively and are well understood [11] although less is known about the release of P from soil P_o.

In areas with intensively cultivated agricultural lands and/or concentrated large-scale animal production units, the excessive use of external P inputs can lead to P accumulation, thus increasing pollution risks and promoting eutrophication of water bodies, if such accumulated P finds its way to streams and rivers. In those areas there are serious environmental concerns about P losses from both point and diffuse P sources. Point P sources include waste waters containing manures and slurry from dairy and animal production farms and seepage from manure stores. Diffuse sources are related to P losses from individual fields through sheet erosion and leaching through the profile to groundwater. It is reported that the relative contribution of P sources to waters in Europe is on the average 50–75% from point sources, 20–40% from diffuse sources (agriculture) and 5–15% from natural loading [12]. Therefore, soil, crop, water, P fertilizer management practices, including climatic conditions are important factors to be considered when attempting to formulate sound P-fertilizer recommendations to obtain adequate crop yield responses while protecting the environment.

1.2. Phosphate plant nutrition

Plants can take up P only from the soil solution. The concentration of soluble P in soils is very low, usually less than 10 µmole P m^{-3} and often as low as 0.01 µmole P m^{-3}. In most soils, P in the soil solution at any given time is about 1 kg ha^{-1} or less than 1 % of the total P in the soil [13]. The P is incorporated into plant tissue with concentrations of about 10 m mole m^{-3} [14]. Thus P uptake occurs against a massive P concentration in the plant tissue. Because soil P is very immobile, it does not move very far in the soil to get to the root. Most P reaches the root surface via diffusion and not by mass flow. Only 1–5% of a plant's P demand is met by mass flow and only half of this amount is by root interception.

Due to the low concentration of P in the soil solution, plants depend on replenishing the soil solution with phosphate from soil P forms or from P fertilization. The bulk of soil phosphates are in mineral P forms or in soil organic matter and a large proportion of these are in very stable and unavailable P forms. Applications of P fertilizers are therefore essential to increase and maintain pasture and crop yields [15]. However, mineral P fertilizers are scarce in most parts of the world and when applied to soils they are rapidly transformed into organic and inorganic forms with limited plant availability.

1.2.1 P acquisition mechanisms by plants

Plants have developed a diverse array of mechanisms to obtain adequate P to cope with the problem of low P availability in soils. These may be divided into (a) those which are directed towards conservation of P use and (b) those which enhance P acquisition or uptake. Some of the processes which conserve P use involve decreased growth rate, increased growth per unit of P uptake, remobilization of internal Pi, modification of C metabolism to bypass P–requiring steps, and alternative respiratory pathways.

1.2.2. Plant phosphorus efficiency, plant P response and P fertilizer utilization.

There are many definitions of P efficiency, utilization and responses [16–17]. In general, plant P efficiency is the ability of a plant genotype to acquire P from the rhizosphere solution and/or to incorporate P to produce above or below ground biomass or utilizable plant material. Some definitions focus on P uptake, others on P utilization. According to [18] three categories of P efficiency are: (a) uptake efficiency, (b) incorporation efficiency and (c) utilization efficiency. Criteria for P uptake efficiency are based on root (e.g. P uptake per unit root dry weight); incorporation efficiency on shoot yields (e.g. shoot DM per unit P of shoot) and utilization efficiency on the whole plant (e.g. plant DM per unit P uptake).

Many workers separate nutrient use efficiency into agronomic efficiency or physiological efficiency [19]. Agronomic efficiency is defined as the biomass or harvestable yield of the plant per unit of nutrient applied [20] or the amount of nutrient required to achieve a given per cent of the maximum attainable yield in a growth medium, also referred to as the “external nutrient requirement”. Screening plants for genotype variation has been proposed as a possible means for overcoming P deficiency stress in soils [21] to optimize P fertilizer applications [19].

1.3 Phosphorus sources

Major P sources in agroecosystems include natural (indigenous soil and atmospheric deposition) and anthropogenic or external (inorganic and organic fertilizers) sources. Major P sources reflect the inputs of P to agricultural lands and soil reservoirs, which may represent the long term potential of P enrichment and transfer to surface freshwaters in the wider terrestrial environments. Riverine loads of P have increased in many river basins globally due to intensified agriculture, urban and industrial development and atmospheric deposition [22].

External sources of P commonly used to supply adequate amounts of P to plants include phosphate rock products, inorganic manufactured P fertilizers and organic P fertilizers such as manures, composts, crop residues and sewage sludge or effluents. The amount of P present in the fertilizer is usually expressed as either total P (% P) or P pentoxide or phosphoric anhydride (% P_2O_5). The conversion factors are: P_2O_5 x 0.44 = P and P x 2.3 = P_2O_5. Phosphate fertilizers are of great economic importance to the productivity of farming systems and to the sustainable intensification of agricultural production in many parts of the world. Although both inorganic and organic P fertilizers are available, inorganic manufactured fertilizers are more commonly used.

1.3.1 Phosphate rocks as fertilizers

Phosphate rocks (PR) are phosphate–bearing minerals found in geological deposits widespread throughout the world, occurring in all continents with the possible exception of the Antarctica [23]. Rates of depletion of these PR reserves are difficult to predict but estimates of exhaustion cited are around 90 years while the reserves in the USA would last only about 25 years [23]. The mineralogy of high P content PRs is complex but they are characteristically members of the mineral apatite group, which may be represented as:

$$Ca_5\,(PO_4, \pm CO_3, \pm OH)_3(OH, F, Cl)$$

Apatite can vary from the mineral fluorapatite ($Ca_{10}(PO_4)_6F_2$) to minerals of the francolite type ($(Ca_{10-\alpha}(Na, Mg)\ PO_4)_{6-\beta}(CO_3)F\gamma$), where α and γ are functions of β, and $\beta = 1.5$ in the most substituted form [24].

Although phosphate rocks (PRs) are used mainly (>90%) as raw materials for the manufacture of phosphate fertilizers, their use for direct application, especially those from indigenous sources is becoming increasingly important in developing countries, particularly on acid soils (e.g. [25–28]. In addition, in developed countries (e.g. New Zealand), the direct application of reactive phosphate rocks (RPRs) has been shown to be as effective as soluble P fertilizers in the field per kg of P applied [24, 29–30]. Several long term studies on the use of PRs in tropical soils demonstrated that their residual value can exceed those of soluble P fertilizers, especially for plantation estate crops [29, 31]. However, all the above advantages of PRs must be considered against some of their major disadvantages such as low P availability resulting in low plant yields, high transportation and spreading costs, particular soil and climatic conditions and crop requirements.

Although the availability to plants of the P in PRs depends on the rate of PR dissolution in a given soil, the agronomic effectiveness of PRs is influenced by soil, climate, plant and management factors. A large number of factors affect the agronomic effectiveness of PRs and it is difficult to predict their relative importance for a particular situation [24, 29, 32]. Not all soils and cropping situations can benefit from direct application of PRs from different sources. Unsatisfactory results occur when low reactive PRs are used, when the soil pH is too high or the period of crop growth is too short [33]. Thus, an understanding of the properties of different PR sources and the soils themselves, methods of PR application, climatic conditions and plant P requirements and their ability to acquire P is necessary for effective management of PRs in a given situation.

1.3.2 Inorganic phosphate fertilizers

A wide range of inorganic phosphate fertilizers are available commercially. The nature of the P components in these fertilizers varies. Various extractants (e.g. water, 2% citric acid) are used to compare their solubility. This is an arbitrary procedure and the results obtained are not necessarily closely related to the P availability to plants upon fertilizer application to the soil. The water soluble P is regarded as the most readily available form and the citric soluble P as the form with intermediate solubility. For quick-starting (short growth cycle) crops, fertilizers with high water soluble P are most suitable and can be placed in bands next to the seeds but not too close as to cause salt damage to germination. Citric-soluble P is ideal for slow-growing crops or for applications before planting. The sum of the water soluble and citric-soluble P is considered as the “total available P” in the fertilizer trade in some countries (e.g. USA).

1.3.3 Organic phosphate fertilizers

Since ancient times, organic materials were the main nutrient sources used in agriculture. Bones and guano (seabird droppings) were the early sources of P. The Peruvian guano, which is relatively high in N (12–14%) and total P (4.5–5.5%), was imported as a commercial fertilizer in both North America and England in the 1840s but it was depleted in 1860. In general, organic phosphate fertilizers are largely plant (crop) and animal residues such as by-products of farm animals (cows, sheep, poultry), meat processing and waste treatment plants (biosolids). These materials contain extremely variable amounts of P in addition to other nutrients (e.g. N) according to the source and methods of processing. Their P content is relatively low compared with inorganic phosphate fertilizers and thus is expensive per kg P, if purchased. By-products of the meat processing industry (e.g. blood and bone) contain relatively more P (7–12%P) than other organic fertilizers (e.g. manure) and are classified as non-bulky organic fertilizers, while plant residues, animal manure, compost, and biosolids (e.g. sewage sludge) are known as bulky organic fertilizers. In some instances, bulky organic fertilizers are applied to the soil as soil conditioners (amendments) to improve soil physical conditions rather than as suppliers of P and other nutrients.

1.3.3.1 Crop residues and composts

Crop residues are the parts of plants left in the field after crops have been harvested or pastures are grazed by animals. The total amount of P in crop residues varies with the crop, soil and fertilizer practice. It ranges from 0.4 to 2.0 kg per tonne of residue and can be a significant source of P if retained or returned to the soil after the plant harvest and not burned or used as animal feed or housing materials. Major factors and their interactions influencing residue decomposition and the release of P to plants and their effects on crop yields are residue quality, particle size, age of residue, crop, edaphic (soil) and climatic factors and management practices [34]. Biochemical characteristics of the residues (e.g. lignin, polyphenol) in addition to their N and C: N ratios are useful for predicting residue decomposition rates [34–35].

Composting is a biological process of aerobically converting organic materials to a more stable form through decomposition and oxidation reactions [36]. Overall, composting results in the enrichment of total P in the composted product [37]. Composting of manure reduces transport costs since it reduces manure mass and volume. It also allows the composted manure to be transported over greater distances to areas of deficiency, especially for the restoration of crop productivity on degraded soils [38]. Composts provide a means for recycling wastes and getting rid of large quantities of municipal wastes in industrialized countries.

The application of composts has been reported to increase crop yields and improve soil physical, chemical, and microbiological conditions [39–40]. Although considerable potential exists for using composts for vegetable production in urban / peri urban areas or in close proximity to poultry farms, the yield responses have been variable. The amount of P that can be extracted from composts usually varies considerably from about 3% when water is used to 98% when strong acids (e.g. citric acid) is used [41]. Likewise, the amount of P taken up by plants from a soil/compost mixture varies from 10–264 % compared with that taken up from a water soluble mineral fertilizer at comparable P application rates. This large variability was attributed to differences in compost and soil properties, plant species studied, and the methodologies used [42].

1.3.3.4 Manures

Farm animal manures are largely raw faeces, urine, waste feed, spilled water; absorptive bedding materials and other materials added to the waste stream of livestock farms. According to a recent review by [6], the total P content in manure is very variable and nearly 70% of total P in manure is labile. In manure, Pi accounts for 50% to 90%. Animal manures are grouped into three broad categories based on the moisture content, namely solids (>20 % solids), semi-solids (10–20% solids) and slurries or effluents (< 4–10% solids). Land application of manure to improve soil nutrient and physical conditions has been a well-established and accepted practice in many countries for many decades. In terms of serving as a means of replacing inorganic phosphate fertilizers, the economics of using manures on an individual farm depend on the availability of local supplies and the costs associated with the transport and spreading of the manure. Many factors affect the chemical composition of manures such as type of animal, animal feed used, type of housing, waste handling and storage, type of waste management system, amount and type of bedding used, amount of water and waste feed, and climate [43]. In general, manure P is considered to have lower plant availability than inorganic fertilizer P.

1.3.3.5 Farm effluents

Effluents from dairy farms or piggeries (swine sheds) are a mixture of faeces; urine and water generated from the washings of the sheds and contain more than 98% water and 2% solids. Their P concentrations average about 65 to 70 g litre^{-1}, with higher concentrations from piggery than dairy effluent. Regular applications of farm effluents to agricultural land generally result in increased pasture and crop yields, enhanced soil microbial activity and often reduced soil acidity [44]. Farmers can benefit from land application of farm effluent by reducing fertilizer costs, although increases in pasture yields vary according to application rate, method, time (season) soil P status and climate [45]. In legume-based pasture, effluent irrigation was found to decrease the clover component of the white clover-ryegrass pasture [45]. This was attributed to the N in the effluent inhibiting biological N fixation of the clover and consequently decreasing the clover content in the pasture.

A sustainable land application of farm effluent should be efficient in both retaining the effluent in the soil and the subsequent uptake of the effluent nutrients by plants The longer the effluent stays in contact with the soil, especially in the active plant root zone, the greater is the opportunity for the soil to filter the effluent whilst absorbing its nutrients and making them available to plants. Few studies have been conducted to evaluate the ability of plants to remove effluent P especially the mechanisms of manure-induced P transformation processes between Pi and Po in soil.

1.3.3.6 Bio solids (sewage sludge)

Biosolids are the solid residue remaining after wastewater treatment, and contain waste mineral matter, microbial cell debris and undecomposed organic matter. Sewage sludge and industrial by-products can be a valuable source of P, N, K and trace elements. However, their nutrient content varies markedly both between and within treatment plants and industries [46]. For example, total P concentrations in biosolids generally range from 1–5% but could vary from < 0.1% to as high as 14% [47]. Most of this P is in inorganic forms due to the breakdown of Po and polymeric P in wastewater during treatment. The bioavailability of P in biosolids varies from 10–100% of that in soluble fertilizers [48]. The release of P from Pi and Po in biosolids depends on many factors, including the presence of Fe, Al, or Ca and the forms of P and C in the biosolid.

1.4 Losses of phosphorus sources from agricultural lands and water quality.

The widespread use of P fertilizers in these countries over the last century has led to increased soil P levels in surface and deeper layers [49]. This P, which is surplus to plant requirements, not only increases the cost of using P fertilizers but also enhances the depletion of rock phosphate reserves used for manufacturing P fertilizers. More importantly, it has become a risk to water quality and the environment. Excessive or inappropriate P fertilizer applications have led to considerable losses of P from agricultural land and degradation of surface water resources through eutrophication [50]. Achieving a correct balance between maintaining agricultural production and minimizing P transfer to water resources should therefore, be an important part of future strategies for establishing sustainable agriculture and water quality.

1.4.1 P losses and eutrophication

In terms of their impact and potential for affecting water quality in terrestrial aquatic environments, P sources are often considered as point and non-point (diffuse) sources. Point sources are P discharges from a specific point such as from applied P fertilizers, manures, a milking shed, a sewage treatment plant or an industrial facility, such as a pulp paper factory. Phosphorus from these sources can be traced to a specific “point” or discharge pipe. A non-point P source is diffuse and non-specific, and could arise from any point other than the specific source. Nonpoint sources are generally considered as being approximately equivalent to both (a) the part of P originating from all sources other than sewage and industrial wastewaters, and (b) the part of P originating from agricultural activities and soils. The primary anthropogenic non-point P sources include (a) land areas being mined for phosphate deposits, (b) agricultural areas, and (c) urban and residential areas. As P has a strong affinity for soil, little P is transported in runoff. Most P is transported to the water bodies as eroded sediments from mining and agricultural areas. Non-point source P inputs to a watershed could be derived from diffuse source areas, ranging from a few km to the area of an entire watershed. Only part of the P input from these sources reaches the stream channel; the remainder accumulating within the watershed or lost through human activities such as crop harvesting or animal export. Natural non-point P sources derive largely from phosphate deposits and phosphate-rich rocks which release P during weathering, erosion, and leaching. Phosphorus may also be released from lake and reservoir bottom sediments during seasonal overturns. Separating the relative contribution of point and non-point sources of P to water pollution in catchments is difficult and subject to considerable uncertainty [51]. A diversity of both empirical and modelling approaches is used to estimate these sources.

Eutrophication is the process of enriching surface waters with nutrients causing natural aging of lakes and streams. Phosphorus is generally considered as the macronutrient most frequently responsible for eutrophication problems in freshwater and to a lesser extent in estuarine ecosystems [52]. This process is greatly accelerated by human activities that increase nutrient loading to water especially the inputs of P [53–54]. Eutrophication has been identified as the main cause of impairment of surface water quality in the USA [55], Europe [56], Australia [57], and New Zealand [58]. It restricts water use for recreation, industry, fisheries, and drinking due to the increased growth of undesirable algae and aquatic weeds and the oxygen shortage caused by their death and decomposition. Associated periodic surface blooms of *Cyanobacteria* (blue-green algae) occur in drinking water supplies and may pose a serious health hazard to humans and animals..

Agricultural sources of P inputs from fertilizers and manures are important non-point sources causing eutrophication of water bodies. Since the late 1960s, point P source (e.g. municipal and industrial effluents) pollution of water bodies has been effectively reduced. However, many problems still remain in controlling non-point P source pollution, which impacts on freshwater and seawater biogeochemical cycles [59].

1.4.2 Forms and processes of phosphorus losses

It has generally been assumed that leaching of P is negligible in most soils because P is strongly held by the soil matrix. However, it is now recognised that P leaching losses can be significant in high P, coarse textured soils with macro pore networks. For example, significant leaching of orthophosphate has been reported in soils only partly saturated with P due to excess applications of manure [60]. Continuous applications of organic wastes or manures have raised the soil P to an excessive content while decreasing P sorption capacity thus enhancing P leaching losses [61].

Generally, P losses in grasslands are less than 2 kg ha^{-1} $year^{-1}$, which can be regarded as agronomical insignificant. They are, nevertheless, significant from a water quality perspective because only a few tens of g l^{-1} P can cause eutrophication [62]. In waterways, where the primary production is limited by P, it has been reported that increasing P supply by a few parts per billion led to high growths of algae and associated eutrophication [63]. The general consensus is that all soils are prone to some degree of P leaching losses and that the degree of loss is significantly enhanced in soils, which receive regular applications of P fertilizers and farm manures [64].

Forms of P losses are largely total P (TP) and dissolved P (DP). Particulate P (PP) or sediment-bound P is the dominant form of TP loss. The definitions of DP and PP are arbitrary and based on analytical convenience as P can occur in a continuum of sizes down to near molecular dimensions [65]. Most research on the transport of soil P have used the 0.45 µm filter to separate the "dissolved" and the "particulate" P forms. The DP is sometimes referred to as the unreactive P or the <0.45 µm fraction and the PP as the unreactive P or the >0.45 µm fraction. Particulate P is sediment-bound and includes P associated with soil particles and organic materials eroded during flow events. It constitutes about 80 % of P transported in surface runoff in most cultivated soils but considerably less in surface runoff from grasslands, forests, or non-cultivated soils, where DP predominates (80% of P loss) [65].

Soil P losses from agricultural lands may be divided into three broad categories: (1) flash losses of soluble P soon after fertilizer or manure application, (2) slow-leak losses of soluble P and (3) erosion losses of PP. Manures and phosphate fertilizers contain higher amounts of soluble P than soils. If rainfall occurs immediately or soon after surface application of these fertilizers, the soluble P in the flash runoff can be 100 times higher than that of other runoff events [66]. The soluble P in the flash runoff is readily available to aquatic organisms.

1.4.3 Main factors affecting phosphorus losses from agricultural lands

Nonpoint sources of P loss from agricultural land to water bodies are affected by many factors, the main ones being related to transport and source factors. In most cases, P lost from feedlots and barnyards is greater than from manure application sites or grazing areas [67].

In catchment studies, it has been shown that P loss does not occur from the entire catchment but from small areas within the catchment, which can dominate the P loss to water streams [68]. These areas known as critical source areas (CSAs) are dependent upon many factors such as soil type, topography, management (e.g. inputs of fertilizer and manure/effluent, and take-off in crops or forage) and transport processes related to environmental and hydrological conditions. The interactions between these factors are complex and vary spatially and temporally. In general, CSAs are defined as areas with a high concentration of P available to flow and a high potential for water flow, equating to a high potential for P loss. The identification and mapping of CSAs using geographic information systems (GIS) may enable farmers to better target management practices for mitigating P loss from CSAs.

1.5 The need for sustainable P management strategies in agroecosystems

The world population is expected to reach 8billion by 2020. The projections on population pressure and availability of land and water resources worldwide, several developing countries will face major challenges to achieve food security in a sustainable manner, considering their available per capita land area, severe scarcity of fresh water resources and particular infrastructure and socio-economic conditions. This is further compounded by severe global soil degradation, in particular Sub-Saharan Africa and South Asia and increased risks of soil erosion, in particular desertification. Worldwide soil degradation is currently estimated at 1.9 billion hectares and is increasing at a rate of 5 to 7 million hectares each year [26, 69].

Soil degradation and food insecurity are linked with long term social, economic and environmental degradation impacts that result in human migration and socio-political unrest. Enhancing sustainable food production will require the combined use of the following strategies for land and water resources: (a) agricultural intensification on the best arable lands that are already being farmed with minimum environmental degradation; (b) rational utilization of the marginal lands, and (c) arrest land degradation and restore degraded soils [26, 69]. In order to increase the intensification, diversification and specialization of agricultural production systems towards supporting productivity gains and income generation, innovative soil-specific technologies will have to be developed, pilot tested and transferred in a relatively short time. These technologies needs to address priority issues such as: (i) enhancing cropping intensity by exploiting genotype differences in adaptation to particular environments and nutrient use efficiency; (ii) increasing nutrient use efficiency and recycling through integrated nutrient sources management in cropping systems; (iii) soil and water conservation through crop residue management and conservation tillage; and (iv) improving water use efficiency through the development of efficient methods of irrigation, water harvesting and recycling.

An integrated soil fertility management imply the use of inorganic P fertilizers and other alternative sources of phosphorus, such as phosphate rocks (PRs), biological nitrogen fixation (BNF), and animal and green manures, in combination with the recycling of crop residues [70]. The utilization of these technologies requires the assessment of the nutrient supply from the locally available materials applied as nutrient sources, their tailoring to specific cropping systems and the provision of recommendations for their application [71–73]. Whilst N inputs can be obtained from sources such as BNF, crop residues and other organic sources, external P inputs, in particular inorganic P fertilizers need to be applied in order to improve the soil P status and ensure normal plant growth and adequate yields. Water soluble phosphate (WSP) fertilizers such as superphosphates are derived from rock phosphates and commonly recommended for correcting soil P deficiencies. However, most developing countries import these fertilizers, which are often in limited supply and represent a major outlay for resource poor farmers. In addition, intensification of agricultural production in these regions necessitates the addition of P inputs not only to increase crop production but also to improve soil P status in order to avoid further soil degradation.

Therefore, it is imperative to explore alternative P inputs. In this context, under certain soil and climate conditions, the direct application of reactive indigenous PRs is considered an agronomic and economically sound alternative P source to the more expensive superphosphates in the tropics [74].

Besides these pressing productivity issues, several environmental changes and related degradation problems, which would also need to be addressed include: (a) Increasing risks and impacts of global warming and climatic variability; (b) rising energy demands, in particular renewable energy sources; (c) expanding urbanization and industrialization and related infrastructure development; and (d) deteriorating water and air quality. All of them will likely have negative impacts and induced changes on agroecosystems, thus placing increased pressures on sustainable land and water resources to produce sufficient food, feed, fibre and fuel for the ever increasing world population [75].

In summary, modern agriculture is mostly dependent on the adequate supply of inputs of P fertilizers, which are derived from rock phosphates. The current PRs geological reserves are a non-renewable resource of finite nature and they are estimated to be depleted before the end of the century [76]. From the above it may be inferred that the main challenges for the future management of P are: (a) to supply adequate P inputs to improve soil P status to achieve sustainable intensification of agricultural production and ensure food security in the long term, and (b) to minimize the adverse effects of excess P on the environment. The twin aims of a sustainable P management in agroecosystems should, therefore, be:

Maximize P use efficiency through the judicious use of P fertilizers and other P sources.

Minimize P losses from agricultural land to protect fresh water resources and promote environmental quality.

In order to achieve these goals, it would be necessary to review/analyse thoroughly the global P cycling in terrestrial ecosystems and define integrated strategies to better manage global P resources for food production. These may include current mining and processing systems of PRs, manufacturing, transport and storage of P fertilizers, utilization of P fertilizers in agriculture, reduction in soil erosion and related P losses, crop harvesting, food processing, storage and final consumption as well as recycling of used P in human and animal excreta and food and crop residues [76].

1.6. Research Activities to address P constraints in tropical acid soils conducted by the Joint FAO/IAEA Programme

The development, evaluation and standardization of new technologies using nuclear, isotopic and related methodologies is done through the IAEA Research Contract Programme by promoting global and regional thematic research and development networks called Co-ordinated Research Projects (CPRs). The IAEA provides financial support to conduct research activities agreed in the work plan of the project through the formation of CPRs, which involve scientists from developing countries (5–7 contract holders) and from developed countries including CGIAR Centres, other IARCs and ARIs (3–5 agreement holders). The project duration is normally 5 years with Research Co-ordination Meetings (RCMs) every 18 months [77].

In the frame of the subprogramme on sustainable intensification of crop production systems, the Joint FAO/IAEA Programme of Nuclear Techniques in Food and Agriculture through the Soil and Water Management & Crop Nutrition Section has implemented two CPRs on approaches and strategies to address soil P constraints in tropical acid soils with a view to develop sustainable technologies for intensification of agricultural production systems in these regions [78].

1.6.1 Assessing soil P status and developing improved management practices of P fertilizer inputs

The first two CPRs addressing soil P constraints in tropical acid soils were: "The Use of Nuclear and Related Techniques for Evaluating the Agronomic Effectiveness of Phosphate Fertilizers, in Particular Rock Phosphates" (1993–1998) and "The Development of Management Practices for Sustainable Crop Production Systems in Tropical Acid Soils through the Use of Nuclear and Related Techniques" (1999 to 2004).

Under the first CRP, activities focused on the following topics related to phosphorus in soil-plant systems: (a) to assess the initial available soil P status and fertilizer-induced changes when amended with rock phosphate (RP) products and water soluble P fertilizers using conventional (chemical) and isotopic techniques; (b) to quantitatively evaluate the uptake and utilization of P fertilizers, in particular rock phosphate-based products, thus the project aimed at evaluating the agronomic effectiveness of natural rock phosphates and where necessary to finding ways/means of enhancing their effectiveness, and (c) to obtain agronomic and economic recommendations on the use of P fertilizers, in particular rock phosphate products in acid soils [79].

Under the second CRP, an integrated approach to crop, soil, water and nutrient management in predominant cropping systems grown in tropical acid soils was adopted [78]. The objective was to develop management practices for improving sustainable crop production in tropical acid soils along three main areas of investigation: (i) use of acid-tolerant and P efficient plant genotypes (ii) ameliorating soil acidity and infertility of tropical acid soils, and (iii) develop integrated crop, soil, water and nutrient management for the sustainable agricultural production in acid savannah soils [80].

Both projects generated a wealth of information on soil and fertilizer P management practices, in particular the potential use of reactive indigenous PRs to build up the soil P capital in tropical acid soils. The participants have produced many publications on these topics. Among them, two special issues in scientific journals, two IAEA publications and a FAO Bulletin on the direct application of rock phosphate in agriculture have been produced [26, 79–82]

The generated information has been compiled in a PR database with chemical and agronomic entries and a decision support system for the direct application of phosphate rock (PR-DSS) was developed in a joint venture with IFDC. A dedicated website on direct application of phosphate rock (DAPR) has been also developed for wide dissemination of the results to land managers and policy makers [83].

1.6.2. Adapting plants to the soil P constraints

The identification of plant genotypes with adequate yield potential, efficient in nutrient use and tolerant to specific soil and environmental stresses (drought, acidity, salinity, frost, etc.) will be of strategic importance. This approach is currently being utilized for the sustainable management of P deficient acid soils [78, 79, 84,].

Plants differ greatly in their ability to grow on low P soils because they have developed specific physicochemical mechanisms/processes to utilize P compounds in these low P fertility soils, often with intervention of micro-organisms present in the soil-root interface called rhizosphere. Some authors prefer to use the term acquisition rather than uptake [85]. These mechanisms include (i) alterations (morphological and physiological) of root systems, i.e. mycorrhizal plants have better water uptake and Al tolerance in acid soils [86] (ii) secretion of low-molecular-weight organic compounds (exudates production), i.e. malonic, oxalic, citric, malic and piscidic acids secreted by roots of pigeon pea help to release low-soluble P compounds in soils [87–89] (iii) secretion of enzymatic compounds, i.e. phosphatases, and (iv) plant molecular changes such as enhanced expression of P transporters. The role of plant root morphology and architecture for enhanced soil exploration and P acquisition has been extensively reviewed [90–91]. Exploiting these mechanisms in P acquisition and utilization by crop genotypes is one of the strategies recommended to enhance the agronomic effectiveness of phosphate rocks for direct application to P deficient acid soils.

In this context, a TECDOC “Optimizing productivity of food crop genotypes in low nutrient soils” generated a lot of information on root traits related to N and P acquisition and provided valuable resources for plant breeding programs aimed at enhancing P and N use efficient in cereal and legume crops. ^{32}P tracer methodologies to evaluate the differential ability of cereals and legumes to utilize soil P for plant growth from total P, available P, and inorganic (Fe-P, Al-P and Ca-P) soil P pools have been developed [92].

The IAEA has also implemented a research network on the application of irradiated sewage sludge to agricultural lands to: (i) characterize irradiated an non-irradiated sewage sludge in terms of physical and chemical properties, content of pathogen organisms and toxic organic compounds; (ii) study the crop response to sewage sludge application and measure nutrient (N and P) uptake using isotopic techniques and (iii) assess risk contamination of soils and crops by sludge-derived heavy metals. Irradiation increased N but not P availability in sludge and increased response of a variety of crops to sludge application under variable soil and climatic conditions. Sludge was a good source of P, particularly in soils of high fixation capacity [93].

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CHEMICAL, NUCLEAR AND RADIOISOTOPIC TRACER TECHNIQUES FOR STUDYING SOIL PHOSPHORUS FORMS AND ESTIMATING PHOSPHORUS AVAILABILITY, FLUXES AND BALANCES

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Abstract

Estimations of P balances and fluxes are used in achieving the major objectives of improving P use efficiency in sustainable agricultural production and minimizing potential P losses to the environment. Farm P balances and fluxes when considered together with the results of soil test measurements would provide the first indication of where P inputs or outputs could be managed to achieve these objectives. The use of ^{32}P and ^{33}P isotopes in P flux and balance measurements offers considerable advantages over conventional techniques to identify P sources and quantify their impacts

1 INTRODUCTION

Numerous procedures have been developed and used to conduct phosphate studies in soil-plant systems and their individual compartments. Isotopic methods are becoming increasingly important, not so much as routine methods but more in investigating the soil P kinetics processes and the soil and plant factors that affect the availability of P to plants. The paper describes a range of conventional (chemical), nuclear and isotopic techniques to identify soil P forms and determine plant available P in soils, and estimate P balances (inputs and outputs), and fluxes in farming systems.

1.2. ^{31}P Nuclear Magnetic Resonance (^{31}P NMR) Spectroscopic Methods

Application of the ^{31}P NMR technique to soil P studies is a recent and rapid development [1–3]. More than 350 publications dealing with the use of the technique for agronomic and environmental studies have been cited [4]. It is an ideal analytical technique for differentiating and quantifying elements in different environments, being particularly well suited for P characterization because the ^{31}P nucleus is NMR-sensitive (more so than ^{13}C or ^{15}N) with 100 % natural isotopic abundance and a nuclear spin of ½ that ensures relatively easy detection and spectral interpretation. In addition, the technique provides the opportunity to identify simultaneously many important classes of P compounds in soils, especially soil Po. Thus, it eliminates the elaborate and often time-consuming chromatographic preparation and separation involved in identifying specific Po species in soil extracts [5].

The identification of compounds by ^{31}P NMR is based on their chemical shift relative to that of an external H_3PO_4 standard [6]. The chemical shift, δ, is defined as:

$$\delta \ = \frac{V_s - V_R}{V_R} \times 10^6 ppm$$

where V_S and V_R are respectively the frequencies of the sample and reference standard relative to that of the applied magnetic field.

The δ values are dimensionless and are expressed in parts per million (ppm) with the external standard set to 0 ppm. As δ values depend primarily on the degree of molecular shielding around the P nuclei, they can be modified by surrounding chemical factors, such as ionic strength, pH, probe temperature and the presence of paramagnetic ions (e.g. Fe).

Most solution ^{31}P NMR studies of environmental samples rely on chemical shifts of model compounds reported in the literature, added as a spike to soil extraction solutions. To partly overcome this problem, [7] studied the chemical shifts of a wide range of P compounds in a soil NaOH-EDTA extract matrix and recommended from their results that a standard operating temperature of 20°C be used for solution ^{31}P NMR.

Both solution and solid state ^{31}P NMR have been used to characterize P in soils and related materials. According to [8], each mode has its inherent advantages and disadvantages. Solution NMR spectra provide much better resolution than solid state NMR but are restricted to soluble species only. However, there is no general agreement on the best extractant to use for solution ^{31}P NMR. A number of extractants have been investigated by various workers such as NaOH [9], bicarbonate [10] and 0.01 M $CaCl_2$ [11]. Nevertheless, the most favoured extractant used in many studies is a combination of NaOH and EDTA [12–13]. For manure samples, [14] showed that 0.25 M NaOH-0.05M EDTA provided a good compromise between efficient soil Po extraction and minimizing hydrolysis to yield the highest possible peak diversity in spectra.

Solid state ^{31}P NMR spectroscopy has the unique advantage of identifying P forms in soils as solids without the need for extraction or pre-treatment. This technique has been mainly used for the characterization of Pi in soils and other materials [11, 15] although it has also been used for Po in some studies [16]. The inferior resolution compared with solution ^{31}P NMR has limited the wider use of solid state ^{31}P NMR [17]. In addition, paramagnetic species, especially Fe, also limit the quantitative potential of solid state ^{31}P NMR. Significant improvements in solid state ^{31}P NMR are possible based on non-frequency parameters, such as observability, chemical shift anisotropy and relaxation rates [8].

Among the different forms of P identified in soils by ^{31}P NMR, orthophosphate diesters, including phospholipids and nucleic acids are most readily converted to plant available P under favourable soil conditions [18]. Monoester phosphates are regarded as being more stable than diester phosphates due to the formation of monoester phosphate complexes with Fe and Al [13]. The ratio of diester: monoester has been used as a measure of Po lability [19–20]. An increase in this ratio indicates increased microbial activity since phosphate diesters are considered to be primarily of microbial origin [21].

The greatest proportion of labile orthophosphate diesters occurred in native, uncultivated soils while only recalcitrant orthophosphate monoesters were found in soils that had been cultivated annually for 70–80 years [22]. A report from [23] showed in 24 diverse pasture soils in New Zealand, monoesters comprised the major class of Po (24–60% of extracted P), consisting of 14–91% *myo*-inositol hexakrisphosphate. The next largest Po class was diesters (0–4% of extracted P), which were higher in volcanic ash soils (monoester to diester ratio = 14) compared with non-volcanic ash soils (ratio = 30). This difference was attributed to a combination of decreased mineralization, high natural organic C and microbial biomass in volcanic ash soils. According to [24] the concentrations of orthophosphate monoesters in pasture soils in the United Kingdom (UK) were indicative of the potential chemical stabilization (i.e. protected against mineralization) of Po. However, [25] reported that in New Zealand grassland soils, orthophosphate monoesters were biologically active, being mineralized by radiate pine (*Pinus radiata* D. Don) seedlings and ryegrass (*Lolium perenne* L.).

In addition to identifying the above soil Po forms, ^{31}P NMR has revealed the presence of Pi compounds in soils such as orthophosphate, pyrophosphate and polyphosphates [22].

The forms of P in composts have been studied by various workers using ^{31}P NMR spectroscopy techniques. For example, [26], showed that composts made from peat and fish and crab wastes contained orthophosphate, calcium phosphate and organic phosphate, while [27], using solid state ^{31}P NMR, reported the presence of a range of slightly soluble and ill-crystallized Ca-P compounds such as apatite or octa-calcium phosphates in alkaline composts made from garden and solid kitchen wastes. Using isotopic exchange and sequential extraction techniques, [27] reported that composts contained relatively large concentrations of rapidly available Pi, confirming the results of other workers [28–29].

1.3. Conventional soil testing techniques for assessing available soil P.

Conventional techniques for assessing P availability in soils are based on soil testing methods for phosphorus (P). These soil P tests have been developed over more than 100 years [30] and have been used as routine procedures for making P fertilizer recommendations in the USA since 1940 [31]. These chemical methods have also been widely used in many developed countries for the past 65 years as important tools for managing P in agricultural production.

Excellent reviews on the topic including the advantages and disadvantages of the various methods have been published by several workers (e.g. [31–34]. According to [33–34], specific aims of soil tests include: (a) to accurately estimate the P status as an index of the amount of P a soil can supply to the crop over a growing season, (b) to clearly indicate P deficiency or excess for the crop, (c) to predict the probability of a crop response to P fertilizer application and thereby to use this as a basis for P fertilizer recommendations, and (d) to provide results for economic evaluation and recommendations. Thus, a soil test is more than simply a chemical analysis since it involves soil sampling, extraction, interpretation of results and making a fertilizer recommendation. Each of these steps in the whole process is important to ensure success and has to be based on extensive research.

Conventional soil test methods are based on the use of either direct chemical extractant methods to extract a portion of the soil P, or using ion sink methods based on P sorption-desorption processes. A wide range of chemical extractants are used for direct extraction of soil P including water [35], dilute acids [36], dilute acids plus a complexing agent [37], buffered alkaline solutions [38] and multi-nutrient extractants [39–41]. Some of the more common chemical extractants (or mixtures of extractants) and the soil: extractant ratios used are shown in Table 1.

TABLE 1 SOME COMMON CHEMICAL EXTRACTANTS USED IN SOIL TESTS (Source: [modified 31, 34].

Extractant	Soil:Extractant Ratio	Name of Procedure
0.025N HCl + 0.03N HH_4F	1:10	Bray 1
0.1N HCl + 0.03N NH_4F	1:17	Bray 2
0.5N $NaHCO_3$ at pH 8.5	1:20	Olsen
0.05N HCl + 0.025N H_2SO_4	1:4	Mehlich 1
0.2N CH_3COOH + 0.2N NH_4Cl + 0.015N NH_4F + 0.012N HCl	1:10	Mehlich 2
0.2N CH_3COOH + 0.25N NH_4NO_3 + 0.015N NH_4F + 0.013N HNO_3 + 0.001M EDTA	1:10	Mehlich 3
0.005N H_2SO_4 buffered at pH 3.0 with $(NH_4)_2SO_4$	1:100	Truog
0.54N HOAc + 0.7N NaOAc at pH 4.8	1:10	Morgan
0.02N Ca lactate + 0.02N HCl	1:20	Egner
1% citric acid	1:10	Citric acid

Ion sink methods are relatively more recent and include the use of an anion exchange resin and an iron oxide impregnated filter paper or strip [34, 42–43]. Early resin methods used beads that were freely mixed in the soil-water suspension [44], while later methods involved placing beads in nylon netting bags immersed in the soil suspension [45]. However, fine root materials and soil particles could be trapped in the bags and therefore this method was improved by using anion exchange resin in membrane form (AERM) [34, 46] to facilitate separation of beads for routine analysis.

The iron oxide impregnated method uses strips of filter paper saturated with iron chloride ($FeCl_3$) and then exposed to NH_3 to convert the $FeCl_3$ to iron oxide [47–49]. The soil P is extracted by placing the paper strip in a suspension of soil in a 0.01M $CaCl_2$ solution. Like the resin method, the iron oxide strip test acts only as a sink by adsorbing and retaining the P entering the soil solution. Phosphorus ions are removed from the soil onto the iron (hydro) oxide surfaces of the reactive strip. The P adsorbed by the strip is extracted with 0.1 M H_2SO_4 after the strip has been washed free of soil. The method was found to be effective for extracting plant available P [48].

1.3.1 Factors affecting extractable soil phosphorus

The value obtained in a soil test is affected by many factors including those associated with the extraction technique and conditions in the laboratory, and external factors such as soil sampling, soil properties and variability, analysis of P in the extracted solution, and interpretations of results. Most laboratory procedures use closed batch systems where the soil:extractant ratio is fixed, and inter-laboratory accreditation schemes have improved the accuracy and reproducibility of analytical results [50]. However, the amount of P extracted varies not only between methods but also with the ratio employed and the individual soil samples. Obtaining a soil sample for analysis that is representative of a whole field is an area of concern. The soil sample collected for a soil test usually represents only one part per ten million of the bulk sample it is considered to represent [51]. Since soils are heterogeneous, there is often disagreement as to what constitutes an appropriate sample [33].

In addition to spatial variability, many soil properties affect the amount of P extracted by soil test methods including extractable Fe, Al, and Mn oxides, clay content, $CaCO_3$, organic matter content, soil pH and soil P sorption capacity [52–53]. The depth of soil sampling is also known to affect soil P test values [54–55], and the standard 0–75 mm soil depth recommended for grassland soils [56] is not suitable for deeper rooting crops or trees. However, in reduced tillage systems a shallower soil sampling depth is preferred [33].

The approach used for soil sampling by most testing laboratories is based on classical statistics and involves collecting and bulking a large number of soil cores from random locations across the area to be sampled for analysis as allowed under given logistics and cost conditions.

Soil test results are also affected by the method used to analyse the P in the extracted solution. The P in most extracts is generally analysed colorimetrically using the phosphomolybdate reaction. Inductively coupled plasma (ICP) methods have become more widely used [31]. These have the advantages of being quicker and allowing the quantitative determination of P and other plant nutrients in a single analytical operation. Several workers reported that the amount of P measured by ICP could be 50% higher than that obtained using colorimetric methods [57–59]. It was recommended that methods using ICP needed to be calibrated differently from those based on traditional colorimetric methods [60], and it has been suggested that the higher P levels measured by ICP methods were due mainly to Po but no consistent relationship has been found between the additional P measured with ICP and manure or soil organic matter [61].

1.3.2 Comparisons of direct chemical extraction and ion sink methods

Direct chemical extraction methods are rapid, inexpensive, and amenable to automation and can, therefore, handle a large number of soil samples for routine soil testing. The principal aim of the direct chemical extraction method is to extract the labile Pi in the soil (i.e. Pi fraction that can move into soil solution). No attempt is usually made to determine the possible contribution of Po to plant P uptake. Some extractants may extract more than labile Pi and include non-labile or stable soil P [52], or fail to extract labile Pi in soil types for which they are inappropriate [62]. For example, acid extractant such as Bray-1 cannot be used on calcareous soils because neutralization of the extractant occurs. On the other hand, Bray-1 and Mehlich-3 extractants are designed to extract P from non-calcareous soils or soils with a pH less than 7.4 [37, 39], while the Olsen test is preferred for calcareous soils although it can also be used for soils with a pH near 5.0. The Mehlich-3 test has been found to be similar to Bray-1 in acidic or neutral soils but is better than Bray-1 in many calcareous soils in Iowa in the USA [63].

The Olsen P test is also widely used for pasture soils in New Zealand and has been found to be a useful test. However, it can produce variable results, often in the order of 20%. Olsen P values do not decline in direct proportion to the amount of P removed by harvested crops suggesting that P uptake by plants is replenished from sources other than those measured by this test [64].

Unlike chemical extractants, P ion sink methods do not alter the chemical and physical characteristics of the soil. The resin and iron oxide strip acts as a sink for P by absorbing and retaining the P entering the soil solution in the same manner as plant roots [65]. One of the main advantages of resin methods is that resins can be re-used several times without losing their extracting power [66]. The resin and iron oxide strips are regarded as being superior to the traditional chemical extraction methods because they are less influenced by soil type and can be used in acid, alkaline and calcareous soils [67–68]. In biosolid-amended soils with relatively high P retention capacity, the iron oxide paper strip method [69] was effective in assessing available P. In paddy soils of Tanzania [70] the iron oxide strips were effective for extracting P from wet soil samples after flooding or by direct embedding of the strips in the flooded soils. In three soils in Zambia, the iron oxide strip method was consistently more related to P uptake and dry matter yield of maize than was the Bray-1 extraction method [43].

However, there are some disadvantages of using P ion sink methods. For example, the resin method is affected by the soil: solution ratio [41]. The resin strip size and total area need to be standardized [53, 71–72]. Also, the iron oxide impregnated paper strips are not readily available [73], and soil particles can contaminate the paper strips during shaking [74], leading to error in estimating the desorbable P.. It was reported that the resin and iron oxide sink methods over-estimated the P status of soils which had received PR applications. This occurred in soils with low PR dissolution rate [75].

1.3.3 Interpretation of soil test results for fertilizer recommendations

An important practical aspect of soil tests is their use in obtaining critical P values, i.e. P concentrations for interpreting probable crop or pasture responses to P fertilizer applications. These values are calibrated against results obtained over several years for plant yield responses to fertilizer rates applied through experiments in the field or pot trials in the glasshouse. The calibration involves determining the relationship between soil test P values and either the yield of the crop or pasture or their likely response to P fertilizer applications. The interpretation assumes that above a critical P value there is a low probability of response (generally no response) to P fertilization, and below this value crops are likely to respond. This soil test information is generally incorporated into a model for fertilizer recommendations which takes into account the climatic conditions and estimated specific crop yield responses to applied fertilizer rates [32]. The early model used was the Mitscherlich response curve incorporated into the “Decide” model [76], and later the Mitscherlich-Bray [77] and other mechanistic models were developed [78].

P fertilizer recommendations are based on either fertilizing the soil or the crop. Fertilizing the soil is aimed at building the soil P test value to a level determined by field calibrations [79], to be adequate for optimum crop or pasture yield before maintaining this optimum yield over time by replacing the P removed by the crop or pasture [56]. This approach works well with periodic soil testing strategies. Difficulties for accurately predicting the amount of P required to maintain soil P test values are overcome by using assumptions to keep these values close to the optimum range. The “fertilizing the crop” approach is based on applying sufficient P to achieve an optimum crop response at a given soil test value [80]. This approach is most suitable for short term economic and land tenure conditions [79].

Soil P test interpretation and P fertilizer recommendations are largely empirical. For example, [80] in comparing the iron oxide strip method and four other chemical extractant methods for four crops on lateritic soils in south-western Australia found that for each soil test method and plant species the relationship between yield and soil test values varied with the fertilizer type and year, requiring different calibrations. Because of the very wide range of conditions under which soil P tests are used even within a given geographical area, the amount of calibration and response data required to support soil tests becomes astronomically large [79]. Furthermore, the search for a soil P test method capable of predicting plant responses suitable for routine soil testing under a wide range of soil, crop and climatic conditions across different regions or countries has not been successful [48].

1.3.4 Supplementary soil tests to improve interpretation of conventional soil P test results

The interpretation of conventional soil P test results for fertilizer recommendations can be improved by supplementing the results with additional information from other soil tests and measurements such as those for soil properties (e.g. soil pH, oxalate-extractable Fe and Al, free carbonate content, etc.), P dynamics (e.g. soil P retention, sorption and buffering capacities), land fertilizer history, farming practices used, plant species grown, their requirements and also plant tests [81–82]. In addition, relating P extracted by different conventional chemical extractants to estimates of P balances and fluxes can also aid in identifying where and how P inputs and outputs could be better managed.

The measurement of available soil P needs to consider the amounts and rate of release of P from the soil solid phase. The dynamic nature of soil P and the response of soil test value to actual quantitative soil P changes are not known [83]. Little information is available on the relations between soil P test values and exchange characteristics relating to P sorption on soil surfaces (P quantity, Q), in solution (P intensity, I) and P buffer power (dQ/dI). In New Zealand, phosphate retention measurements are conducted to aid interpretations based on Olsen P test results [84]. The P retention test, now known as the anion retention capacity test, measures the amount of added phosphate (1000 μg P ml^{-1}) retained by five g soil in 24 h, shaken at 20 °C in 25 ml of sodium acetate-acetic acid buffered at pH 4.6. It provides an estimate of the soil's capacity to fix P and is related to the amount of short range order Fe and Al compounds present in the soil. A soil with a high P retention value (i.e. well buffered) requires more P fertilizer to increase P soil test values and to maintain these once the P critical value has been obtained.

In Australia, the soil test method most commonly used is the Colwell method [85]. This method uses 0.5 M $NaHCO_3$, a soil: solution ratio of 1:100 and a 17 h extraction period. It has been shown that Colwell test values are affected by the soil buffer capacity [86]. Numerous methods have been used to measure P buffer capacity, the most common in Australia being based on the amount of P sorbed between P concentrations of 0.25 and 0.35 mg P $litre^1$ [87]. A single addition of P sorption index known as the P Buffer Index (PBI) was developed recently and was found to be highly correlated with the buffer capacity measured by the Ozanne and Shaw method [88]. However, a combination of the Colwell-P method and the PBI offers the most efficient approach for assessing P status and availability for five crops in Australia [83]. Both PBI and Colwell-P methods are amenable to commercial laboratory operations [89].

Soil P fractionation schemes, especially those involving sequential fractionation, have been employed by several workers (e.g. [90–93] to determine the fate and long term availability of added P fertilizers in soils and also the effects of cropping and management practices (e.g. cultivation) on P status and availability [94–96].

The basic assumption of sequential fractionation methods is that readily available P or fractions with higher lability are extracted first with the mild extractants and the less available and /or unavailable P fractions are extracted later by stronger acids and alkalis. Soil P fractions have been grouped into readily available, sparingly available, and reversibly available P functional pools [97]. Relationships between these P fractions have been identified in sorption studies [98] and quantified in path analysis [99]. While differences between P fractions due to management and fertilizer practices have been reported, it has generally not been possible to isolate an individual P fraction as the dominant contributor to plant P availability [100–101].

The limitations of P fractionation methods have been discussed by several workers, the main difficulty being finding a relationship between the bioavailability of soil P to plants and its chemical solubility (e.g. [97, 102–106]. The division of soil P into fractions or functional pools remains arbitrary as available P is a dynamic continuum which changes with time.

1.4 Radio isotopic techniques

Radio isotopic techniques were first proposed [107] to study P uptake by crops from phosphate fertilizer. Since then they have been used extensively to assess soil P availability and study soil P dynamics in ecosystems [108]. These techniques provide a powerful alternative means for characterizing soil P availability with minimum modifications to soil P forms compared with conventional chemical extraction methods. Earlier applications of these techniques were related to measure the quantity of available P in soils in determining the E-value or exchangeable P in the laboratory [109], and the L value or labile P [110] and the A value or available P [111] using plants. The basic assumption of the A value is that when a plant is presented with two sources of P (soil and fertilizer), it will absorb P in direct proportion to the respective amount available from each source. The A value has been used widely not only to estimate the amount of plant available P in soils but also to evaluate residual P from previous P fertilizer applications, P placement, and other factors. Detailed definitions, principles, calculations, and procedures for determining E-, L-, and A- values are presented in the next paper.

1.4.1 Comparisons of E, L, and A values

Comparisons of these values are well documented although more comparisons were reported for E- and L- values than with A values. Several workers have compared E- and L- values many times (e.g. [112-115]. Good correlations between these values were reported [115], and also found to be better in assessing soil P availability than A-values [116].

E and L values have a similar conceptual basis (see paper 3). Also, unlike the L value, the E- value has the advantage of providing a quick measure of exchangeable Pi in soils in the laboratory without the need of having to grow plants. However, since it is measured in a dilute soil solution the E-value does not reflect the same conditions of being exposed to plant roots in the soil. Hence the E-value has been reported to be less successful in soils with high P retention [112] and also in soils with very low P levels such as soils in the tropics [117–119]. Different E and L values have also been reported [42]. These discrepancies could be due to (a) specific sorption of the labelled orthophosphate on soil surfaces, (b) the difficulty of determining very small amounts of Pi accurately, and (c) the assumed isotopic equilibrium had not been reached between the added Pi and soil orthophosphate at a given time [42]. The interference of seed P was also cited as a possible factor [117].

The L value has the unique advantage of being a biological measurement. However, it is based on the assumption of an equilibrium being attained between the added ^{32}P and the exchangeable P in the soil [110, 120–121]. Such equilibrium may not be established particularly in soils where fertilizer P has been applied recently. Thus an L value measured long after labelling may over-estimate the exchangeable P value [108]. For acid tropical soils, [43] E and L values were suitable for ranking treatments but not precise enough to identify plant species or cultivars in terms of their ability to take up P from slowly or non-exchangeable P pools or to quantify the rate of P mineralization in soil organic matter.

The A value approach has been found to be very useful for assessing the P availability of PRs because it is not possible to label PRs with ^{32}P in the same manner as with fertilizer P without making significant changes to their properties. This method has been used for determining the agronomic effectiveness of PRs [122–123]. However, A values have been found to vary with many factors such as rate and method of fertilizer application [116].

A review on the use of tracers to investigate phosphorus cycling in soil-plant systems proposed three most challenging research areas that need attention [124]. These include (1) extending modelling efforts to predict the rate of soil solution replenishment with Pi as a function of soil properties and management (2) the measurement of organic P mineralization to soils that contain very little available P and that have a high sorbing capacity for Pi and (3) assessing the importance of pool substitution in assessing the fate of P from organic exogenous sources in soil-plant systems

1.4.2 The isotopic exchange kinetics (IEK) method for determining soil phosphorus status and its availability

Soil P status and its availability is governed by a combination of intensity, quantity and capacity factors, and these methods provide only the quantity factor of soil available P [125].

The isotopic exchange kinetics (IEK) method, which has been described in detail elsewhere [124, 126–127], can be used to describe the three parameters of intensity, quantity and capacity and has been used to characterize P availability in a wide range of soil types, fertilizer- and bio solid-amended soils [124, 126–127] and also soils treated with natural or modified PRs (e.g. [77, 128–130].

In the IEK method, the quantity factor is defined as the isotopically exchangeable P (Et) measured in a soil suspension (water) at a time t. It represents the plant available P reserve [124, 131]. The capacity factor is described by the rate at which P disappears with time from the soil suspension [132] while the intensity factor is represented by the P concentration in the soil suspension.

According to the IEK method, when ^{33}P (or ^{32}P) ions are added to a soil system that is in steady-state equilibrium, the radioactivity in solution decreases with time according to the following equation:

$$r(t)/R= \{r(1)/R\}\times\{t + [r(1)/R]1/n\}-n + r(\infty)/R \qquad (1)$$

where: R is the total radioactivity introduced; r(1) and r(∞) are the radioactivity remaining in the solution after 1 min and at infinity respectively; and n is the parameter describing the rate of disappearance of the radioactive tracer from the solution after the first min of exchange. The n is calculated as the factor (slope) of the linear regression between log [r(t)/R] and log (t). The ratio r(∞)/R, is the proportion of ^{33}P in the soil solution when the isotopic equilibrium or maximum possible dilution is reached [133]. For isotopic exchange of less than 60 min, Eq. (1) can be simplified as follows because [r(1)/R]1/n and r(∞)/R can be ignored:

$$r(t)/R = [r(1)/R] \times t\text{-}n \qquad (2)$$

The quantity, E (t) (mg P kg^{-1} soil), of isotopically exchangeable P at time t can be calculated by assuming that ^{31}P and ^{33}P ions have the same fate in the system, and at time t the specific activity of the phosphate ions in the soil solution is similar to that of the isotopically exchangeable phosphate ions in the whole system:

$$r(t)/(a \times Cp) = R/E(t) \qquad (3)$$

where: a represents the soil: solution ratio and Cp is the water soluble P (mg P L^{-1}). The term (a x Cp) is equivalent to the water soluble P in the soil expressed as mg P kg-1 soil. By combining Equations (2) and (3), E(t) can be obtained as:

$$E(t) = E1min\ t \qquad (4)$$

For t = 1 min.,

$$E1min = a\ x\ Cp/[r(1)/R] \qquad (5)$$

r(1)/R is the ratio of the radioactivity remaining in the solution after 1 min to the total radioactivity introduced and is considered as an estimate of the P buffering capacity of the soil [119, 132].

Soil P is considered as a continuum of P pools and not as a number of distinct pools of plant available P in the IEK approach. The pools release P via one another into the soil solution over time [103, 124]. Many investigators have defined P exchangeability operationally into that exchangeable within discrete time frames. For example, the data derived from the short term (100 min) kinetics of isotopic exchange can be used to derive P exchangeable over at least 3 months by using a model [133]. The compartments of P that is exchangeable with plant available P [105] is well defined as P exchangeable between:

One min and 24 h which corresponds to the time frame where a root can take up P actively;

Twenty four h and 3 months which correspond to the time frame of growth for a root system annually;

Three months and a year; and

Periods of 1 year and longer

The two major methodological advantages of the IEK method are that it can be used to generate multiple estimates of P availability from only one IEK measurement, and there is no requirement for the system to reach equilibrium [134]. However, the amount of added tracer must be small in comparison with the total pool of P that receives the tracer [126]. In addition, and as mentioned earlier, for soils in the tropics with very little P present, accurate determination of this small amount of P may be a problem [42], although improved methods for measuring very small concentrations of P have been developed [124, 135–136].

1.5 Using soil P tests for predicting soil phosphorus losses

In the last two decades, there has been considerable interest in using conventional agronomic soil tests, also known as soil test Ps (STPs), as indicators of the potential for P losses from agricultural land [137, 138, 142]. Some of the major advantages of using STPs are that they are relatively inexpensive and are readily available since routine soil testing is widely conducted. Thus, more emphasis has been given to using STPs to assess potential P losses (e.g. [151, 138–139]. Several researchers found good correlations between STPs and P losses in runoff, with results showing higher P losses with higher STP values (e.g. [83; 140–141].

Three main problems of using agronomic STPs on their own to indicate potential P losses have been identified by [142]. These include: (a) transport processes connecting a site with surface waters, (b) management factors such as manure applications and tillage practice, and (c) proximity to a water body sensitive to P inputs. Another major deficiency of using STP measurements to infer environmental P losses is the soil sampling depth. In general, most mobilization of P resulting in P losses occurs in the top ca. 0–20 mm soil [143], but the root zone soil depth (i.e. 0–100 or 0–150 mm) is used in STP measurements. In addition, STP measurements are not precise enough to include measurements of important soil attributes that affect P losses such as P accumulation at the soil surface, water-extractable P in soil organic matter, and organic matter interferences with P sorption. Thus, a universal STP threshold limit is not likely to adequately protect water quality within a landscape or across all soils and regions.

In order to overcome some of these problems, several new STPs known as environmental soil tests have been developed and used by different workers. For example, the iron impregnated filter paper strips and the anion exchange resin methods presented earlier have been used [144] as well as the water soluble P (WSP) [140, 145]. Another environmental soil test is the degree of phosphate saturation (DPS) test, calculated as the ratio of acid ammonium oxalate P to [Al + Fe] [146–147]. This test has been found to be closely correlated with P concentrations in leachate waters [138, 148]. Much research has shown that the dissolved reactive P (DRP) concentration in runoff is related to the STP concentration in the topsoil (e.g. [149–150]. However, in their review [151] concluded that the relationship between DRP and Bray 1 P varied among soils.

The relationship between runoff P and soil P were compared [152] by using simulated rainfall on three soils and a number of soil and environmental test measurements such as Mehlich 3 P, WSP, ammonium oxalate saturation index (PSI_{ox}), water soluble P saturation index (PSI_{wsp}), P saturation index calculated from Melich 3 P, and P_{sat} calculated from P adsorption isotherm maximum (S_{max}). Significant relationships were obtained between DRP and the different P saturation indices but the regression relationships of these indices also showed significant differences indicating that these relationships were site specific. Using the

IEK method, [153] P loss to overland and subsurface flow was best related to P exchangeable within one min and less to that determined up to 24 h. It was postulated that with further research the IEK approach may provide a useful means of predicting potential P losses from agricultural soils to overland and subsurface drainage waters.

In general, most researchers have reported that agronomic STP and environmental soil tests are well correlated to each other and that the latter generally show slightly higher correlation coefficients when compared to P losses in runoff and leaching [144]. However, agronomic STP [144] is a better predictor of plant P uptake than environmental tests and hence environmental tests are not likely to replace STP for routine soil tests. The lack of a clear indication that environmental soil tests can provide a better prediction of soil P losses indicates that there is little justification in conducting a second soil test [142]. The Mehlich 3 P test has been suggested as a possible single soil test to fulfil the dual objectives of agronomic and environmental tests since the Mehlich 3 extraction generates the agronomic Mehlich 3-P as well as the environmental Mehlich 3-P saturation ratio (defined as molar ratio P/(Al + Fe) or P/A) [152, 154]. As a compromise, it was proposed that agronomic soil tests could be used to identify soils which are likely to pose a risk of excessive P losses and environmental soil tests could then be conducted on those soils which pose such a risk [155].

1.6 Determination and estimation of phosphorus balances, inputs, outputs, and fluxes

1.6.1 Phosphorus balances, inputs and outputs

The P balance approach employs a system of accounting the amounts of each material and the P concentrations entering (inputs) and leaving (outputs) a farm or a given system for a defined period. The main objective of establishing a P balance is to achieve adequate levels of the P inputs and outputs in the field or farm to meet the crop and animal requirements while at the same time not exceeding levels that could cause a potential risk of P loss to the environment. Once the balance has been established, land treatment practices may then be applied to overcome P losses or deficits.

In a given field or system, when P inputs consistently exceed outputs (i.e. balance is positive), an excess of P is present in the system [156]. This is regarded as a P imbalance which could result in: (a) direct P loss to the environment; and/or (b) an increase in P reserves in the soil enhancing the risk of environmental P losses over time [157–158]. This imbalance is increasingly being referred to as a P “surplus” and represents inefficiency in the production system. If the difference between P inputs and outputs is negative, it implies that P is depleted from the system. If the soil P status is high due to high P accumulation, then this may be beneficial but if P status is low, this may result in low soil P test values and crop deficiency.

A P balance can be constructed by various means including interviewing farmers or land users to collect the information on inputs and outputs of materials and P to the farm in order to construct the P budget. Very few nutrient budgets are derived from direct *in situ* or field measurements of all inputs or outputs [156] and this has caused difficulties in the accuracy and ease of constructing nutrient budgets [159].

Phosphorus balances can be constructed for different scales (individual farm, county, region, watershed, state, or even entire country) and for different purposes [160–161]. The knowledge of the P balance at different scales allows the identification of “areas” that require to be managed differently to reduce excess P or overcome P deficiency. Within farm systems, three basic types of nutrient balance (Table 2) are commonly used, and there may be variants within each [157, 159]. The farm gate balance (i.e. a black box approach) includes simple assessments of farm gate inputs and outputs, while the soil surface balance requires more detailed data on fluxes across the soil surface. The soil system balance requires even more detailed information and involves partitioning the net loading changes between system components (Table 2) [157, 159].The different levels of balance provide specific benefits, but the increasing complexity increases uncertainties associated with more detailed data acquisition. The farm gate approach is preferred because of its simplicity, being easier to construct and more accurate than the other approaches [157, 159].

TABLE 2. PHOSPHORUS INPUT AND OUTPUT PARAMETERS USED IN THE FARM- GATE SOIL SURFACE AND SOIL SYSTEM BUDGET (ADAPTED FROM [159].

Budget	Farm gate	Soil Surface	Soil system
Inputs	Purchased fertilizer Purchased feed Purchased cattle Purchased bedding material Atmospheric deposition Total	Applied fertilizer Urine and dung deposits Applied animal manure Recycled forage losses Atmospheric deposition Total	Applied fertilizer Urine and dung deposits Applied animal manure Recycled forage losses Atmospheric deposition Total
Outputs	Exported milk Exported cattle Exported animal manure Exported animal feed Total	Harvested grass by grazing animals Harvested silage, maize and grass Total	Harvested grass by grazing animals Harvested silage, maize and grass Phosphorus adsorption/desorption Leaching and runoff Net immobilization in soil Net mineralization in soil Total

Detailed records of P inputs and outputs can be used to identify opportunities for improving balances and ensuring specific goals are achieved [33] as well as to create awareness among farmers to re-examine their routine practices [157,162]. These records provide early warning indications of potential problems arising from P surplus or deficit and also help farmers or researchers to identify the factors affecting P status in soils or specific field sites of P accumulation or depletion. Farm gate P balances may provide a cheaper means of obtaining farm nutrient loss data and environmental impact than by more costly and difficult conventional method using water quality monitoring [163–164].

The quantification of nutrient inputs and outputs has led to the development of a number of indicators of farm nutrient performance to satisfy the increasing requirements of policy makers for easy to interpret and understand indicators that can assess the environmental performance and sustainability of agriculture (Organisation of Economic

Cooperation and Development, [165]. From farm perspectives, the term “nutrient use efficiency” is used as an indicator of the nutrient conversion efficiency of a particular land use. It is defined as the per cent farm nutrient inputs that is exported as farm produce. The farm nutrient surplus indicates the potential for off-site nutrient impact. When these two terms are considered together, they can indicate the extent to which efficiency could be improved by better management using voluntary management practices of farmers. [157, 166].

Another indicator commonly used is “eco-efficiency”, which implies “doing more with less” i.e. increasing the value of production with less environmental impact [167]. The idea is to produce more value out of raw materials with less waste and less pollution ([168]. In agriculture, this means getting more farm production for a given level of nutrient (i.e. effectiveness of farm nutrient utilization) while reducing waste and nutrient loss to the environment [164].

In spite of the many advantages of P balances as presented above, a number of factors such as the lack of standard and accepted guidelines in making nutrient budgets, large differences in the nature and complexity of agroecosystems and spatial variability and temporal changes within systems have introduced many uncertainties in nutrient budgets [158, 159]. In addition, few studies measure all inputs and outputs of a nutrient in a system [156] or use isotopes (^{32}P or ^{33}P) to identify more accurately and specifically the various sources of P or focus more on nutrient pathways which are more difficult to measure [169]. Thus, the results of many studies provide only apparent quantitative balances, and are not only regional and site specific but also case-specific. However, these uncertainties are due to biases and errors [159].

Five possible sources of bias and two sources of error have been identified [170]. These are: personal, sampling, measurement and data manipulation biases and biases due to fraud and sampling and measurement errors. Four options to deal with uncertainties in nutrient budget studies and in the subsequent decision-making were suggested [159]. These are:

- Ignore nutrient uncertain budgets;
- Consider the result but ignore the uncertainty;
- Qualitatively consider the uncertainty and adopt conservative assumptions and apply safety factors to deal with them; and
- Address explicitly and quantitatively the uncertainty and its simplifications

The application of “quality assurance and quality control” may help to remove the uncertainties in nutrient budget research [159] .

1.6.2 Comparing phosphorus balances in organic and conventional farms

As mentioned earlier, organic farming excludes the use of synthetic P fertilizers [171–172] and relies on P supply from internal P cycling such as the recycling of on-farm P from farmyard manures, slurries, composts, green manure, crop residues and mulches. Rock phosphates may also be used as external P sources. Due to the lower input of P in organic farms compared with conventional systems, several workers have reported lower available soil P under organic management [173–174].

Negative P balances have been reported by several workers [175–176]. The depletion of P from past P fertilization in organic crops due to the scarcity of organic P fertilizers was reported [175]. The negative P balance (average 6.3 kg ha^{-1} $year^{-1}$) in organic dairy farms in Norway was not a problem in the short term [177]. The negative P balances in organic systems may be particularly high in dry and semiarid regions due to low cattle densities and thus low availability of farmyard manure [178]. Extractable P concentrations were significantly lower in soils under organic than paired conventional farms in England [174] and that the largest difference occurred in the oldest farm (54 years). Thus, organic systems may be mining the P reserves accumulated during prior conventional management and may gradually deplete soil P reserves compared with conventional systems. This has been cited as an advantage as organic farming may reduce the accumulation of surplus P in soils resulting in reduced diffuse P losses to water bodies [179]. This has not yet been proven.

However, positive P balances have also been reported in Australian organic vegetable [180] and cereal farms [181], and in organic dairy farms in Europe and Norway as cited by [182]. In organic dairy farms in Norway, there was P transfer from topsoil to subsoil with time [182]. These workers also found that although available P levels in organic dairy farms were less than those of comparable conventional farms, crop yields were comparable. Nevertheless, the general trend was decreased yields and [182] suggested that P inputs from external sources would be necessary to maintain yields. However, in long term (21 years) trials in Switzerland [183], soils from organic treatments had adequate level of available P and that comparable yields were obtained in the organic plots compared with those of conventional plots.

Similar results on P status in organic and conventional vegetable farms in Queensland; Australia has been reported [184]. Examination of the farm records revealed that there were substantial overlaps between P inputs in the two systems as the conventional farms also received organic inputs such as green manure and composts. In their surveys, many conventional growers used substantial inputs of organic fertilizers in their farms [185]. Thus, the distinction between organic and conventional systems became less well defined. Based on the above it is clear that results of P balances (positive and negative) in organic systems are contradictory, suggesting that it is not possible to generalize on the effects of organic farming on P balances as these will depend on the soil (P status and reserves), crop, climate, and farm management practices. In addition, animal stocking rates affect P balances in organic dairy farms. Results reported by other workers, which showed that an average field P surplus of 2 kg P ha^{-1} $year^{-1}$ was changed to a P shortage of –4.5 kg P ha^{-1} $year^{-1}$ when the stocking rate was reduced from 1.4 to 0.8 units ha^{-1} [182]. Furthermore, average field P balances generally showed larger P shortages than farm level P balances [182].

1.6.3 Phosphorus fluxes

The flows of P into or out of a system are regarded as the fluxes of P. These can be estimated, measured or modelled [186]. A nutrient monitoring (NUTMON) system involving input-output analysis of nutrients in SSA agriculture systems was initiated [187], and this methodology has been widely used. These workers used fertilizers, mineral and organic, wet and dry deposition, N_2 fixation and sedimentation as inputs for N, and harvested crops and residues, leaching, denitrification, and erosion as N outputs. Nutrient fluxes as fertilizers and crop harvests were measured or estimated from interviews with farmers, and where fluxes were difficult to quantify (e.g. leaching, erosion), they were modelled by transfer functions mainly elaborated by the NUTMON initiators [187]. The methodology was improved [188] by making it spatially explicit, improving the various transfer functions, and modelling the uncertainties in the estimations.

An example of the major fluxes of P in a dairy farm is shown in Figure 1 [189]. Major P fluxes that enter the farm include feed concentrates, straw bedding, atmospheric deposition and fertilizer input while fluxes which leave the farm include milk, calves, losses to water and excreta to pasture. These fluxes (Figure 1) are regarded as external fluxes of P entering or leaving the farm. Within the farm itself, there is internal cycling and fluxes of P mineralization/immobilization, root uptake fluxes, adsorption/desorption and other internal P cycling processes which are not included in farm gate balances [177, 190]. These internal fluxes need to be considered together with P balances for improving P utilization in a farm or system.

Phosphorus fluxes through the plant root zone of soils have been studied. The P fluxes using suction cups and lysimeters were compared [102], but the data were not used for P balance studies. Phosphorus isotopes (^{32}P, ^{33}P) have been used in many studies to measure processes such as P dynamics [34, 191], P kinetics [124, 126], gross mineralization of soil Po [191], mycorrhizal acquisition of Pi [192], and for investigating the effects of tillage and ploughing on the fate of ^{33}P-labelled crop residues [193].

Several models have also been developed and published on modelling P fluxes and balances in farms [161, 194], catchments [195], watersheds [196], landscapes [197], and high-rate algal ponds [198]. However, none of these studies used P isotopes to measure P fluxes or some of the input and output processes. ^{32}P and ^{33}P isotopes can specifically identify P sources and quantify their fluxes [126, 194], considerable advantages can be gained by using these to assess P fluxes in balance studies.

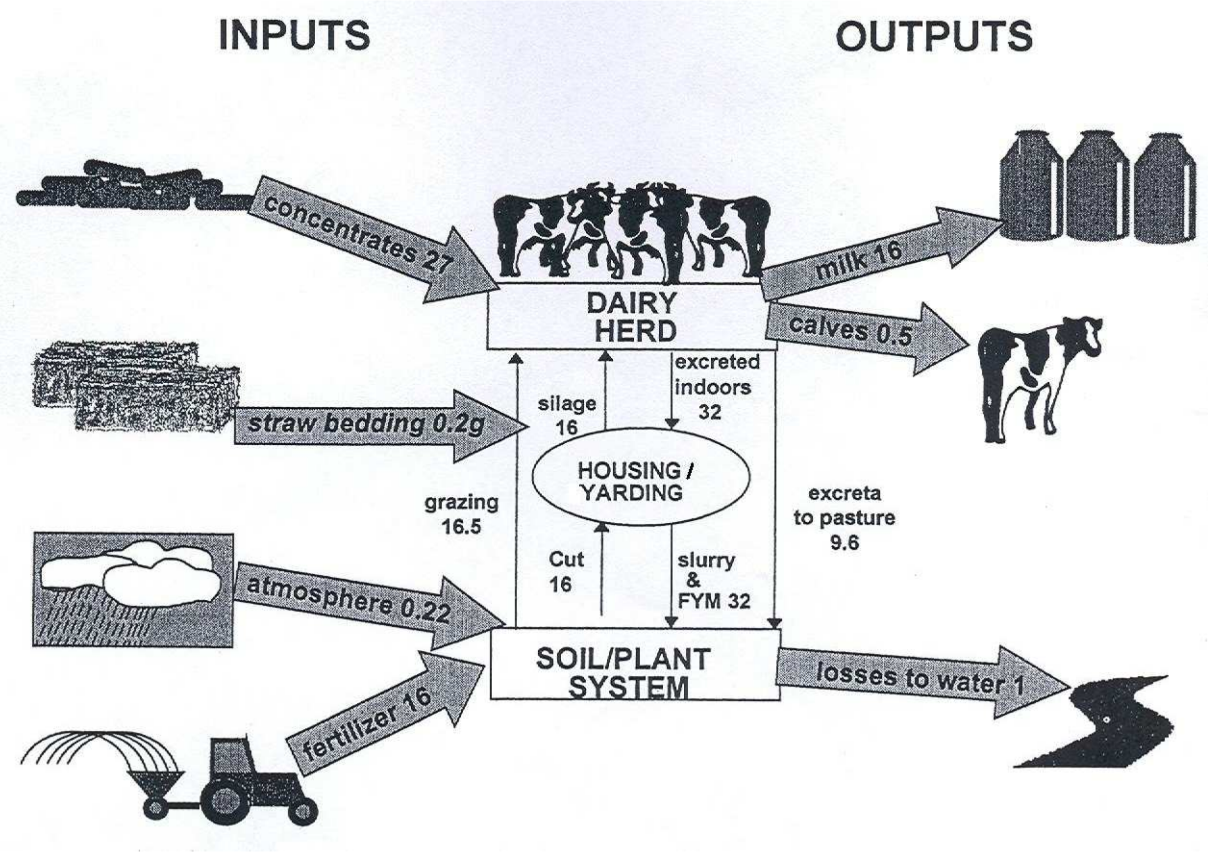

FIG.1. A detailed illustration of phosphorus fluxes in a model dairy farm in the UK. Amounts are expressed as kg ha^{-1} except for straw bedding which is measured in g ha^{-1}. Source: [189].

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PHOSPHORUS ISOTOPE TRACER TECHNIQUES: PROCEDURES AND SAFETY ISSUES

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Abstract

Detailed procedures used in isotope tracer techniques including problem set and calculations are provided. In addition, the application of radioisotopes as tracers in agricultural research requires suitable facilities including laboratory and measuring/monitoring equipment and adequate training of the personnel to handle these nuclides safely, ensuring that radiation workers are not exposed to undue external or internal radiation hazards. The last part of the paper examines the operational personal safety practices that ensure adequate radiation protection of the workers.

1. INTRODUCTION

Isotopic methods have been developed and used to conduct phosphate studies in soil-plant systems and their individual compartments. They are utilised to investigate the soil P kinetics processes and the soil and plant factors that affect the availability of P to plants. The use of tracers to investigate phosphate cycling in soil-plant systems has been reviewed [1]. This paper provides definitions, principles, calculations, and procedures for determining E, L, and A values described briefly in paper 2 to assess available soil P. It also describes the phosphorus tracer techniques commonly used to study P availability from a range of nutrient sources. As phosphorus isotopes commonly used in agricultural systems are radioactive, relevant radiation protection and safety issues are presented.

2. PHOSPHORUS ISOTOPES IN AGRICULTURAL STUDIES

2.1 Radioactive P isotopes

Phosphorus has one stable isotope (^{31}P) and several radioisotopes (from ^{26}P to ^{30}P and from ^{32}P to ^{38}P), but only two of them (^{32}P and ^{33}P) are suitable for agronomic studies [2]. The main characteristics of these radioactive P isotopes, i.e. half-life, decay mode, i.e. radiation type and energy emitted are shown in Table 1.

TABLE.1. SUMMARY OF MAIN CHARACTERISTICS OF P ISOTOPES USED IN SOIL-PLANT STUDIES

Isotope	Half-life (days)	Radiation characteristics		Typical applications
		Type	Energy (E_{max}) in MeV	
^{32}P	14.3	β^-	1.71	Exchangeable P in soils P availability from P fertilizers Plant root distribution/activity Residual P fertilizer availability
^{33}P	24.4	β^-	0.248	Auto-radiography Diffusion in soils Double labelling with ^{32}P

Detection efficiencies for both radioisotopes are high using modern liquid scintillation counters/analysers. The high beta energy of the photons emitted by ^{32}P allows the use of Cerenkov counting, which makes the technique cheaper. Conversely, the low beta energy of the photons emitted by ^{33}P requires the use of scintillation fluors or cocktails, which are commercially available and more expensive. The lower energy emitted by ^{33}P presents less radiation hazard, and its longer half-life (24.4 days) allows studies to be conducted for relatively longer time periods. The ^{32}P can be easily monitored because of its high beta energy but its use is limited to studies for approximately 10 half-lives.

The availability of these two isotopes also makes it possible to use double labelling techniques in root activity studies and P placement experiments [3–4]. An additional factor to be considered is the cost of the isotopes, ^{32}P being far cheaper than ^{33}P and also easier and faster to obtain from commercial suppliers.

It should be noted that the handling and use of these radioisotopes require compliance with regulations concerning radiation protection and safety set by international standards and the National Radiation Protection Authorities This involves, among others, special laboratory facilities and trained personnel as well as the licensing to perform all the activities including ordering, dispensing, experimental use and waste disposal [5–6].

2.2 Analytical techniques

As both P radioisotopes are beta emitters, the measurement of their activities is made using liquid scintillation counting (LSC) methods. Relevant procedures are briefly described below [7]. A detailed treatment of this can be found in treatises of radioactivity measurement [8].

2.2.1 Principles of liquid scintillation counting

Radioactive decay is a spontaneous reaction occurring when there is nuclear instability. Nuclides vary considerably in their instability and unstable nuclei emit subatomic particles through a series of decay reactions.

Beta decay occurs when an unstable nucleus with an excess of neutrons returns to stability equilibrium through the conversion of a neutron to a proton with the emission of an electron and an antineutrino as follows:

$$\text{Neutron (n)} \longrightarrow \text{Proton } (p^+) + \text{Electron } (e^-) + \text{Antineutrino } (\nu)$$

This process occurs within the nucleus of an isotope like phosphorus-32, which has 15 protons and 17 neutrons but as a result of beta decay, transforms into stable sulphur with a nucleus of 16 protons and 16 neutrons. The total energy of beta decay, E_{max}, consists of the combined energy of the emitted the beta and antineutrino particles. Very few of the emitted beta particles have maximum energy, as energy is shared between the beta particle and the antineutrino. Most of the emitted beta particles have an average energy of approximately one third of E_{max} (FIG. 1)

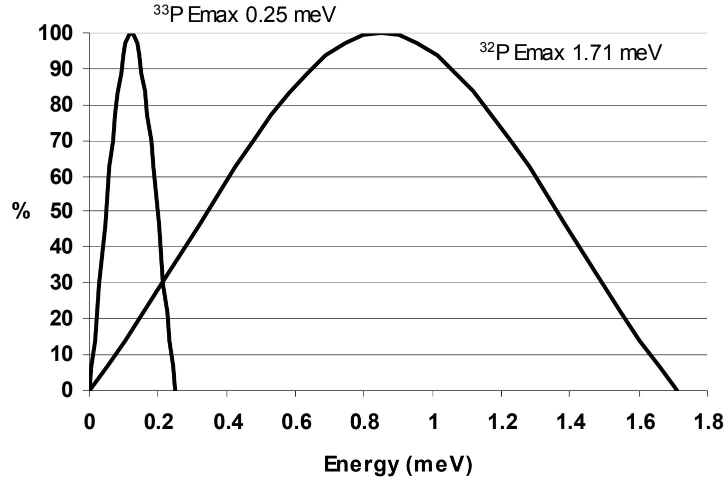

FIG. 1. Average energy of emitted beta particles spectra for ^{32}P and ^{33}P

The windows can be set on the liquid scintillation counter LSC to capture β particles of particular energies. These window settings can also be used to simultaneously count two or more isotopes that have different energy spectra such as the ^{32}P and ^{33}P isotopes in FIG. 1.

2.2.2 Use of Scintillation Mixtures

In liquid scintillation counting a solvent is used to ensure that the liquid to be counted is in solution. An emulsifier or detergent is added to enhance the mixing of organic and inorganic solutions and a compound which fluoresces when struck with an electron (fluor) is added. In some instances the fluorescence that occurs cannot be detected by a photomultiplier tube, so a secondary wave shifter is added.

The solvent is the first compound in the scintillation cocktail to capture the energy of the beta particle and the solvent molecule achieves an excited state. The excess energy is transferred from solvent molecule to solvent molecule. The solvent remains in the excited state for an extended period of time, decaying into the ground state without the emission of light. The fluor then absorbs the excitation energy of the solvent, and quickly returns to the ground state by emitting light photons. If a wave shifting fluor is used this absorbs the signal of the first solute and emits a second burst of light at a longer wavelength and this is detected by a photomultiplier in the counter.

2.2.3 Preparation of a Scintillation Mixture

There are many "cocktails" used for the preparation of radioactive samples. Following, are the details for the preparation of a cocktail, which can be successfully used with most samples [7].

2.2.3.1 Reagents

Toluene - scintillation grade

p-terphenyl

POPOP

Teric

2.2.3.2 Procedure

1. Heat 1L of toluene in a beaker on a heater/stirrer.
2. Add 16.92 g of *p*-terphenyl and 0.73 g of POPOP (1, 4-bis-2-(5-phenyloxazolyl) benzene or phenyl-oxazolyl-phenyl-oxazolyl-phenyl) to the toluene.
3. Heat and stir until dissolved.
4. The toluene/*p*-terphenyl/POPOP solution is then added to 2080 mL Teric (A detergent manufactured by Shell) in a 5 L volumetric flask.
5. Make the solution to volume with toluene once the solution is cool.

2.2.3.3 Sample/ scintillant ratio

This mixture can be used at a ratio of 3 mL sample: 17 mL of scintillant, to give a final volume of 20 mL (See Table 2 below). However, if the mixture of the sample and scintillant prove immiscible, the ratio of scintillant to sample can be varied (e.g. 18–19 mL scintillant to 2–1 mL sample) or the mixture acidified using a concentrated mineral acid (e.g. 2mL sample, 1mL acid and 17mL of scintillant). These ratios may be altered until a clear emulsion results.

2.2.3.4 The Phenomenon of Quenching

Chemical constituents and colour in the sample can result in a reduction in the number of β^+ particles leaving the sample. This is termed quench. This can be accounted for by adding known quantities of the isotope to the matrix and using this count data to correct the counts measured in the samples. This is termed quench correction [7].

To compensate for quenching losses, a calibration curve must be prepared against which the unknown samples can be compared. The quench curve can be established by counting a series of samples containing a known constant amount of radioactivity, but varying concentrations of a quencher.

In theory, the construction of one calibration curve should suffice for all mechanisms quenching the same isotope, provided that the calibration is for the same scintillator and constant settings. However, most users calibrate for each particular sample preparation, unless using a sophisticated machine which can compensate for colour and photon quenching.

A prepared quench curve should cover the range in which the unknown samples are to be measured. The standards should be prepared in duplicate and there should be 5–10 calibration points. Two substances that can be used as quenching agents are chloroform and benzoic acid. Chloroform is a very effective quencher, but, due to its volatility, it can be difficult to measure accurate volumes. When using chloroform, use in a cool, draught-free area, to minimise errors.

TABLE .2. contains a suggested method of preparing a quench curve. Chloroform is used, but the user can modify this to suit the particular sample matrix required. The isotope activity and volume of quench can also be varied.

TABLE .2. VOLUMES USED IN PREPARING QUENCH STANDARDS

Identifier	Volume of quench (eg chloroform) (mL)	Volume of water (mL)	Volume of isotope solution (eg.1500mBq/mL) (mL)	Volume of scintillant (mL)
Background 1	0	3.00	0	17.00
Background 1	0	3.00	0	17.00
Quench 1a	0	2.00	1.00	17.00
Quench 1b	0	2.00	1.00	17.00
Quench 2a	0.05	1.95	1.00	17.00
Quench 2b	0.05	1.95	1.00	17.00
Quench 3a	0.10	1.90	1.00	17.00
Quench 3b	0.10	1.90	1.00	17.00
Quench 4a	0.15	1.85	1.00	17.00
Quench 4b	0.15	1.85	1.00	17.00
Quench 5a	0.20	1.80	1.00	17.00
Quench 5b	0.20	1.80	1.00	17.00
Quench 6a	0.25	1.75	1.00	17.00
Quench 6b	0.25	1.75	1.00	17.00
Quench 7a	0.30	1.70	1.00	17.00
Quench 7b	0.30	1.70	1.00	17.00
Quench 8a	0.35	1.65	1.00	17.00
Quench 8b	0.35	1.65	1.00	17.00

When running the quench curve on the LSC, set-up the measurement conditions and load the curve so that the background samples are read first, followed by the unquenched standards, then the quenched standards in increasing volumes of quench.

To measure dual labelled samples (e.g. both ^{32}P and ^{35}S), two quench curves must be prepared for each isotope, i.e. the two isotopes are not mixed together in the same standard. This is because the LSC cannot differentiate between the two different radioisotopes; it simply combines the energies. To run a quench curve for dual labelling, the lowest energy nuclide is loaded first (e.g. ^{35}S) followed by the highest energy nuclide (e.g. ^{32}P). Many modern LSCs use sophisticated software to separate the counts for the different nuclides.

2.2.3.5 Cerenkov counting

When β particles are emitted they leave the nucleus at speeds approaching that of light in a vacuum. However, in the surrounding medium the speed of light is lower and consequently the passage of particles through the medium causes shock waves from which light photons are emitted. This light can be counted to give a measure of the radioactivity present. The minimum energy required to produce light in an aqueous solution is 0.263 MeV. This means that only those radionuclides with high-energy emissions, such as ^{32}P, may be counted by this method.

2.3 Basic concepts in radiotracer experiments

2.3.1 *Artificial labelling with ^{32}P and/or ^{33}P labelled sources*

Phosphate tracer studies are based on artificial labelling approaches. For this purpose, a range of products/materials labelled with $^{32}P/^{33}P$ (open radioactive sources) have been utilised:

a) ^{32}P carrier free materials, i.e. contain only ^{32}P atoms, are normally utilized as tracers (commercially available, upon request)

b) ^{32}P labelled orthophosphate solutions of high specific activity (commercially available, upon request)

c) ^{32}P labelled fertilizers such as superphosphates labelled during manufacturing (commercially available, upon request)

d) ^{32}P labelled solutions of known concentration prepared for use in greenhouse and field experiments.

e) ^{32}P labelled plant materials can be prepared for use as labelled organic matter. Labelled white clover (*Trifolium repens*) was prepared as follows [9]: A sward of clover was taken from the field and clipped to near the soil surface. Carrier free ^{32}P in a solution (1700 mBq/g P) was applied at the rate of 360 mBq /m^{2}' and watered into the soil surface. The clover was grown for 19 days, after which the clover plants were removed from the soil, retaining as many roots as possible, and oven dried. The dried whole clover plants were crushed and the roots, stems and petioles cut into pieces less than 1cm long. Because insufficient labelled organic matter was produced in the zero phosphorus soil, the labelled material was mixed intimately with unlabelled material, grown under the same conditions, in the ratio 2.28 labelled: 1 unlabelled. The plant material added to the soils contained 0.161 % P and 75.81mBq/g P in the low P treatment. The high P treatment was 0.333% P and 38.11mBq/g P.

2.3.2 *Primary data and abbreviations used in the equations*

In ^{32}P labelled fertilizer studies, the following parameters and abbreviations are used in the equations [7]

P_{py}= Total P in plant yield

P_{fa}= Total fertilizer P applied

P_f = P concentration in fertilizer

$^{32}P_f$ = ^{32}P activity in fertilizer

P_p = P concentration in plant

$^{32}P_p$ = ^{32}P activity in plant

P_a = P concentration in soil "available P" pool

$^{32}P_a$ = ^{32}P activity in soil "available P" pool

P_{pfa} = P concentration of plant derived from the soil available P pool

P_{pff} = P concentration of plant derived from the fertilizer

PP_{pff} = proportion of P in the plant derived from the fertilizer

SR_p = Specific radioactivity of plant P

SR*f* = Specific radioactivity of fertilizer P

SR*a* = Specific radioactivity of available soil P

In radiotracer studies the specific radioactivity (SR), also called specific activity (SA) is used to describe the amount of radioactivity per unit of material as well as the amount of radiotracer per unit of the common element. Consequently care must be taken to avoid confusion between the SR of the plant dry matter, which is expressed in units such as Bq/g DM and the SR of the phosphorus in the plant (SR*p*) = $^{32}\mathrm{P}p/\mathrm{P}p$ which is expressed in units such as Bq/mg P [7].

2.3.3 Radioactivity units

By definition the activity of a radioactive source or radionuclide sample is a measure of the total radiation emitted. In other words it is the number of nuclei decaying per unit time. The SI unit of radioactivity is the Becquerel, (symbol Bq). The Bacquerel is one nuclear disintegration per second (dps). The old unit was the Curie (Ci). For details and equivalency see Table 3 [10].

Another important property is the energy of radiation, which is expressed in terms of millions (Mega) of electron volts (MeV). One MeV is equivalent to the kinetic energy acquired by an electron accelerated through a potential difference of one million volts.

TABLE 3. ACTIVITY UNITS OF RADIOSOTOPES

Curie (Ci)	Becquerel (Bq)	Disintegration per second (dps)	Disintegration per minute(dpm)
1 Ci	3.7×10^{10} Bq = 37 GBq	$3.7. \times 10^{10}$	2.22×10^{12}
1 mCi	3.7×10^{7} Bq = 37 MBq	3.7×10^{7}	2.22×10^{9}
1 µCi	3.7×10^{4} Bq = 37 KBq	3.7×10^{4}	2.22×10^{6}
1 nCi	3.7 x 10 Bq	3.7 x 10	2.22×10^{3}
1 pCi	3.7×10^{-2} Bq	3.7×10^{-2}	2.22
	1 Bq	1	6 x 10
27,027 nCi	1 KBq	1×10^{3}	6×10^{4}
27,027 µCi	1 MBq	1×10^{6}	6×10^{7}
27,027 mCi	1 GBq	1×10^{9}	6×10^{10}

Other units utilised in radiation protection are the Gray, Gy (unit of absorbed dose) and the Sievert, Sv (unit of equivalent dose exposure).

3. PHOSPHORUS RADIOTRACER TECHNIQUES TO ASSESS SOIL AVAILABLE P

Earlier applications of these techniques were developed to measure the quantity of available P in soils by determining the E-value or exchangeable P in the laboratory and the L value or labile P using plants in the greenhouse, and the A value or available P using plants grown in the field (Paper 3, section 3.4.1). These techniques have been applied to make comparative studies of the amount of soil available P (quantity factor) among different soils and between soils untreated (native) and treated with fertilizer P sources. It was also noted in

Paper 3, section 3.4.2 that a full characterization of the soil P status and its availability through the isotopic exchange kinetics (IEK) method provides better information for P management in agroecosystems. A detailed description of the latter method can be found elsewhere [1, 11]. In this section only procedures and calculations for the techniques to assess soil available P using ^{32}P tracer are described.

3.1 Isotopically exchangeable soil P – (E value)

The E value is an estimation of the amount of P which is immediately available to plants by measuring the isotopically exchangeable P pool in a soil, i.e. the solid phase phosphorus in equilibrium with that in solution at a given time [12]. Unlike the A and L value methods in the E value method the isotope is mixed intimately with the soil under laboratory conditions. The change in the specific radioactivity of the P is used to determine the isotopically exchangeable P. This method assumes that the ^{32}P and ^{31}P come to equilibrium, which is known not to happen, but this is not a severe limitation of the method.

3.1.1 Procedure

In the procedure soil is shaken with a specified concentration of P and a spike of ^{32}P added for 1 hour and the concentration of both ^{31}P and ^{32}P determined.

1. Weigh duplicate lots of 5 g of soil into 100 mL centrifuge tubes and add 49 mL of KH_2PO_4 in 0.01 M $CaCl_2$ solution. The sorptivity of the soil will determine the concentration of P required but it is suggested to start with a solution of 2 µg P/mL. An aliquot of this solution is needed to determine the exact P concentration.
2. Add 2 drops of toluene to each tube and shake for 23 hours.
3. Remove the tubes from the shaker and add exactly 1 mL of a carrier free ^{32}P solution (4.93 KBq/mg P) to each tube. The sorptivity of the soil will determine the activity of the ^{32}P required but it is suggested to start with a solution of 150 KBq/mL.
4. Return the tubes to the shaker and shake for exactly 1 hour.
5. Remove the tubes from the shaker and filter the solution through a 0.025 µm filter. If such a filter is not available centrifuge at 10000 rpm for 15 min or until a clear supernatant is obtained.
6. Take aliquots of each solution for determination of ^{32}P activity and ^{31}P concentration.

3.1.2 Calculations

The E value for a ^{32}P carrier solution is calculated as follows:

$$E = \left(\frac{r_i}{r_f} * {}^{31}\mathrm{Pf} \right) - {}^{31}Pi$$

Where r_i and r_f are the initial and final activity (cpm/mL) respectively, and

$^{31}P_i$ and $^{31}P_f$ are the initial and final solution P concentrations, respectively expressed as µg P/g soil.

TABLE 4. ^{31}P CONCENTRATION AND ^{32}P ACTIVITY IN INITIAL AND FINAL SOLUTIONS FROM TWO SOILS

Soil	^{31}P (µg P/mL)		^{31}P (µg P/g soil)		^{32}P (cpm/mL)	
	Measured P concentration of KH_2PO_4 added (initial)	Measured P concentration of filtered soil solution after 24 hr shaking (final)	Initial	Final	Initial	Final
Vertisol	1.966	0.045	19.66	0.45	18155	160
Ferrosol	2.014	0.013	20.14	0.13	18155	55

Using the data presented in Table 3.4, the E values of the soils are calculated as follows:

Vertisol, $E = ((18155 / 160)^{*} 0.45) - 19.66 = 31.44$

Ferrosol, $E = ((18155 / 55)^{*} 0.13) - 20.14 = 22.77$

3.2 Labile P– (L value)

L value is the amount of available soil P determined growing plants in the greenhouse where the added P is thoroughly mixed with the soil [13]. Calculations for the L value are identical to those for the A value. The important difference between the two measures is that when determining the L value the amount of P fertilizer added must be small and it must be thoroughly mixed with the soil. In addition, the amount of isotope added must be high to allow measurement. This means that fertilizer with a very high SA must be used and preferably carrier free ^{32}P material. In order to get the degree of mixing required it is often necessary to apply aqueous solutions. These conditions severely limit the utility of this procedure.

3.2.1 Procedure

In order to determine an L value, under as ideal conditions as possible, carrier free ^{32}P should be used. The ^{32}P activity required will vary with soil but an application of 2 MBq/kg soil is a good starting point.

The procedure requires that the added ^{32}P and the soil ^{31}P come to equilibrium, which is not often attained. If this condition is not met the L value obtained can provide an index of available P rather than an absolute value.

3.2.2 Calculations

The L value is calculated as follows:

$$L = \text{amount of P fertiliser added x} \left[\frac{\text{SA fertiliser}}{\text{SA plant}} - 1 \right] \text{mg P/100 g soil}$$

In the experiment reported in [14], an additional treatment to that shown for the E value was added where the 49 mL of 2 µg P/mL KH_2PO_4 in 0.01 M $CaCl_2$ solution was replaced with 49 mL of 0.03 µg P/mL solution. When the 1 mL of ^{32}P solution was added this resulted in a SA of 3580640 KBq/mg P as shown in Table 5.

TABLE 5. SPECIFIC ACTIVITY (SA) OF FERTILIZER AND PLANT AND CALCULATED L VALUE.

Soil	SA fertilizer KBq/mg P	SA plant KBq/mg P	L value using carrier ^{32}P mg P /100 g soil
Clay loam	3580640	0.206	135
Loam	3580640	0.156	178
Sandy loam	3580640	0.184	151

The L value for the clay loam soil is calculated as follows:

$$L = [0.00000775 \text{ mg of fertiliser P/100 g soil}] \times \left[\frac{3580640}{0.206} - 1\right]$$

$$= 135 \text{ mg P/100 g soil}$$

3.2.3 Relationship between L and E values

The relationship between E and L values was studied [18]. They found a good correlation between the L values determined on 10 P fertilized or unfertilized soils growing *Agrostis communis* for 13 weeks and the E values determined after 23 weeks of isotopic exchange (Fig. 2). The short half-life of ^{32}P prevented studies over a longer period.

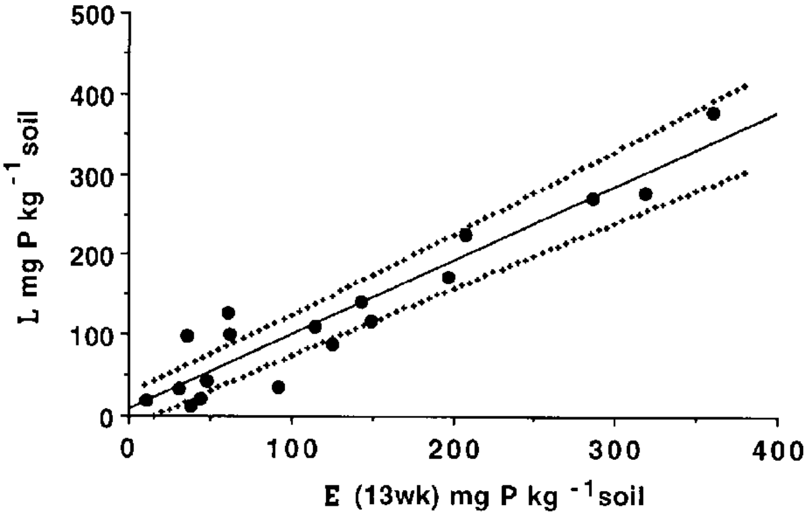

Figure. 2. Relationship between L and E values determined on 10 soils.

Several authors have conducted comparative studies between E and L values to assess soil available P (Chapter 3, section 3.4.1). For instance, a critical analysis of L and E values in assessing soil isotopically exchangeable phosphorus has been reported [15]

3.3 Available P (A value)

The “A” value concept was developed [16]. The measurement relies on determination of the specific radioactivity (SA) of a P fertilizer added to the soil and the consequent SA of the plants grown in that soil. It is particularly useful in comparing the P status of different soils, the efficacy of P sources that can be labelled, placement methods and timing of P application.

The inherent assumption in this method is that when a plant is confronted with two sources of P (soil and fertilizer) it utilizes them in direct proportion to the availability of P in each source.

$$A = \frac{B[\text{Fraction of plant P derived from soil}]}{\text{Fraction of plant P derived from fertiliser}}$$

or

$$A = \frac{B[1-(S_p/S_f)]}{S_p/S_f}$$

where $(1 - S_p / S_f)$ is the fraction of P derived from the soil, and

S_p / S_f is the fraction of P derived from the labelled fertilizer.

or

$$A = \frac{B[\text{Pdfs}]}{\text{Pdff}}$$

Where: B is the rate of P fertilizer added, Pdfs is the fraction of P derived from the soil and Pdff is the fraction of P derived from the fertilizer.

3.3.1 Procedure

1. Prepare a fertilizer P source/s (eg. a phosphate solution containing between 10 and 50 kBq/mg P. The SA of the fertilizer or solution produced depends on the duration of the experiment, the expected sorption of the P onto the colloid surfaces and immobilization of P into organic forms.
2. Determine the rate of P addition required.
3. Apply the labelled P source/s (e.g. banded and broadcast).
4. Retain samples of the labelled sources to determine the SA.
5. Grow the plants for the required time and harvest them.
6. Measure the ^{31}P concentration and ^{32}P activity of the plant samples.

3.3.2 Calculations

Calculation of the A value in terms of mg P/100 g soil is as follows:

$$A = [\text{mg of fertiliser P/100 g soil}] \times \left[\frac{\text{SA of fertiliser}}{\text{SA of plant}} - 1\right]$$

Results from an experiment where band and broadcast (mixed) application of KH_2PO_4 solution were compared in three soils are presented in Table 6 ([14]. The data are used to demonstrate the calculations necessary.

The ^{32}P labelled fertilizer was added at the rate of 24.2 mg P/ 2000g soil (equivalent to 21.8 kg P/ha) The SA of the fertilizer was 25.45 KBq/mg P.

A subsample of 200 mg of dried plant was digested in acid and diluted to 50 mL prior to P determination. A 1 mL aliquot was counted in a liquid scintillation counter to determine ^{32}P activity.

Using the band treatment in the clay loam soil as an example, the calculation of plant SA is as follows:

Plant ^{32}P activity (KBq/g DM) = 697 cpm/mL *50 mL./200 mg sample * 60/1000 (to convert to KBq)

= 10.45 KBq/g DM

The P concentrations in the plant material were not presented so a constant value of 0.15%P (15 mg P/g DM) has been assumed.

Plant ^{32}P activity (KBq/mgP) = 10.45 KBq/ 15 mg P

= 0.697 KBq/ mg P

TABLE 6. RESULTS OF A VALUE AND L CALCULATIONS

Soil	Count (cpm/mL)[A]		^{32}P activity (KBq/g DM)		SA of plant material (KBq/mgP)[B]		A value (kg P/ha)		L value (kg P /ha)
	Band	Mixed	Band	Mixed	Band	Mixed	Band	Mixed	Mixed
Clay loam	697	311	10.45	4.66	0.697	0.310	43	98	135
Loam	512	296	7.67	4.43	0.512	0.296	59	103	178
Sandy loam	415	197	6.23	2.96	0.415	0.197	73	155	151

[A] Scintillation count corrected for decay and efficiency

[B] Assuming a constant plant P concentration of 0.15%

Using the data from the banded treatment for the clay loam soil, the A value calculation is as follows:

$$A = \left[1.21\,\text{mg of fertiliser P/100 g soil}\right] \times \left[\frac{25.457}{0.697} - 1\right]$$

= 43 mg P/100 g soil

Using the data from the mixed treatment for the clay loam soil, the A value calculation is as follows:

$$A = \left[1.21\,\text{mg of fertiliser P/100 g soil}\right] \times \left[\frac{25.457}{0..310} - 1\right]$$

= 98 mg P/100 g soil

A values estimated for the other soils and fertilizer treatments are presented in Table 6.

4. PHOSPHORUS RADIOTRACER TECHNIQUES IN SOIL FERTILITY AND PLANT MINERAL NUTRITION STUDIES

The first extensive use of isotopes as tracers in plant nutrition was made in the 1940's. The radioactive isotope of P (^{32}P) was used to study the utilization of P fertilizers by various crops in a series of greenhouse experiments [15–17] and field trials [18]. International research networks using isotopic tracers ^{15}N and ^{32}P were extensively conducted over two decades to develop effective fertilizer practices by grain crops [19].

In the direct labelling method, essentially a tracer was incorporated into a fertilizer material or the nutrient source of interest, and the amount of tracer taken up by the plant was measured directly (ordinary direct isotope dilution). An ideal tracer should have exactly the same behaviour as the material being traced, and should have no effect on the components of that material in the system under study. Since tracer detection is very sensitive, the amount of radioactivity added to the system in a tracer experiment is usually very small compared with the amounts already present in, or added to the system. Thus, very little disturbance of the system is made.

In case of natural P fertilizer sources, like phosphate rocks (PR), it is not possible to directly label these materials with P isotopes, because of the changes induced in their physical and chemical characteristics during labelling. Therefore, techniques based on reverse or indirect isotopic dilution have been widely used to investigate P availability from PR sources to plants [20].

4.1 Measures of fertilizer P uptake

Two distinct measures of fertilizer P uptake can be made in isotopic studies, each with their own particular merit [7]. They are:

1. Total amount of fertilizer P taken up by the plant that is a yield-dependent parameter. We need to know the total amount of fertilizer P applied (P*fa*), its specific radioactivity (SR*f*), and the concentration of phosphorus in it (P*f*). Also the P in the total plant yield (Ppy), the phosphorus concentration in the plant (P*p*) and its specific radioactivity (SR*p*). This will allow a direct calculation of the amount of fertilizer P utilization (also called recovery) by the plant and will rarely be the same as other non-isotopic estimates of "fertilizer P efficiency".

2. Proportion of phosphorus in the plant derived from fertilizer is a yield-independent parameter. The same measurements of nutrient concentration and amounts of tracer as those in 1 (above) are needed but it does not require quantitative measurement of total plant P yield. This is an easier measure to make, and in many ways is more meaningful when comparing the relative "efficiencies" of different fertilizers.

4.2 Determinations for the quantification of fertilizer P uptake

The phosphorus isotopic composition, i.e. the ^{32}P/total P ratio, of any material is called specific radioactivity (SR). It is customary to express the specific activities of plant samples and fertilizer in Bq ^{32}P/g P, at the time the samples were counted. It is important to note that the concept of specific radioactivity (ratio ^{32}P/total P) for radioisotopes is identical to that of ^{15}N atom excess (ratio ^{15}N/total N) for stable isotopes [21].

The determination of the specific radioactivity (SR) of a sample requires two independent measurements:

1. Determination of the activity (Bq or dps) of the radioisotope by radio assay techniques using appropriate detectors, i.e. liquid scintillation counting or Cerenkov counting (for high-energy β emitters).
2. Determination of the total P concentration by any conventional chemical method, i.e. total P by colorimetry (metavanadate yellow, molybdate blue, or malachite green) method and a spectrophotometer.

The fraction of P in the plant derived from the ^{32}P or ^{33}P labelled fertilizer material is termed Pdff. It also follows from the isotope dilution principle that:

Pdff = (SR plant sample / SR labelled fertilizer)

or as a Per centage:

%Pdff = (SR plant sample / SR labelled fertilizer) × 100

How is Pdff determined?

Both the ^{32}P activity and total P content in the plant and fertilizer samples must be measured to determine Pdff.

4.3 Calculation exercises

The following exercises illustrate common ways for calculating these parameters

Exercise 1

An aliquot of a wet digested plant sample containing 8 mg P gives an activity of 800 Bq. If an aliquot of the dissolved ^{32}P labelled fertilizer containing 10 mg P gives an activity of 4000 Bq then the following relationship can be written:

4000Bq = 10 mg P in the fertilizer

800 Bq = X mg P in the plant, and

X = (800 × 10) /4000 = 2 mg P in the plant came from the fertilizer

The next step is to calculate the Pdff by relating the amount of P in the plant which came from the fertilizer (2 mg P) to the total amount of P in the plant sample (8 mg P). Thus 2 mg out of 8 mg was derived from the fertilizer and:

Pdff = 2/8 = 0.25

or % Pdff = 25%

Exercise 2

In a greenhouse experiment, 20 mg/kg P as ^{32}P labelled single superphosphate was applied to pots containing 2 kg soil with barley as the test crop. After 2 months, the plant material was harvested and analysed for ^{32}P activity and total P concentration. The ^{32}P labelled single superphosphate (standard) used in this experiment was analysed in the same way.

Results:

Plant sample: 5 g dry matter yield and 0.2 % total P

An aliquot containing 2 mg P gave 250 Bq ^{32}P by Cerenkov counting. Since the counting efficiency was 50% the activity of the plant sample was 500 Bq ^{32}P.

Thus the SR plant = 500 Bq ^{32}P / 2 mg P = 250 Bq ^{32}P/mg P.

Fertilizer: An aliquot containing 10 mg P counted by Cerenkov gave 6250Bq^{32}P. Considering also 50% counting efficiency the activity of the fertilizer sample was 12500 Bq ^{32}P. Thus the SR fertilizer = 12500 Bq ^{32}P / 10 mg P = 1250 Bq P/mg P

Questions:

I. What was the fraction of P in the plant which was derived from the fertilizer or % Pdff?
2. What was the fraction of P in the plant which was derived from the soil?
3. What was the total P content of the crop?
4. What was the fertilizer P content of the crop?
5. What was the fertilizer P utilization or recovery by the crop?

Calculations:

1. % P derived from the fertilizer:

%Pdff = (SR plant / SR fertilizer) x l00

= (250/1250) x 100 = 20%

2. % P derived from the soil

%Pdfs = 100 – %Pdff

= 100–20 = 80%

3. P content of the crop = Yield (g DM) × (%/100)

= 5 g × (0.2/100) = 0.01g P/pot

= 5000 mg × (0.2/100) = 10 mg P/pot

4. Fertilizer P uptake by the crop = P content of the crop × (%Pdff/100)

= 10 × (20/100) = 2 mg P/pot

5 Fertilizer P utilization or recovery by the crop: Since 20 mg P/kg soil was applied to each pot containing 2 kg soil, thus the P rate was 40 mg P/pot and

% Fertilizer P utilization = (Fert. P uptake by the crop / Fert. P rate applied) × 100

= (2/40) × 100 = 5%

Exercise 3

In a rice field, 20 kg P/ha as ^{32}P-labelled single superphosphate was applied at transplanting time. After about six weeks, plant samples were harvested from these treated plots. The dry matter yield was 2500 kg/ha and the total P concentration of 0.30 %.

A representative plant dry matter sample was dry, ashed and extracted with a known amount of 2N HCl. An aliquot of this extract containing 0.2 mg P was counted by Cerenkov and was found to give a count rate of 320 Bq. At the same time an aliquot of an acid extract of the ^{32}P labelled superphosphate containing 0.3 mg P was counted and was found to have a count rate of 3450 Bq. The counting efficiency was found to be 40 %.

Question: What was the fertilizer P utilization?

Calculations:

1. % Pdff is calculated as follows:

   Plant sample activity = 320 / 0.4 = 800 Bq

   SR plant sample = 800 / 0.2 = 4000 Bq/mg P

   Fertilizer activity = 3450 / 0.4 = 8625 Bq

   SR fertilizer = 8625/ 0.3 = 28750 Bq/mg P

   % Pdff = 4000 / 28750 × 100 = 13.9%

2. The total P yield or uptake

   P yield = 2500 × (0.3 /100) = 7.5 kg P/ha

3. The fertilizer P yield:

   Fertilizer P yield = 7.5 × (13.9 / 100) = 1.04 kg P/ha

4. The fertilizer P utilisation:

   % Fertilizer P utilisation = (1.04/20) × 100 = 5.2%

Exercise 4

Basic primary data from the experiment reported in [14] where band and broadcast application of KH_2PO_4 solution were compared in three soils are presented in Table 6 (section 3.3.3, this paper).

Using the band treatment in the clay loam soil as an example, the calculation of %Pdff is as follows:

$$\%\,\text{Pdff} = \frac{\text{KBq/g P in plant}}{\text{KBq/g P in fertiliser}} * 100$$

$$\%\text{Pdff} = \frac{0.697}{25.457} * 100 * = 2.7$$

And % Pdfs = 100 – % Pdff

= 100 – 2.7 = 97.3

Data for all the treatments with estimated plant yields and a constant P concentration of 0.15% is presented in Table 7 below. The % recovery (or utilization) of fertilizer P is calculated as follows:

$$\%\,\text{recovery of fertiliser P} = \frac{(2.7/100) * (0.15\%\,\text{P} * 3.6\,\text{g DM})}{24.2\,\text{mg fertiliser P added}} * 100$$

$$\%\,\text{recovery of fertiliser P} = \frac{0.027 * 5.4\,\text{mg}}{24.2\,\text{mg}} * 100$$

$$= 0.61\%$$

TABLE 7. DATA USED IN THE CALCULATION OF FERTILIZER P RECOVERY

Soil	Estimated Yield (g/pot)		%Pdff		%Pdfs		% recovery of fertilizer P	
	Band	Mixed	Band	Mixed	Band	Mixed	Band	Mixed
Clay loam	3.6	2.1	2.7	1.2	97.3	98.8	0.61	0.16
Loam	4.2	3.8	2.0	1.2	98.0	98.8	0.52	0.27
Sandy loam	5.4	4.8	1.6	0.8	98.4	99.2	0.55	0.23

An alternative method for calculating the % recovery of fertilizer P is as follows:

SA of fertilizer = 25.45 KBq/mg P

1 KBq = 1/25.4 mg P = 0.03929 mg P

Fertilizer P in plant = 1.045 KBq/g DM * 3.6 g DM * 0.03929 mg P

= 0.147 mg

% recovery of fertilizer P = (0.147 mg / 24.2 mg fertilizer P added)*100

= 0.61%

4.4 Quantification of P uptake from nutrient sources that can be labelled (ordinary/direct isotope dilution)

4.4.1 Introduction

P fertilizers are commonly applied as sources of nutrients to agricultural lands to ensure normal growth and achieve adequate yields of cultivated crops. Best fertilizer P management practices are required to ensure sustainable crop production and profitability and minimise adverse environmental impacts [18]. Fertilizer management practices such as source, timing, placement, etc. may be studied in the presence and absence of the effects of the fertilizer treatments on plant development, root distribution and crop yield. The use of special experimental designs using isotopes such as the single treatment fertility experiments allows the study of fertilizer uptake without a plant-fertilizer interaction [22]. As ^{32}P labelled fertilizers (direct labelling) are usually employed in these studies, the ordinary simple dilution principle applies.

4.4.2 Ordinary isotope dilution principle

In applying this technique it is assumed that the tracer is uniformly mixed in the particular 'pool' of material and that the rates with which the isotopes participate in the various processes are not substantially different from the unlabelled material; i.e. isotope effects are small [7].

Note that in some cases even though the isotope effects are very small they can provide valuable information on system operation.

The SR of the phosphorus in new plant growth reflects the integrated effective SR of the “soil available” phosphorus pool over that time interval

$$SRp = {}^{32}Pp/Pp = SRa = {}^{32}Pa/Pa \qquad (1)$$

According to the Ordinary Isotope Dilution (OD) using ^{32}P labelled Fertilizer

Specific radioactivity of fertilizer $SRf = {}^{32}Pf / Pf$ (eg Bq / g P) (2)

Specific radioactivity of plant P $SRp = {}^{32}Pp / Pp$ (eg Bq / g P) (3)

The ^{32}P in the plant can only have come from the fertilizer and this must be accompanied by the corresponding amount of fertilizer P. The SR of the fertilizer and the ^{32}P concentration in the plant are measured so the plant P derived from the fertilizer can be calculated

$$Ppff = {}^{32}Pp / SRf \qquad (4)$$

The proportion of plant P from the fertilizer $PPpff = Ppff / Pp$ (5)

from equations 4 and 5 $PPpff = {}^{32}Pp / SRf / Pp = SRp / SRf$ (6)

The proportion of the P in the plants from the fertilizer is the specific radioactivity "ratio" (SRR) of the SR's in plant and fertilizer. ie. $PPpff = SRR(OD)$

Fertilizer P utilization (recovery) or fertilizer P use efficiency can be calculated from the total ^{32}P uptake divided by the total ^{32}P applied in fertilizer

$$\text{Efficiency} = (SRp \times Ppy) / (SRf \times Pfa) = SRR \times Ppy / Pfa) \qquad (7)$$

4.4.3 Calculation exercises

The application of this technique in fertilizer studies are illustrated by the following exercises [21].

Exercise 1

Comparison of two ^{32}P labelled fertilizers such as superphosphate and nitro phosphate. (A Greenhouse experiment).

Treatments

^{32}P labelled superphosphate applied at a rate of 50 mg P/kg soil

^{32}P labelled nitro phosphate applied at a rate of 50 mg P/kg soil

Results:

Superphosphate treatment:

% Pdff = 20% and % Pdfs = 80%

From the fractional utilization relationship 20/50 = 80/x

Where: X = available amount of soil P or 200 mg P in superphosphate equivalent units.

Nitro phosphate treatment:

% Pdff = 10% and % Pdfs = 90%

From the fractional utilization relationship 10/50 = 90/x

Where X = available amount of soil P or 450 mg P in nitro phosphate units

Quantitative comparison of superphosphate and nitro phosphate

200 mg P as superphosphate = 450 mg P as nitro phosphate

1 kg P as superphosphate = X

1 kg P as superphosphate is equivalent to 450/200 = 2.25 kg P as nitro phosphate.

Exercise 2

Comparison of the efficiency of powdered and granulated triple superphosphate

Treatments

Powdered and granulated ^{32}P-labelled triple superphosphate

Both applied at a rate of 40 kg P/ha.

Results

Powdered ^{32}P labelled triple super (TSP)

% Pdff = 15% and % Pdfs = 85%

From the fractional utilization relationship 15/40 = 85/x

Where x = available amount of soil P or 227 kg P as powdered TSP units

Granulated ^{32}P labelled TSP

% Pdff = 20% and % Pdfs = 80%

From the fractional utilization relationship 20/40 = 80/x

Where x = available amount of soil P or 160 kg P as granulated TSP units

Quantitative comparison of powdered and granulated TSP

227 kg P as powdered TSP = 160 kg P as granulated TSP

1 kg P as powdered TSP = X

1 kg P as powdered TSP is equivalent to 160/227 = 0.70 kg as granulated TSP.

If the application of 40 kg P/ha as powdered TSP was the farmer's practice then the farmer should now apply 28 kg P/ha as granulated TSP to get the same amount of fertilizer taken up.

4.5 Quantification of P uptake from nutrient sources that cannot be labelled (Reverse or indirect isotope dilution method)

4.5.1 Introduction

In case of natural fertilizer sources, like phosphate rocks (PR), it is not possible to directly label these materials with P isotopes, because of the changes induced in their physical and chemical characteristics during labelling. Because of this techniques based on reverse or indirect isotopic dilution have been widely used to investigate P availability from phosphate rock sources to plants ([19, 22–23]

This methodology can be used in the following cases:

a) When it is impossible to label fertilizer P sources such as natural products (phosphate rocks) and organic materials, i.e: guano, green and animal manures, compost, agricultural wastes, crop residues, etc.

b) When it is impractical to label nutrient sources such as special fertilizer formulations required for a particular study are not commercially available.

c) When the cost of the required labelled fertilizers for the experiment, e.g. study of residual effect from P fertilization is too high.

4.5.2 Reverse/indirect dilution principle

Reverse dilution (RD) essentially consists of labelling the soil with a ^{32}P labelled solution and using the plant to measure the changes in specific radioactivity (SR) of the P supplied by the labelled soil. This method is usually referred to in the literature as "the isotope dilution technique", although this is not a true isotope dilution as defined in isotope tracer chemistry.

In phosphate studies, a solution of KH_2PO_4 or NaH_2PO_4 (at low P concentration: 10–50 mg P/L) labelled with ^{32}P carrier free or a high specific radioactivity orthophosphate solution (directly available from commercial firms) can be used for labelling the soil.

The rate of isotope application (irrespective of the P rate of application) should be about 7–18 × 10^6 Bq ^{32}P /m^2 to field plots and 4–7 × 10^6 Bq ^{32}P /kg soil in greenhouse experiments [20].

In the RD method, dilution of P in the labelled soil by phosphorus released from the unlabelled P source is monitored by measured the changes in SR of P in plants growing in the soil. A control treatment (without application of the unlabelled source) is also required. A diagrammatic representation of the reverse dilution and direct labelling (ordinary dilution) procedures is presented in Figure 3. In the direct labelling (ordinary dilution) the control treatment C, which receives no isotope has a SR of zero whereas in the reverse dilution the SR of the control is always higher than the fertilised treatments T as the SR of is reduced by the P released from the unlabelled P sources [7].

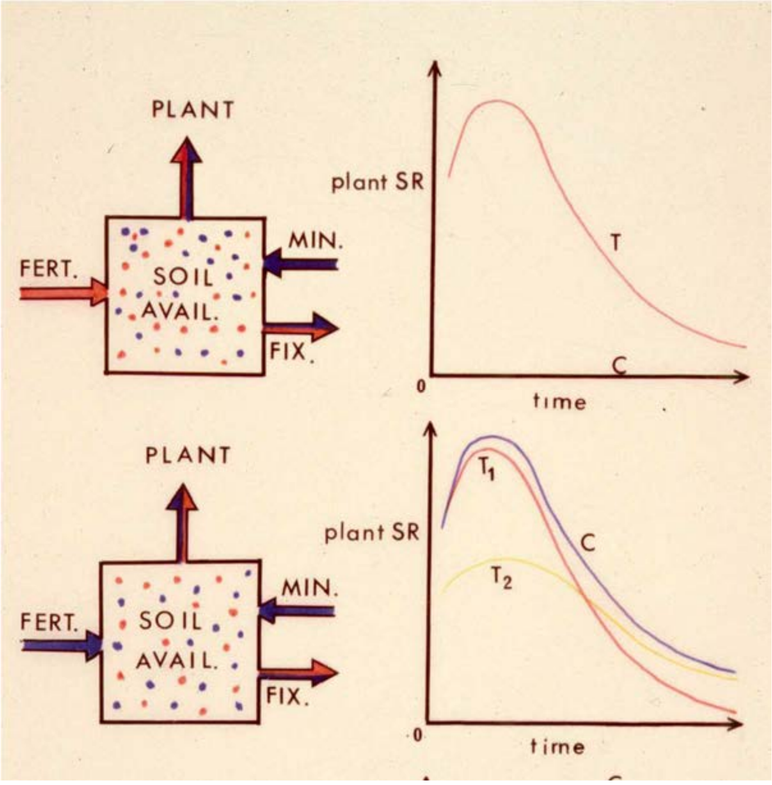

FIG. 3. Diagrammatic representation of direct labelling/ordinary dilution (top figure) and reverse dilution (bottom figure). Red dots represent ^{32}P and blue dots unlabelled P.

In an ideal situation the tracer would be introduced into the soil and in time all the components would end up with the same SR of the tracer nutrient. Unlabelled fertilizer would then be used and the system measurements and interpretation made in a similar manner to the direct labelling (ordinary dilution) situation. However, even if enough time could be left for this equilibrium to be established the moment any perturbation is introduced the equilibrium is upset and the SR of the nutrient in the various system components will not remain constant, thereby complicating the interpretation of some results. The problem is that we need to be able to make an estimate of the effective SR of the plant available phosphorus pool at any particular time. The assumption* is that this is provided by measuring the SR of plants growing in the system without added fertilizer i.e. control plants [7].

*Note: This is really the same assumption that we make about the plants echoing the SR of the soil available pool in the direct labelling (ordinary dilution) method.

In addition, for the fertilizer treatments, it has to be assumed that because the fertilizer treatment is usually small in relation to the total amount of P in the soil and does not mix with the available pool immediately, the flow of ^{32}P into the soil available pool is dominated by the other processes in the soil and changes relatively slowly ie. in the treated plants the change in SR is due to uptake of unlabelled P from the fertilizer.

Plant P and uptake from the soil available pool and applied fertilizer [7].

The concentration of P in the fertilizer is Pf and $^{32}Pf = 0$ the $SRf = 0$

It is assumed that the values of ^{32}P and P in the control plants (^{32}Ppc and Ppc) give an on-going estimate of the SR of the available soil P.

$$^{32}Ppc / Ppc = SRpc = SRa \qquad (1)$$

For the fertilizer treated plants : -

$SRp = {}^{32}Pp/Pp$ and $Pp = Ppff + Ppfa$ (2)

The proportion of the total plant P derived from the fertilizer is :

$PPpff = Ppff / Pp = (Pp – Ppfa) / Pp$ (3)

The ^{32}P in the plant could only come from the labelled soil available P pool and must have been accompanied by the corresponding amount of P from that pool.

The plant P concentration derived from the soil available P pool is given by:

$Ppfa = {}^{32}Pp / SRa$ (4)

and substituting in equation 3 for SRa (Eq 1) and Ppfa (Eq 4) the PPpff is given by :

$PPpff = (Pp – {}^{32}Pp / SRa) /. Pp$

$= 1–{}^{32}Pp / Pp \times 1 / SRa$

$= 1 – SRp/ SRpc$ (5)

In the reverse dilution the SRR is defined as (SRp (fertilised plant) / SRpc (control plant)

$PPpff = 1–SRR$

Note: – This SRR is not the same as SRR used in ordinary dilution.

The efficiency of the fertilizer P utilisation by plant is :

$Efficiency = PPpff \times Ppy / Pfa$

$Efficiency = (1 – SRR) \times Ppy / Pfa$ (6)

Even if the assumption of using the control plants to monitor the SR of the available P pool does not hold it is still possible to get valid RD comparisons between different fertilizers by using a range of rates of each and interpolating to get the application rates that give equivalent uptake of ^{32}P[7].

4.5.3 Calculation Exercise

Evaluation of the agronomic effectiveness of a phosphate rock in terms of a water soluble phosphate source such as superphosphate:

Both fertilizer P sources are unlabelled [21].

Experimental Treatments

1. Soil + ^{32}P labelled solution
2. Soil + superphosphate (60 kg P/ha) + ^{32}P labelled solution
3. Soil + phosphate rock (200 kg P/ha) + ^{32}P labelled solution

Results:

Specific activities (SR) of the harvested plant material per treatment are:

1. SR plant = 2000 Bq/mg P
2. SR plant = 1200 Bq/mg P
3. SR plant = 1400 Bq/mg P

Calculations

% Pdff = (SR plant sample / SR labelled fertilizer) x l00

% Pdfl = P derived from labelled source = (SR plant sample/ SR labelled source) x l00

Since SR labelled source = SR labelled soil

% Pdfl = (SR plant sample / SR labelled soil) x l00

and SR labelled soil = SR of the plant in treatment

= 2000 Bq/mg P

Treatment 2

% Pdfl = (1200/2000) x l00

= 60%

% Pdf. unlabelled fertilizer (super) = 100 – 60

= 40%–

From the fractional utilization relationship 40/60 = 60/x

Where x = available amount of soil P or 90 kg P/ha as superphosphate equivalent units.

Treatment 3

% Pdfl= (1400/2000) ×100

= 70%

% Pdf unlabelled fertilizer (rock phosphate) = 100 – 70

= 30%

From the fractional utilization relationship 30/200 = 70/x

Where x = available amount of soil P or 467 kg P/ha as rock phosphate equivalent units.

Quantitative comparison of rock phosphate and superphosphate

90 kg P as superphosphate = 467 kg P as rock phosphate

1 kg P as superphosphate = x

1 kg P as superphosphate is equivalent to 467/90 = 5.2 kg P as rock phosphate

4.6. Radiation Protection and Safety issues in handling phosphorus radioisotopes

The application of radioisotopes as tracers in agricultural research requires suitable facilities including laboratory and measuring/monitoring equipment and adequate training of the personnel to handle these nuclides safely, ensuring that radiation workers are not exposed to undue external or internal radiation hazards. Each Member States is required to establish radiation safety infrastructure to ensure safe use of radioisotopes. In this regard the users of radioactive material should always consider specific national legislation and regulations that controlling its use.

Occupational exposure to ionizing radiation can occur as a result of various human activities, including the use of radioactive sources in industry, agriculture, medicine and many fields of research, and occupations that involve the handling of materials with enhanced concentrations of naturally occurring radionuclides. This is the particular case when working with the most common radiotracer nuclides (β-emitters) used in agricultural research, i.e. ^{32}P (β^-, 1.7 MeV, t/2=14.3d), ^{33}P (β^-, 0.25 MeV, t/2=25.3d), ^{35}S (β^-, 0.17 MeV, t/2=87d) and ^{14}C (β^-, 0.15 MeV, t/2=5730a), being handled as so called "unsealed sources".

4.6.1 IAEA Safety Fundamentals

The fundamental safety objective and associated principles to protect people and environment against harmful effects of ionizing radiation, including safety of facilities and activities that give rise to radiation risks are presented in the IAEA safety publication entitled Fundamental Safety Principles, IAEA Safety Standard Series SF-1 [6, 24–25]. It has stated ten (10) principles: These are (1) Responsibility for safety (2) Role of government (3) leadership and management of for safety (4) Justification of facilities and activities (5) Optimization of protection (6) Limitations of risk to individuals (7) Protection of present and future generations (8) Prevention of accidents (9) Emergency preparedness and response and (10) Protective actions to reduce existing or unregulated radiation risk. The current basic safety standard of the Agency is based on this Fundamental Safety Principles [5].

4.6.2 IAEA Safety Standards

The IAEA Safety Standards publication series comprising Safety Fundamentals, Safety Requirements and Safety Guides are binding the IAEA for its operations, are applied by other sponsoring organizations for its own operations and are recommended for use by Member States and national authorities in relation to their own activities. According to IAEA these safety standards are not legally binding on Member States, but may be adopted by them, at their own discretion, for use in national regulations with respect to their own activities. Governments, however, have responsibility for establishing a national radiation safety infrastructure in support of applications of ionizing radiation in different activities. The IAEA Safety Requirements publication on the Governmental, Legal and Regulatory Framework for Safety [26] lists the responsibilities and functions of the government for safety. Other IAEA safety standards establish detailed requirements relating to those responsibilities and address in particular the protection of workers, patients and the public, and protection of the environment in all exposure situations and in a variety of facilities and activities.

4.7. Operational Radiation Protection and Safety procedures

Publication GSR Part 3 " Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards", jointly co-sponsored by EC, FAO, IAEA, ILO, OECD/NEA, PAHO, UNEP and WHO, details the requirements for the protection of people and the environment from harmful effects of ionizing radiation and for the safety of radiation sources [5]. Requirements established in this publication, as well as specific safety requirements and guidelines established in other IAEA documents [25, 26–27] could serve as a basis for the preparation and implementation of local rules and procedures directed to ensure an adequate level of radiation protection of workers and the members of the public against the radiation risks associated with the different applications of radiation sources.

Several examples [28-30] exist of the applications of radiation protection standards in those facilities and activities dealing with unsealed sources.

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APPENDIX

THREE CASE STUDIES ON THE APPLICATION OF P RADIOTRACERS TO EVALUATE VARIOUS P SOURCES IN SOILS

Case Study 1–1. Agronomic efficiency of Indian phosphate rocks in acid soils using radiotracer A-value technique

Case Study 1–2. Phosphorus uptake from green manures and phosphate fertilizers applied in acid soils

Case Study 1–3. Comparison of greenhouse and ^{32}p isotopic laboratory methods for evaluating the agronomic effectiveness of natural and modified rock phosphates in some acid soils

1–1 AGRONOMIC EFFICIENCY OF INDIAN PHOSPHATE ROCKS IN ACIDIC SOILS EMPLOYING RADIOTRACER A VALUE TECHNIQUE

1. INTRODUCTION

Phosphorus is an essential element for plant growth and its deficiency poses a major constraint to sustainable crop production especially in tropical and subtropical regions with acid soils. The application of P fertilizers is needed to overcome this constraint. In many developing countries, due to the high cost of mineral P fertilizers and limited access to fertilizer supplies, this is often difficult or impossible. However, phosphate rocks (PR) deposits have been found in many countries and their distribution is worldwide [1–2]. Direct applications of PRs (finely ground) including local deposits where possible, provide one of the cheapest and cost- effective ways to supply P to crops grown in tropical acid soils. As presented earlier, various factors affect the agronomic effectiveness of PRs and their capability to supply P to crops with time, especially the type of PRs used. It is, therefore, necessary to evaluate the agronomic effectiveness of different PRs for their effectiveness.

Radiotracer techniques have been used to evaluate the agronomic effectiveness of P fertilizers [3–4]. This is usually achieved by labelling the fertilizers during the manufacturing process with ^{32}P or ^{33}P [5]. However, this practice cannot be conducted on PRs because the process would drastically change the physical and chemical characteristics of PRs [6]). To overcome this problem the isotopic dilution technique (Paper 3) is used for comparing the P availability from different PRs to plants [7].

The protocol as described below demonstrates the use of the isotopic dilution technique involving the A value (available P) approach, which has been presented in Paper 3, for evaluating the agronomic effectiveness of two Indian PRs.

2. MATERIALS AND METHODS

Greenhouse pot experiments were conducted using sieved (2 mm) soil samples. Two acid soils (Aruvanthklu termed Aru soil, Dapoli termed Dap soil) were used in the study with two Indian rock phosphates (PRs) from Mussoorie (MRP) and Purulia (PRP). Single superphophate (SSP) labelled with ^{32}P containing 9.0% P and initial specific activity of 32 MBq ^{32}P g^{-1} P was used as a tracer.

The soils (2.5 kg pot^{-1}) in the pots were subjected to four treatments: (i) unfertilized control soil, (ii) soil + ^{32}P-labelled SSP, (iii) soil + ^{32}P-labelled SSP + MRP, (iv) soil + ^{32}P-labelled SSP + PRP, and thoroughly mixed. Rates of PRs and ^{32}P-labelled SSP used were 250 and 50 mg P kg^{-1}, respectively. A completely randomized block design was used with four replicates of each treatment. Soils were kept at field capacity for two days and basal N (60 mg N kg^{-1} as urea) and K (30 mg K_2O kg^{-1} as KCl) were applied. Maize (*Zea mays* L cv Ganga) plants (four per pot) were grown for 42 days and harvested. Dry matter yield (DYM) was determined and the plant materials were wet ashed in HNO_3-$HClO_4$ mixture (5:1) and total P determined. Radio assay of ^{32}P was conducted using a Geiger Muller counter.

2.1 Calculations

The followings were calculated according to Zapata (1991), and Zapata and Axmann (1995):

Per cent P derived from fertilizer (%Pdff) = (SA plant / SA fertilizer) × 100

where SA = specific activity (dpm mg P^{-1}).

^{32}P-SSP uptake (U_f) = (U_T × %Pdff) / 100 (mg pot^{-1})

where U_T = total P uptake (mg P pot^{-1}).

Per cent utilization ^{32}P-SSP (Ut_f) = Ut x 100/ R_f

where R_f = P rate applied as ^{32}P-SSP (mg pot^{-1}).

A value of soil (A_s) = [(100 – %Pdff) / %Pdff] × R_f (mg pot^{-1})

A value of RP soil (A_{RP}) =A value$_{(soil+RP)}$ – A_s (mg pot^{-1})

Plant P derived from ^{32}P-SSP (P_f) = (R_f × Ut_f) / 100 (mg pot^{-1})

Plant P derived from soil (P_s) = (A_s × Ut_f) / 100 (mg pot^{-1})

Plant P derived from RP (P_{RP}) = (A_{RP} × Ut_f) / 100 (mg pot^{-1})

Per cent utilization of RP = [PRP (mg pot^{-1}) × 100] / R_{RP}

where R_{RP} = P rate as RP (mg pot^{-1}).

Substitution ratio (SR) = R_{RP} (mg pot^{-1}) / A_{RP} (mg pot^{-1})

The SR compares the effectiveness of the PRs by calculating the amount of kg P as RP equivalent to 1 kg P as SSP.

3. RESULTS AND DISCUSSION

A summary of the agronomic evaluation is shown in Table 1. The A values for the Aru soil were higher than those of PRs, indicating higher P availability in Aru soil than PRs. This was not apparent in the Dap soil. Higher A values were shown by PRs in Aru than in Dap soil suggesting that PRs showed greater P availability in Aru soil compared with Dap soil. This was attributed to the lower pH in the Aru soil, probably causing greater dissolution of PRs.

The results of this case study show that the A value technique is very useful in quantifying the P availability from PRs in different soil types and provides basic information on P sources.

TABLE 1. AGRONOMIC EVALUATION OF INDIAN ROCK PHOSPHATES IN TWO SOILS.

from RP	A values (mg P pot^{-1})			Plant P partition (mg P pot^{-1})			P utilization (%)
Treatments	Soil+RP	Soil	RP	^{32}P-SSP	Soil	RP	RP
Aru soil							
^{32}P-SSP	—	141	—	2.009	2.181	—	—
^{32}P-SSP+MRP	222	141	81	1.653	1.841	1.072	0.172
^{32}P-SSP+PRP	242	141	101	1.362	1.536	1.101	0.180
Dap soil							
^{32}P-SSP	—	83	—	4.360	2.890	—	—
^{32}P-SSP+MRP	151	83	68	3.041	1.994	1.654	0.265
^{32}P-SSP+PRP	162	83	79	3.450	2.284	2.180	0.349

Source: [8].

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1–2 PHOSPHORUS UPTAKE FROM GREEN MANURES AND PHOSPHATE FERTILIZERS APPLIED IN AN ACID TROPICAL SOIL

1. INTRODUCTION

The supply of P to plants can be provided by both organic and inorganic P sources. It is important to have information on the relative effectiveness and contribution of P sources to plants so as to be able to choose the most cost effective source to provide P to crops.

Radio-isotope techniques provide direct and indirect means of assessing the capacity of various P source to plants [1–3]. When two sources of P are present, a double ^{32}P–^{33}P labelling technique can be used to compare the relative contribution of each P source.

The protocols of this study as described below demonstrates the use of this dual P isotope technique in a glasshouse experiment to assess the relative contribution of two different P sources (green manures, GMs and PR fertilizers) to a test plant grown in a tropical acid soil.

2. MATERIALS AND METHODS

Setaria (*Setaria sphacelata*) grass was used as a test crop with three different GM sources (*Calopogonium caeruleum, Gliricidia sepium, Imperata cylindrica*) and four P fertilizer sources (PRs from North Carolina, NCPR, China, CPR, Algeria, APR and triple superphosphate, TSP). The GMs were labelled with ^{33}P and the PR contribution was assessed by the isotopic dilution technique [4–6] using ^{32}P-labelled soil.

An acid topsoil (0–200 mm) and finely ground (<100 µm) or granulated (<250 µm) PRs were used. The plants were first grown for 15 months in separate aluminium containers before being labelled by applying a solution containing 3.33 MBq of ^{33}P and 18 µg of P (KH_2PO_4) as carrier to the top of 100–150 mm soil layer in each container. Labelled GM plants were harvested after another 3 weeks of growth.

Similarly, 1-kg subsamples of the soil were each labelled with a solution containing ^{32}P of an activity of 1.85 MBq and 2 mg P kg^{-1} carrier as KH_2PO_4. These soils were set aside to equilibrate for 14 days. The fresh ^{33}P-labelled GMs (50 g dry matter kg^{-1} soil) and P fertilizers (66 mg P kg^{-1} soil) were then applied to the pre-treated labelled soils in a factorial design of three GMs and four P fertilizers treatments replicated three times. Two stem cuttings of Setaria grass (120–150 mm) were then planted in each pot in the same day, and plants manually irrigated daily. Supplementary N and K were each added (33.3 mg pot^{-1}) as urea and KCl to each pot. Plants were harvested at 4, 8 and 15 weeks after established (WAE) and dry matter yield (DMY) was determined. Plant subsamples were ashed at 500° C for 4 hours and the ash was then dissolved in 2 M HCl. ^{32}P and ^{33}P activities were measured in the filtrate by liquid scintillation counting [7]. Total P in the filtrate was determined by the molybdate method [8].

2.1 Calculations

Per cent P uptake from GMs (%PdfGM) was calculated as:

$$\%PdfGM = (SA_{trt}/SA_{GM}) \times 100$$

where SA_{trt} = specific activity of plants in a particular treatment, SA_{GM} = specific activity of the applied GM.

Total P obtained from GMs (PGM) as:

$$\text{PGM (mg pot}^{-1}\text{)} = \%\text{PdfGm} \times (\text{PYLD}/100)$$

Where: PYLD is total P yield in Setaria as:

$$\text{PYLD (mg pot}^{-1}\text{)} = \%\text{P x DMY} \times 10$$

The proportion of P derived from fertilizer treatment (%PdfT) was obtained based on isotope dilution principle as:

$$\%\text{PdfT} = \{1 - (SA_{ctrt}/SA_{control})\} \times 100$$

Where: SA_{ctrt} and $SA_{control}$ are the specific activities of plants in treated soils and control, respectively.

The total P uptake from fertilizer (Pf) was estimated as:

$$\text{Pf (mg pot}^{-1}\text{)} = (\%\text{PdfT} \times \text{PYLD})/100$$

The proportion of P derived from the soil (%PdfS) was estimated as:

$$\%\text{PdfS} = 100 - (\%\text{PdfT and/or \% PdfGM})$$

The P utilization from the GMs (%PGM) and from the P fertilizers ($\%P_f$) was estimated as:

$$\%P_{GM} \text{ utilization} = P_{GM} \times (100/\text{total } P_{GM} \text{ applied})$$

$$\%P_f \text{ utilization} = \text{Pf x } (100/P_f \text{ applied})$$

3 RESULTS AND DISCUSSION

3.1 Relative contributions of P derived from GMs and P fertilizers to P uptake over time

These results are shown in Table 1. The highest contribution from the GMs was <0.5%, whereas that from PRs and TSP exceeded 70%. The fertilizer P uptake at each stage was not significantly different among all PRs except CPR, which gave significantly the lowest value at 4 and 15 WAE.

TABLE 1.. PROPORTION OF P (%) CONTRIBUTED BY P FERTILIZERS AND GMS TO TOTAL P UPTAKE BY SETARIA PLANTS OVER A 15-WEEK PERIOD.

Treatments	4 weeks	8 weeks	15 weeks
Green manures			
Gliricidia	3.1a*	2.5a	0.8a
Imperata	0.5b	1.6a	0.4a
Calopogonium	3.5a	2.2a	0.6a
P fertilizers			
NCPR	71.2 a	69.4a	61.8a
CPR18.8b	49.5a	8.5b	
APR	60.8a	64.7a	9.0a
TSP	63.2a	77.1a	60.0a

** Treatment means within each sampling time followed by the same letter are not significantly different at* $p \leq 0.05$.

3.2 Utilization of P from GMs and P fertilizers

These results are shown in Table 2. The utilization of P in the combined GM + P treatments varied with the GMs, P fertilizer, and time of sampling. For example, Gliricidia significantly reduced NCPR utilization in the first two harvests (8 WAE) but showed little effects on the other P treatments. At 15 WAE (3 harvests), fertilizer P utilization increased in all GM + P treatments and the highest value was obtained with Imperata + APR (48%). The GMs significantly increased P uptake even in the absence of P fertilizers. However, the small %PdfGM (<5%) and the low $\%P_{GM}$ utilized (<1%) clearly showed that GMs were not a major contributor to P uptake by Setaria plants. The greater %P utilization in the GM + P treatments showed that GMs improved the availability of fertilizer P. Even the low-quality Imperata GM augmented the APR utilization from 6 to 48 % in the soil. Improved availability of fertilizer P could be due to to the effects of the decomposition products (organic anions, hydroxly groups) of GMs enhancing the solubility of PRs similar to that reported by [8] for plant residues.

TABLE 2. PHOSPHORUS UTILIZATION (%) FROM GMS AND P FERTILIZERS BY SETARIA.

		Green manures			
Weeks	P treatments	No GM	Gliricidia	Imperata	Calopogonium
8	NCPR	9.03a(b)*	3.0c(c)	13.71b(ab)	19.50a(a)
8	CPR	2.58c(c)	3.57c(c)	12.15b(b)	16.60a(a)
8	APR	5.16b(c)	6.93b(c)	31.38a(a)	11.17ab(b)
8	TSP	6.16b(b)	8.16a(b)	22.11a(a)	2.85b(c)
15	NCPR	11.59a(c)	19.57b(bc)	24.64a(b)	35.71a(a)
15	CPR	3.70c(c)	14.20b(b)	30.39a(a)	29.34a(b)
15	APR	6.61b(c)	35.35a(b)	48.39a(a)	29.34a(b)
15	TSP	9.40a(b)	35.59a(a)	33.94a(a)	37.33a(a)

* For each sampling time, means within a column followed by the same letter are not significant different at $p \leq 0.05$, and means within a row followed by the same letter(s) in brackets are not significantly different at $p \leq 0.05$ according to Duncan Multiple Range tests.

The results of this case study show that the double isotope ^{32}P–^{33}P technique is a valuable tool in quantifying the P uptake from each of the two different P sources (GMs and P fertilizers) over time.

Source: [9].

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1–3 COMPARISON OF GREENHOUSE AND ^{32}P ISOTOPIC LABORATORY METHODS FOR EVALUATING THE AGRONOMIC EFFECTIVENESSS OF NATURAL AND MODIFIED ROCK PHOSPHATES IN SOME ACID SOILS OF GHANA

1. INTRODUCTION

As pointed out earlier, direct application of natural and modified PRs has been recommended as a cost effective method of providing P to crops in acid soils in the tropics [1]. Methods for evaluating the agronomic effectiveness of various PRs usually involved conducting greenhouse or field experiments with or without isotopic tracers [2]. These are expensive and time-consuming. A laboratory method for evaluating P availability can overcome some of these difficulties. The ^{32}P isotopic kinetic method (IEK) to characterize the available soil P was developed by [3]. It was proposed by [4] that the same technique has the potential to replace greenhouse or field experiments to predict the P bioavailability of P fertilizers and enable their agronomic effectiveness to be assessed. A functional model utilizing the ^{32}P isotopic kinetic method (IEK) data was developed by [5].

The study as described below demonstrates the feasibility of using the IEK laboratory method in place of greenhouse experiments to assess the agronomic effectiveness of some natural and modified PRs in some tropical acid soils in Ghana.

2. MATERIALS AND METHODS

The study compared the agronomic effectiveness of PRs assessed by the classical greenhouse pot experiment and the ^{32}P IEK laboratory experiment. Six acid soils from Ghana were used.

Treatments in the greenhouse pot experiment consisted of six soils (Abenia, Aiyinase, Ankasa, Boi, Kwaben, Tikobo), four P fertilizers (TSP, Togo PR or TPR, Togo PAPR 50% or PAPR, Mali PR or MPR), each applied at four rates (0, 30, 60, 120 kg P ha^{-1}). All treatments were arranged in a randomized complete block design with three replicates. One kg soil (< 2mm) samples were wieghed into plastic pots (95 mm diameter) and P fertilizers were thoroughly mixed with the soil and added to pots. Seeds of maize (*Zea mays* L. var. Obatampa) were sown in pots and thinned to two plants per pot after 7 days. A nutrient solution containing 0.99 g $Ca(NO_3)_2.4H_20$, 2.04 g KNO_3, 0.98 g $MgSO_4.7H_20$, and 0.24 g NH_4Cl per two litres were applied at 150 ml per pot in three aliquots of 50 ml per week when plants were at 1, 3 and 5 weeks old. Plants were harvested six weeks after planting and dry matter yield (DYM) determined.

In the IEK laboratory experiments, the six soil samples were each fertilized with 50 mg P kg^{-1} soil using the same four P fertilizers. Controls without P fertilizers were also included. Two sets of soil samples were used, one immediately after P fertilizer addition (without incubation) and the other incubated for six weeks at room temperature of 25° C under moist conditions. Ten g of each soil sample was weighed into 150-ml polyethylene bottles in triplicate and 99 ml of deionised water was added to each bottle and shaken for 18 h. After shaking, the ^{32}P tracer (1 ml carrier free $H_3{}^{32}PO_4$ with radioactivity (R) of about 0.1 to 1 MBq was added at time t = 0 and mixed well with a magnetic stirrer with continuous shaking. At times (t) corresponding to 1, 10, 40, and 100 min, respectively of isotopic exchange, 8 ml of the suspension was removed with a polyethylene syringe and the solution was immediately separated from the soil using a Millipore filter (0.05 µm pore size, 47 diameter). A constant period of 10 seconds was allowed to complete the sampling and filtration. Radioactivity (r) remaining in the solution at each time (t) was measured with a liquid scintillation counter by Cerenkov counting. The concentration of P (Cp) as phosphate ions in solution was determined after the last isotopic exchange sampling by [6] method.

2.1 Calculations

The equations used for calculating the various parameters in the IEK method have been presented earlier (Paper 3). In this study, the amount of phosphate ions exchangeable with ^{32}P at time t, and E(t) are calculated as follows:

$$E(t) = 10\ Cp\ (R/r_t)t^n$$

where E(t) is the isotopically exchangeable P after t min (mg P kg^{-1}), Cp is the total radioactivity introduced as ^{32}P, r_t is the remaining ^{32}P activity measured in the soil solution after t min, 10 is the water: soil ratio, n is a constant that describes the disappearance of ^{32}P from the solution with time. The total P content of the soil was divided into five pools [5] and the size of each pool calculated as:

$$E_{1min} = 10\ Cp\ [R/r_1]$$

$$E_{1d\text{-}1min} = 10\ Cp\ [R/r_{1140} - R/r_1]$$

Where: 1140 = 1 day (d) calculated from previous Equation.

$$E_{1d\text{-}2wk} = 10\ Cp\ [R/_{120960} - R/r_{1440}]$$

$$E_{12wk\text{-}1}yr = 10\ Cp\ [R/r_{525600} - R/r_{120960}]$$

$$E_{>yr} = P_T - 10\ Cp[R/r_{525600}]$$

Where: P_T is the total quantity of P taken up by plants.

The expected values of P in the plant derived from fertilizer (%Pdff) are calculated [5] as:

$$\%Pdff = 100\ [10Cp'/r_{t'}) - (10Cp/r_t)] / (10Cp'/r_{t'})$$

The Relative Agronomic Effectiveness (%RAE) was calculated from the ratio of the Pdff of the PR to the Pdff of TSP.

In the greenhouse experiment, the relationship between DMY or P uptake and rate of P applied was determined using a semi-logarithmic function [7] as follows:

$$Yi = \beta o + \beta i \ln X + \varepsilon i$$

where Yi = DMY of the P uptake obtained with source i, X = rate of P applied, βi = slope of the response function of source i, βo = common intercept, εi = error term of the fitted model. The Relative Crop Response Index (RCRI) was estimated as follows:

$$\text{RCRI} = \beta i/\beta_{\text{TSP}} \times 100$$

where: βi = regression estimate of the treated PRs, β_{TSP} = regression estimate of the standard fertilizer used (TSP) to evaluate the efficiency of response to fertilizer across the range of P rates used [7]. The RCRI represents the marginal increase in DMY or P uptake in per cent of P source compared to a standard source, when a unit of P fertilizer was applied [8]

3 RESULTS AND DISCUSSION

Data showing the effects of PR on IEK parameters and the bioavailability of P are given in the cited publication [9]. These will not be presented and discussed here as the main objective of this case study is to compare the IEK and greenhouse methods of predicting the agronomic effectiveness of PRs.

3.1 Comparisons of results of agronomic effectiveness determined by the IEK method and the greenhouse experiment

These results are shown in Table 1. as predicted %RAE values derived from the laboratory IEK method and %RCRI (P uptake) derived from the greenhouse experiment. On the whole, the estimates by the two methods were similar in some soils. For example, in the Boi soil, the %RAE values for Togo PAPR and TPR were similar to those of RCRI[4]. reported similar results in their experiments. Based on the RCRI results, the P sources were 4 to 92 % as effective as TSP in terms of P uptake by the crop. Except for the Tikobo soil, the RCRI of P sources increased in the order: TSP>MPR=PAPR>TPR. The high RCRI in the Boi soil was attributed to the low exchangeable Ca present in this soil. In the Boi soil, PAPR was as effective as TSP (Table 4.4) as this soil has a relatively high P sorption capacity as reported in the study. Similar findings on the performance of PAPRs were reported by [9,10] concluded that the results of their study support the findings that PR with low reactivity and containing less than 20 g kg^{-1} Fe and Al oxides as shown by Togo PR [11], partial acidulation of the PR would be the most effective method of using such PR for sustainable agricultural production in acid soils in the tropics [8].

The results of this case study showed that the IEK method may be considered as an alternative to the greenhouse experiment for assessing the agronomic effective of P fertilizers in tropical acid soils when the IEK method offers comparative advantages compared to the greenhouse method under a given situation. However, [9] indicated that trained staff and adequate laboratory facilities are needed to perform the IEK method.

TABLE 1. COMPARISONS OF THE AGRONOMIC EFFECTIVENESS AS ESTIMATED BY THE LABORATORY IEK METHOD (RELATIVE AGRONOMIC EFFECTIVENESS, %RAE) AND BY THE GREENHOUSE EXPERIMENT (RELATIVE CROP RESPONSE INDEX, RCRI FOR P UPTAKE).

Soil	P source	Laboratory estimates %RAE	Greenhouse estimates %RCRI
Abenia	TSP	100	100
	PAPR	92.3	62.4
	MPR	–	63.5
	TPR	63.6	37.6
Aiyinase	TSP	100	100
	PAPR	79	75.3
	MPR	–	82.8
	TPR	–	30.6
Ankasa	TSP	100	100
	PAPR	85.7	41.6
	MPR	–	47.9
	TPR	–	18.9
Boi	TSP	100	100
	PAPR	81.2	91.5
	MPR	–	93
	TPR	93.6	78
Kwaben	TSP	100	100
	PAPR	89.6	43.4
	MPR	–	43.7
	TPR	13.9	3.78
Tikobo	TSP	100	100
	PAPR	80.3	85.4
	MPR	–	46.1
	TPR	–	14.8

Source: [9].

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ABBREVIATIONS AND ACRONYMS

AERM	Anion Exchange Resin in Membrane
ARIs	Advanced Research Institutes
BNF	Biological Nitrogen Fixation
Bq	Becquerel
CGIAR	Consultative Group on International Agricultural Research
Ci	Curie
CPR	People's Republic of China
CRP	Coordinated Research Project
CSAs	Critical Sources Areas
DAPR	Direct Application of Phosphate Rock
DM	Dry Matter
DMY	Dry Matter Yield
DP	Dissolved Phosphorus
DPS	Decay per Second
EDTA	Ethylene Diamine Tetra acetic Acid
EUROATOM	European Atomic Energy Community
FAO	Food and Agriculture Organization of the United Nations, Rome
GIS	Geographical Information System
GM	Green manure
IARCs	International Agricultural Research Centres
ICP	Inductively Coupled Plasma
IEK	Isotopic Exchange Kinetics
IFDC	International fertilizer Development Centre
ILO	International Labour Organization
IMO	International Maritime Organization
LSC	Liquid Scintillation Counter
MeV	Mega electron Volt
NMR	Nuclear Magnetic Resonance
NUTMON	Nutrient Monitoring
OECD/NEA	Organisation for Economic Co-operation and Development / Nuclear Energy Agency
PAHO	Pan American Health Organization
Pi	Inorganic Phosphate
PP	Particulate Phosphorus
PRs	Rock Phosphates/Phosphate Rocks
RAE	Relative Agronomic Effectiveness
RCM	Research Coordinated Meetings
RCRI	Relative Crop Response Index
RD	Reverse Dilution
RPRs	Reactive Phosphate Rocks
SR	Specific Radioactivity
SR_f	Specific Radioactivity in Fertilizer
SR_p	Specific Radioactivity in Plant
TECDOC	Technical Document
TP	Total Phosphorus
TSP	Triple Super Phosphate
UNEP	United Nations Environment Programme

WAE	Weeks after Emergence
WHO	World Health Organization
WSP	Water Soluble Phosphate

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