

ESTIMATING DISSOLVED P LOSSES FROM LEGACY SOURCES IN PASTURES - THE LIMITS OF SOIL TESTS AND SMALL-SCALE RAINFALL SIMULATORS

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Introduction

Excessive P concentrations in streams and water impoundments are a feature of many agricultural catchments where P amendments are applied to intensively grazed pastures. In these systems P is lost in runoff, either as part of a solid, attached to a solid, or as a solute (i.e., dissolved in water). The terms “particulate” and “dissolved” are commonly used to define P materials that pass through or are retained by a 0.45 µm filter. Particulate P (PP; i.e., >0.45 µm) comprises crystalline P, adsorbed P and P in organic matter. On the other hand, dissolved P (DP; i.e., <0.45 µm) is generally considered to be dominated by inorganic orthophosphate (H₂PO₄⁻/HPO₄²⁻), the form of P utilised by both terrestrial and aquatic organisms. In well-managed agricultural systems, unless there is a predisposition to erosion (i.e., high slope, gully formation, dispersive soils, excessive animal treading damage), P in runoff is generally dominated by DP that is reactive in an acid-molybdate solution (Murphy and Riley 1962), known as Dissolved Reactive (DRP).

Phosphorus exports in runoff from pasture-based grazing systems can be conveniently divided into “systematic” (i.e., base or background) and “incidental” (i.e., management) components (Haygarth and Jarvis 1999). Phosphorus amendments can contribute directly to “incidental” P exports soon after their application and to “systematic” exports by increasing soil fertility and P cycling. While incidental P mobilized directly from amendments can account for a substantial portion (30-80%) of total farm P exports, when appropriately managed, that figure can be <10% (Nash and Hannah 2011; Nash *et al.* 2019). Of more concern appears to be P surpluses and the increasing P concentrations in the so-called “legacy P” (Kleinman *et al.* 2011) that represents a recalcitrant baseline underpinning systematic exports.

Tools for assessing P export potential are often informed by empirical relationships between soil test P (STP) and P concentrations developed from rainfall simulation studies (Vadas *et al.* 2005). The use of simulated rainfall and small plots (i.e., <100 m²) to study and estimate the effects of legacy P on P exports has been justified on the basis that those systems mimic the processes responsible for DP mobilization and saturated excess overland flow, rather than quantify DP exports *per se* (McDowell *et al.* 2003a; McDowell *et al.* 2003b; Sharpley and Kleinman 2003; Dougherty *et al.* 2008; Burkitt *et al.* 2011). We evaluate the influence of experimental protocols in small-scale rainfall simulation studies on inferences related to P source (i.e., Soil Test P (STP) and runoff P concentrations).

The processes responsible for dissolved P mobilization

Studies of P runoff from pasture soils under natural rainfall are generally consistent in describing an early spike in DP mobilization, then a decline as a storm stabilises at a slightly lower rate and runoff DP concentrations are diluted with growing flow rate (e.g., Figure 1). That proposition is supported by irrigation (Nash *et al.* 2007b; Nash and Barlow 2009) and flume studies (Barlow 2003; Doody *et al.* 2006).

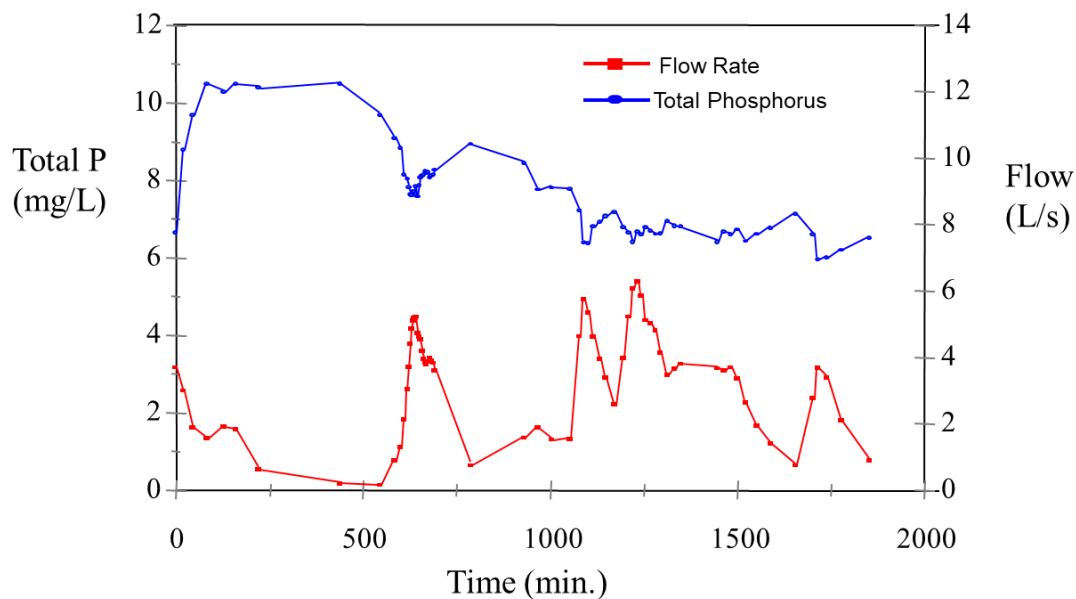


Figure 1. Within storm variation in total P concentration and flow from a field in the Darnum region of West Gippsland, Australia on November 6, 1994. Adapted from (Nash and Murdoch 1997).

For pasture systems, mathematical modelling (Deng *et al.* 2006), rainfall simulation studies where water was applied on successive days (Sharpley 1995), and field studies where strong relationships between overland flow volume and flow-weighted DP concentrations between storms have not been found (Nash *et al.* 2000; Nash *et al.* 2005), all suggest a mixing layer model could be used to describe P mobilisation. In a single layer mixing model, the depth of soil and water mixing determines the quantity of P initially available for mobilization, with a depth of ~ 3 mm expected in many well-managed pastures (Ahuja *et al.* 1981). It is highly unlikely that a discrete layer of fixed depth exists in heterogenous pasture soils or even that true overland flow is the only P transport pathway. The layer of detritus (e.g., decomposing organic matter including thatch, fragments of dead organisms and faecal material, and associated biological communities) near the soil surface is probably a reasonable approximation of a mixing layer that transitions to the soil below. However, while overland flow may occur, in many systems interflow in the surface detritus is common and functionally indistinguishable from true overland flow (Nash *et al.* 2002). Compaction of soil below the mixing layer by animal traffic would help suppress infiltration (Alderfer and Robinson 1947; Drewry 2006; Houlbrooke *et al.* 2009), contributing to interflow that manifests itself in the form of spongy, saturated surface soil that exudes water on compression (e.g., grazing animals). In these systems P is often exported offsite in a few large storms each year and exports continue

after rain, and therefore true overland flow, has ceased (Nash 2002). A single mixing layer model in which chemical dissolution occurs is not consistent with these observations.

It is apparent that DP mobilisation occurs in two phases and can be described using a mixing layer model with chemical transfer. Initially (Process 1), contaminants (e.g., P) are rapidly mobilized from a layer or zone near the surface due to the physical interaction (i.e., mixing) of soil and water. Subsequently, a second (Process 2), slower mobilization dominated by diffusion and hydraulic dispersion (i.e., mechanical mixing by velocity variations at the microscopic level during advective transport) transfers contaminants into the mixing layer from below and facilitates solute egress from aggregates, plants, and detritus both within and to the mixing layer.

Convective transport of dissolved pollutants such as P early in a storm (Process 1) is well documented (Wallach 1991). Initially high rates of pollutant mobilization decline as labile supplies are exhausted (i.e., P mobilization is supply limited). The second slower process on the other hand, Process 2, is rate limited. While slow mobilization (i.e., Process 2) declines exponentially with diffusion path length, the residual pool of accessible P is greater due to an overall slower mobilization rate than Process 1 and access to a larger pool of P, especially from below. It follows that while P mobilization tends to peak early in a storm, it often quickly stabilises and marginally declines thereafter (Wallach and Shabtai 1992; Shi *et al.* 2011).

It is noteworthy that in pastures, P mobilization rates are likely to be influenced by infiltrating water carrying P into the soil and away from the mixing layer (Wallach *et al.* 2001) or conversely, return flow, especially from sub-surface interflow (Snyder and Woolhiser 1985), transporting additional P into the mixing layer (Figure 2) (Govindaraju 1996).

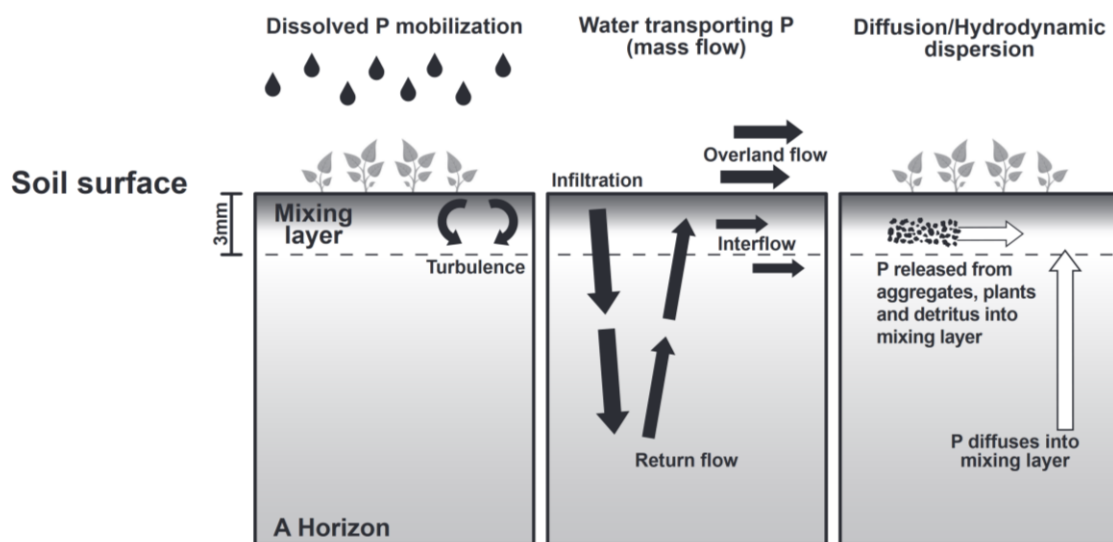


Figure 2. Field-scale processes contributing to DP mobilization.

Sources of DP mobilized from pasture soils.

Rather confusingly, the term “desorption” has often been used to describe DP mobilization into overland flow. While “desorption” may have a broader context in relation to DP mobilization that can include physical processes (e.g., diffusion-controlled desorption) (Sharpley *et al.* 1981; Koopmans *et al.* 2004), it is questionable if the term “desorption” is appropriate for pasture-based grazing systems. Moreover, using the term “desorption” implies that reactions between orthophosphate and adsorption surfaces primarily control DP mobilization.

Dissolved P mobilization commences when rainfall or irrigation-water washes over pasture plants and onto the soil surface. Numerous studies have shown that water can extract significant concentrations of P from the plant canopy (Timmons *et al.* 1970; Sharpley 1981; McDowell *et al.* 2011), especially after grazing (Mundy *et al.* 2003). Plant exudates can contribute to a surface coating of soluble P mixed with dust that can be removed by rainfall. Phosphorus inside standing detritus and intracellular P are more difficult to mobilize (Dougherty *et al.* 2004).

On arrival at the soil surface, water is exposed to both inorganic and organic sources of P in the mixing layer. In pasture-based grazing systems organic P often comprises >50% of total soil P (Perrott and Sarathchandra 1989; Perrott *et al.* 1990; Richardson 1994; Stutter *et al.* 2012; Stutter *et al.* 2015). Although relationships between organic carbon and P in overland flow have been demonstrated (Halliwell *et al.* 2000), estimating the proportion P exports derived from inorganic (e.g., mineral fertilizer) versus organic P sources (e.g., animal manures) remains problematic.

The physical location of P released from organic sources in relation to other soil constituents is also likely to affect P mobilization. While P in the form of orthophosphate (e.g., from plant exudates) on the surface of detritus may participate in adsorption processes with inorganic soil components, a considerable portion of P derived from organic sources would likely be encapsulated by the organic materials themselves. Moreover, at microsites where organically derived P may be sequestered, anionic organic matter may compete with P for adsorption sites in ligand-exchange (Holford 1989; Schulthess and Sparks 1991) and, in acidic soils, organic matter may lower the activity of iron and aluminium (Vijayachandran and Harter 1975), which would otherwise precipitate P from solution (Thomas 1975; Bloom *et al.* 1979; Lobartini *et al.* 1998). There is little quantitative information on these mechanisms.

The role of experimental protocols in rainfall simulation outcomes

Numerous studies have investigated relationships between STP and P exports in simulated overland flow. For a selection of those studies and their experimental protocols refer to (Nash *et al.* 2021). Rainfall simulation experiments can be divided into three classes based on soil or site preparation. For **Repacked trays**, soil is often collected from the field, air dried, processed (e.g., crushed and sieved) and repacked into trays at near field soil bulk density (e.g., (Kleinman *et al.* 2004)). Some of the soil layering may be reconstituted (e.g., 0-20 mm) and/or plant cover established. For **Intact turfs**, wedges of soil and the associated plant cover are recovered from the field and placed in trays. And for **Field plots**, borders of various types are used to hydrologically isolate plots and collect overland flow *in-situ*. The plots are often located in commercial fields or experimental plots. Specific aspects of rainfall simulation experiments that may affect their ability to accurately estimate the effects of legacy P on P exports are considered below.

Soil preparation

Soil preparation prior to the application of simulated rainfall is likely to affect relationships developed using repacked trays. Increased P availability following wetting and drying cycles is well documented (Frossard *et al.* 2000; Blackwell *et al.* 2010) and, even if the soil was sampled in layers, it is highly unlikely that natural soil P stratification (Dougherty *et al.* 2006b) (i.e., the mixing layer and transition zone below it) could be re-established. The “apparent” mixing layer would contain only a fraction of the total soil P that would exist in the field, much like field soils that have been cultivated as part of pasture renovation (Dougherty *et al.* 2006a; Watkins *et al.* 2012).

Drying, crushing, and repacking trays is also highly likely to alter soil physical properties including structure and aggregate stability that affect the diffusion pathways that are important for rate dependant P mobilization (Process 2) and soil infiltration characteristics that affect mass transfer of P into and out of the mixing zone (see hydrology below). The anomalies created by reconstructing the soil profile do not occur to the same extent with intact turfs or field plots and in part explains why small-scale, high-intensity rainfall simulation may underestimate natural runoff P concentrations from pastures (Dougherty *et al.* 2008).

A lack of significant differences in extraction coefficients (i.e., gradient of a linear plot of STP against DRP concentration) between repacked trays and field plots (Vadas *et al.* 2005) has been used to argue that repacked trays with re-established pasture soils adequately represents, and compares well with, P mobilization under field conditions. However, a lack of significant differences is not of itself a measure of similarity. Moreover, it is unlikely that the chemical and physical attributes of a field soil could be reproduced by regrowing pasture in a glasshouse ($20^{\circ}\text{C} \pm 5^{\circ}\text{C}$) for <1 yr. prior to experimentation. More so in the absence of “normal soil biology” and where harvested vegetation is removed. In field-scale studies, pastures that have been cultivated prior to being resown, do not exhibit pre-cultivation P concentrations in soil water (Watkins *et al.* 2012) and runoff (Nash *et al.* 2007b) until long after pasture is re-established (i.e., >>1 yr.).

Scale and measurement duration

Effects of flow path length and velocity are two interrelated parameters that affect soil-water contact time and Process 2, (i.e., P mobilization). The “time of concentration” (i.e., time for the entire watershed to contribute to measured flow and therefore the time available for soil-water interaction) (Grimaldi *et al.* 2012) is a concept used in hydrology to estimate the effect of a rain event and is related to the time to peak flow and rainfall intensity (Michailidi *et al.* 2018). In rainfall simulation studies where P exports are often measured for <60 minutes after overland flow has commenced, the time of concentration is relatively short when compared to field-scale studies where overland flow persists for hours. Consequently, rapid, supply-limited P mobilization (i.e., Process 1) would be expected to dominate P export concentrations in simulated rainfall experiments. However, at the field-scale, most P exports occur in a few major runoff events each year (Owens and Shipitalo 2006) that often last longer than an hour (Nash 2002). It follows that in the field, P exports are more likely to reflect rate dependant P mobilization (i.e., Process 2) rather than P mobilized directly from the mixing layer.

Hydrology

In most rainfall simulation studies the hydrology is referred to using terms such as runoff, surface runoff, overland flow, or saturated overland flow. While the latter description is true for the outlet, it is unlikely to be the case for other areas of the tray or plot. In small scale simulation experiments hydrology often varies between replicates within soil types, as

demonstrated by good relationships between STP and P concentration, and poor relationships (i.e., $R^2 < 0.02$) between STP and P loads (Pote *et al.* 1996). As P concentrations in runoff reflect net P mobilization, understanding the hydrology of simulation experiments is important for interpreting their outcomes (Kleinman *et al.* 2006)

A schematic diagram describing the possible hydrology of experimental trays is presented in Figure 3a. It is likely that infiltration excess overland flow, saturation excess overland flow and interflow are occurring simultaneously in different locations (Nash *et al.* 2002). The predominant hydrology will vary with soil infiltration rate and hydraulic conductivity (i.e., water transmission rate) (Nash 1984), and the degree of anisotropic behaviour (i.e., variation in soil behavioural characteristics, such as hydraulic conductivity, when the direction of measurement is changed, for example from the vertical to horizontal plane).

Hydrological variability associated with small-scale rainfall simulation experiments has been used to justify prewetting soils shortly (i.e., ~1-2 d.) before both tray-based (Burkitt *et al.* 2011) and plot-based experiments commence (Pote *et al.* 1996) (Table 2). Prewetting would be expected to move P from the mixing zone into subsoil storage. In that case, the simulation is assessing the short-term (i.e., < 2 day) ability of Process 2 to resupply P into the mixing layer for a soil at near field capacity. Again, soil P buffering would be expected to affect that resupply.

Where field plots are used, the characteristics of the site (e.g., topography, initial soil water content) determine which of saturation excess- or infiltration excess-overland flow or interflow, is most prevalent (Figure 3b) (Srinivasan *et al.* 2007). Pedological features are also critically important in gaining an understanding of the response of plot runoff to applied rainfall (as simulated or natural rainfall) (Needelman 2002; Buda *et al.* 2009).

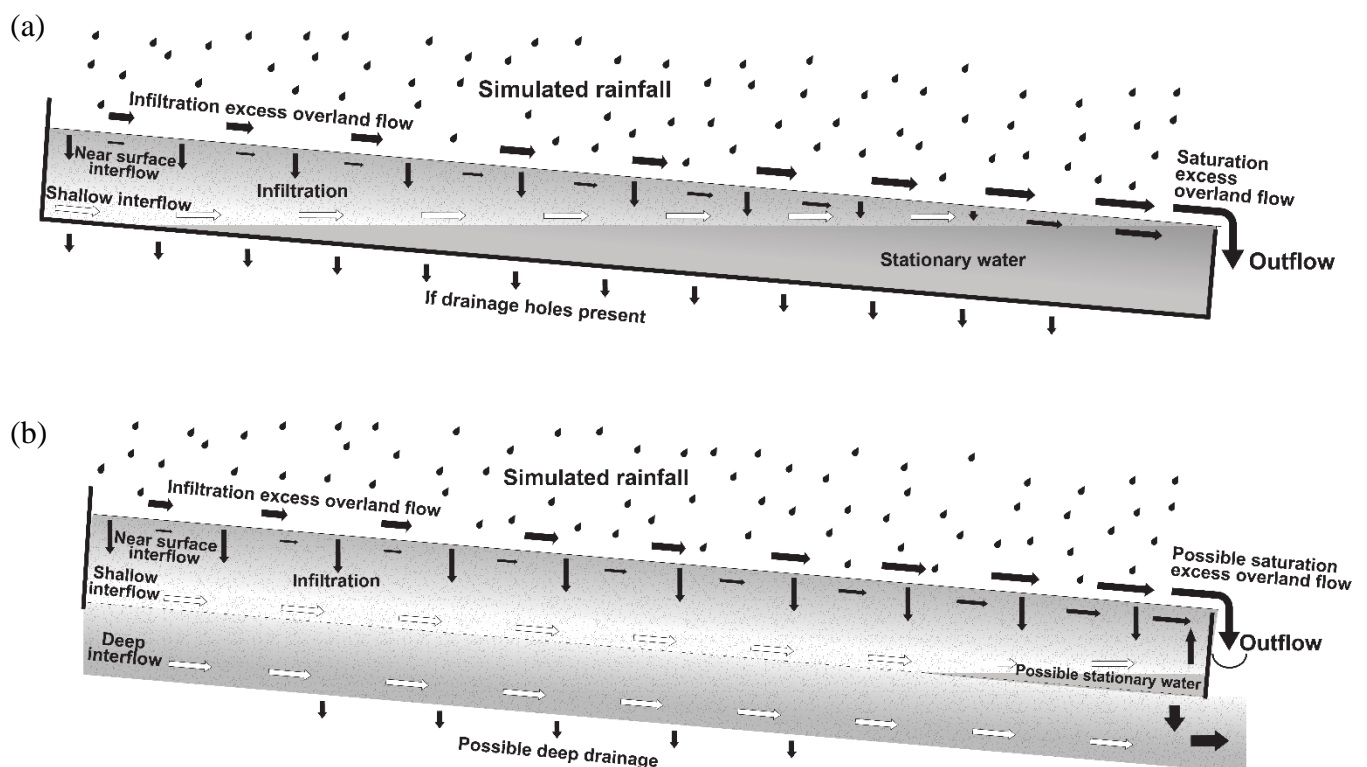


Figure 3. Cross-sectional profiles of possible hydrology in (a) trays and (b) plots used in small-scale rainfall simulation experiments.

As an approximation, early in experiments, infiltrating water would be expected to transport P from the mixing layer into the soil. Conversely, later in an event, especially where subsoil conductivity is impaired, for example by grazing animals, or subsoils have low saturated hydraulic conductivity compared to topsoils, shallow (i.e., <100mm) interflow may re-emerge at the surface, diluting the overland flow and near surface interflow. Both overland flow and interflow increase with scale (e.g., run-on from areas higher in the catchment increases with scale) (Nash *et al.* 2002). It follows that different site preparation (e.g., pre-watering) and experimental protocols (e.g., scale) can emphasise different hydrological processes and thereby experimental outcomes, albeit with similar numerical outcomes in some cases (Sharpley *et al.* 1982; Cornish *et al.* 2002). Because of the effects of scale (McDowell and Sharpley 2002), simply extending the duration of experiments is unlikely to replicate field-scale hydrology and mobilization processes.

Soil test P methodology

Numerous soil tests have been used to infer DP export potential (Sims 1993; Sims 2000; Maguire and Sims 2002; Nash *et al.* 2007a). Agronomic soil tests (i.e., 0-10 cm) were designed to relate soil fertility to plant growth/yield (i.e., predict response to additional fertilizer). They generally measure “quantity”, the concentration of soil P that is potentially available for uptake during the crop cycle, or “intensity”, the immediately available P (i.e., P activity or orthophosphate P concentration in soil water) in soil solution (Moody and Bolland 1999). In Australasia, Olsen P and Colwell P are the two most common agronomic soil tests. Both use bicarbonate solutions (0.5 M NaHCO₃ at pH 8.5) to extract P. The shorter duration (30 min.) Olsen P test measures both P quantity (i.e., supply) and intensity (i.e., concentration), while the Colwell P (16 hr) predominantly measures P quantity (Moody and Bolland 1999).

As P mobilization is both a function of the P concentration in solution and ability to resupply that P, neither test would be expected to reliably predict short-term (i.e., <48 hr) mobilization of DP by water or changes in P availability over the year, especially those attributable to organic sources and organically mediated P availability (Fox *et al.* 1990). The so-called environmental tests include water soluble P and dilute (0.01M) calcium chloride extractable P that both measure P intensity, and P sorption saturation that estimates the extent of soil binding sites occupied by P, and therefore, P desorption potential (Kleinman 2017). Given that most small-scale rainfall simulation studies appear to be focussing on short-term P mobilization from the mixing layer (Process 1), there should be strong relationships (e.g., R²>0.7) between STP and DP in runoff and even stronger relationships for the environmental tests, much as a single layer mixing model would suggest (Sharpley *et al.* 1981). None of the common soil tests consider organic sources of P and their possible indirect (i.e., effects on P sorption) contributions to P exports.

Concluding discussion

An ability to estimate the systematic (i.e., background) component of P exports is necessary for evaluating the effects of legacy P and optimising mitigation measures. While it is widely acknowledged that empirical relationships between STP and P concentrations derived from small-scale simulation studies do not quantitatively translate well to the field-scale, by necessity, STP is currently the tool of choice for assessing systematic P export potential.

Despite the differences in experimental protocols (Table 2), most small-scale rainfall simulation studies find good relationships between STP and P concentrations in runoff. Being of short duration, such studies replicate the rapid mobilization of P early in a storm (i.e., Process 1) in a similar way to laboratory adsorption experiments. Their time scale evens out some hydrological variation, albeit atypical of most field-scale hydrology. And intensive soil

sampling around the time of rainfall simulation, minimizes temporal and spatial variation that would be expected in the field (Mountier and During 1967; Morton *et al.* 2000; Department of Natural Resources and Environment 2002; Simpson *et al.* 2015).

The limited set up conditions imposed by rainfall simulation protocols constrain the evaluation of factors and mechanisms that have produced STP v DP relationships. Consequently, extrapolation to larger scale is precarious (Shepherd *et al.* 2013), especially given that the simulation data from which such equations are derived do not represent the time-dependant, rate-limited process (i.e., Process 2) accounting for most P exports, or field scale hydrology (i.e., transport mechanisms). It is therefore not surprising that most field-scale studies yield poor quantitative relationships (i.e., $R^2 < 0.2$) between STP and systematic P concentrations.

All else being equal, one would expect DP concentrations in runoff to increase with an increase in STP. But in the field all things are rarely equal. Farming systems are complex with interrelated capital (e.g., soil type, topography), management (i.e., history, grazing strategy) and environmental (e.g., climate) components that are conditionally dependant on one another. Is it possible to encapsulate that complexity in a single metric (i.e., extraction co-efficient or soil test) derived from small-scale rainfall simulation experiments that can be used to estimate systematic P concentrations and loads, even within a soil type, without reference to hydrology?

There are modelling platforms (e.g., Bayesian Belief Networks) that use cause and effect relationships and probability theory that can be used to iteratively develop conceptually sound mechanistic (i.e., quasi process) models (McDowell *et al.* 2009; Nash *et al.* 2010; Nash and Hannah 2011; Nash *et al.* 2013b; Lucci *et al.* 2014). Importantly, these systems can interface with conventional modelling (Pollino and Henderson 2010; Barton *et al.* 2012; Nash *et al.* 2013a; Phan *et al.* 2016; Bicking *et al.* 2019). Small-scale rainfall simulation studies have potentially an important role to play in providing input to such modelling efforts. However, more detailed analyses of the hydrology and other scale dependant processes (i.e., the system components), rather than simply reporting apparent relationships, is needed. The emphasis needs to be more on “how and why”, rather than “what” happened and working iteratively towards a more process-oriented approach.

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