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CROPPING, SOIL TYPE AND MANURE APPLICATION EFFECTS ON PHOSPHORUS EXPORT AND BIOAVAILABILITY

(CROPPING, MANURE AND SOIL TYPE EFFECTS ON PHOSPHORUS EXPORT)

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Michaud, A.R. and M.R. Laverdière. 2003. **Effects of cropping, soil type and manure application on phosphorus export and bioavailability.** A simulated rainfall study was conducted on an array of 36 runoff plots (6 m^2 each) deployed on three benchmark soil series of the Missisquoi region in southwestern Québec. The split-plot experimental design tested the effects and interactions of pig slurry treatment as main plots (check *vs*. 59 kg P ha^{-1}) and cropping (tilled vs hay) as subplots, on runoff volume and concentrations in total suspended sediment (TSS), total phosphorus (TP), dissolved reactive soluble P (DRP), particulate P (PP) and bioavailable P (BioP). TP concentration in runoff ranged from a low of 1.17 mg L^{-1} average on non amended Bedford hay, to a peak concentration average of 9.55 mg L^{-1} on manured and tilled Saint-Sébastien plots. Variance analysis indicated significant contributions of treatments in explaining TP concentration in runoff as follows: Soil type effect > Cropping effect > Soil*Cropping interaction > Manure effect. Erosion and sediment transport processes were identified as prime vectors of TP export. Manure effect alone accounted for 35% of overall DRP variability, while soil type alone accounted for 70% of variability in particulate P bioavaibility (BioP/PP). Among practical implications of this study is the importance of assessing PP bioavaibility to adequately predict the adverse impact of runoff on aquatic ecosystems. The high level of interaction among cropping and manure treatment and the site-specific influence of soil physical and chemical properties also calls for a holistic approach to nonpoint P risk assessment and management, that focuses on timely manure P management, control of soil P build-up and agricultural practices minimizing surface runoff.

Key words: phosphorus, P-index, rainfall simulation, runoff, erosion, bioavailability, sediment

Michaud, A.R. et M.R. Laverdière. 2003. **Effets de la couverture végétale, de l'apport de lisier et du type de sol sur l'exportation de phosphore et sa biodisponibilité**. Une étude faisant intervenir une simulation de pluie fut conduite sur un réseau de 36 parcelles expérimentales de 6 m^2 distribuées sur trois séries de sol caractéristiques de la région de Missisquoi, au Québec. Le dispositif expérimental en tiroirs a mis en relief les effets et les interactions des traitements d'apport de lisier de porc en parcelle principale (témoin *vs*. 59 kg P ha^{-1}) et de couverture du sol en parcelle secondaire (sol nu *vs*. prairie) sur le volume de ruissellement et ses concentrations en matières en suspension (MES), phosphore total (PT), P réactif dissout (PRD), P particulaire (PP) et P biodisponible (Pbio). Les concentrations observées en PT ont varié d'un minimum de 1.17 mg L^{-1} sur le loam argileux Bedford en prairie, non amendée, à un maximum de 9.55 mg L^{-1} sur le loam Saint-Sébastien en condition de sol nu et amendé à partir de lisier de porc. L'analyse de variance indiqua que les contributions des traitements et interactions à l'explication de la variabilité de la concentration en PT du ruissellement suit l'ordre suivant : Type de sol > couverture du sol > Sol X Couverture du sol > amendement au lisier. Les processus d'érosion et de transport de sédiments furent identifiés comme les principaux vecteurs d'exportation du P. L'effet de l'application de lisier expliqua à lui seul 35% de la variabilité du PRD, alors que 70% de biodisponibilité du phosphore particulaire fut expliquée par les propriétés des sols à l'étude. Parmi les implications pratiques de l'étude, notons l'importance de considérer la biodisponibilité du PP pour prédire adéquatement l'impact du ruissellement sur l'écosystème aquatique. Le degré élevé d'interaction entre les traitements culturaux, de fumure et les propriétés physico-chimiques des sites appelle à une approche holistique dans l'appréciation des risques et la gestion des pertes de P biodisponible, ciblée notamment sur le mode de gestion des épandages d'engrais de ferme, le contrôle de l'enrichissement des sols en P et des pratiques agricoles qui minimisent le ruissellement de surface.

Mots clés: phosphore, IRP, simulation de pluie, ruissellement, érosion, biodisponibilité, sédiments

Portions of Lake Champlain, a 1124 km^2 body of water shared by the states of Vermont and New York in the United States, and the province of Québec in Canada, are prone to eutrophication. This condition is especially prevalent in the waters of the Missisquoi Bay, at the northern extremity of Lake Champlain, and presents a severe threat to its exceptional recreational and touristic appeal, as well as to local drinking water supplies. Non-point sources of phosphorus (P), account for over 90%

of the annual P load (167 Mg P yr^{-1}) entering Missisquoi Bay (Hegman et al., 1999). Of these sources, 79% are associated with agricultural lands, which cover over one quarter of the area of contributing watersheds. To remedy this situation, a multi-stakeholder Management Conference on Lake Champlain (LCBP, 1994) established the reduction of agricultural non-point source P pollution as a top priority. A comprehensive set of agro-environmental indicators can aid in farm-, catchment- and territorial-scale planning and implementation of efficient strategies to prevent such P losses into the Missisquoi Bay. Based upon this premise, one such indicator, which ranks non-point P export risks according to both source and transport factors, was proposed by researchers and advisory personnel: the P-index (Lemunyon and Gilbert, 1993; Gburek et al., 2000).

Source factors represent P potentially exportable through overland and subsurface flows, ranking a site′s vulnerability according to existing soil test P values and the origin, placement and timing of P inputs. A number of studies have linked P concentrations in surface runoff to soil test P. However, unless employed in conjunction with an estimate of a site′s potential for runoff and soil erosion, the information borne in threshold soil P levels has been deemed insufficient to serve as the sole criterion to guide P management and P applications (Wolf et al., 2000).

Transport factors determine whether potential P-contributing areas will translate into areas of P loss. Surface runoff is generally considered as the major hydrological pathway for P flux. In Québec and Northeastern American catchments, the temporal distribution of precipitation intensities is most likely to favour saturation-excess runoff. Overland flow is generally linked to cumulative rainfall and snowmelt events, rather than to high rainfall intensities (Lapp, 1996; Michaud et al., 2004). Under such climatic conditions, saturation-excess runoff is largely landscape driven and linked to watertable and stream level rises, subsoil permeability, slope breaks, as well as convergent surface and subsurface flows. Throughout the landscape, these processes generate hydrologically-active variable-source areas (VSA; Beven and Wood, 1983), whose boundaries vary within seasonal and precipitation-event time-frames.

Of the agricultural practices prevalent in the watersheds which contribute to Missisquoi Bay, manure management under perennial forage and grain corn (*Zea mays* L.) crop rotations are of particular environmental concern. Plot studies conducted under natural and simulated rainfall conditions have extensively documented the adverse effects of non-incorporated or late-season manure disposal on nutrient export under Quebec′s climatic conditions (Côté et al., 1998; Gangbazo et al., 1997). On a regional scale, surpluses in P budgets have been tied to elevated P levels in soils and streams within the Pike River watershed, a major tributary and non-point P contributor to Missisquoi Bay (Deslandes et al., 2004).

In order to document (i) the effect of soil physical and chemical properties, cropping and manure inputs on the abundance and forms of P in surface runoff, and (ii) aid in the interpretation of spatial and temporal variability in P export documented in a parallel watershed-scale study (Michaud et al., 2004), a runoff plot study was conducted on benchmark soils of the Castors Brook experimental watershed, a small (11 km^2) agricultural tributary of the Pike River.

MATERIALS AND METHODS

Sites Description and Preparation

The experiment was conducted on three hay fields located within the Castors Brook watershed (45E 08' N, 72E 58' W), where dairy and grain production are the dominant agricultural systems. Corn, perennial forages, small grains and soybean are typically cultivated in rotation. At the watershed level, the P mass balance at the soil surface (mineral and manure inputs *vs.* crop uptake) indicated a moderate annual surplus of 10 kg P ha^{-1}. While a detailed agronomic survey revealed that annual mineral and manure inputs were roughly the same, the surplus in the P balance was predominantly attributable to the manure inputs. This reflected the fact that rates of manure application were based on the crop's nitrogen (N), rather than P, needs (Michaud et al., 2004).

The soils of the study area have been described and mapped by Cann et al. (1948). Soil series prevalent in this study have also been described by Grenon et al. (1999). The typical Saint-Lawrence lowlands physiography of the watershed presents a longitudinal gradient reflecting a transition from low-lying poorly drained lacustrine and marine clays, including Sainte-Rosalie clay experimental site (Orthic humic gleysol, 42% clay, 25% sand, ph: 6.2), to loamy glacial calcareous tills, including the poorly drained Bedford clay loam experimental site (Orthic humic gleysol, 30% clay, 31% sand, pH: 5.9). Moderately drained, schisty Saint-Sébastien sandy loam experimental site (Gleyed sombric Brunisol, 23% clay, 47% sand, pH: 6.3) occurs in the highest elevation, in the easternmost portion of the basin. Table 1 presents selected soil physical and chemical properties of the experimental sites.

A split plot within a randomized complete block design with three replications was laid out in each of three experimental hay fields, resulting in a total of 36 experimental simulated rainfall plots (3 site-soils x 3 blocks x 2 manure applications x 2 cropping treatments). Plots (1.5 m wide X 4 m in length) were positioned so as to provide nearly equivalent 3% slopes on each soil type. Manure treatments (Manure *vs.* None) were applied on main plots which were divided into cropping treatment sub-plots (Hay *vs.* Tilled). Simulated rainfall runs were performed on main plot units, covering simultaneously hay and paired tilled plots. Tilled plot preparation began with chemical (glyphosate) burndown of the forage crop one month prior to experiments. Forage residues were harvested manually and plots were roto-tilled and harrowed to simulate seedbed preparation. An alfalfa (*Medicago sativa* L.) stand on Saint-Sebastien site and mixed timothy (*Phleum* pratense L.)

and red clover (*Trifolium* pratense L.) stands on Bedford and Sainte Rosalie sites were maintained at a height of 0.1-0.2 m. Two weeks prior to the simulation experiment, fresh hog manure (4.40 g total N kg^{-1}, 1.47 g P kg^{-1} and 6.05 % dry matter) was applied manually and incorporated on the manure treated plots at a rate of 40 Mg ha^{-1}, resulting in a total nutrient input of 59 kg P ha^{-1} and 176 kg N ha^{-1}. Surface incorporation (50 mm depth) of liquid manure on tilled plots was provided by light harrowing. During simulated rainfall runs on single plots (i.e. paired subplots), neighbouring plots were protected by plastic blankets. The study was performed between August 6th and August 20th, 1998. Over this period a total of 44.2 mm of natural precipitation occurred. The two rainfall events neither yielded any runoff nor affected soil surface conditions of experimental plots.

Simulated Rainfall and Test Storm Characteristics

A calibrated stationary variable-intensity rainfall simulator developed by Michaud (1987), equipped with eight 9.5 mm nozzles (Model MP156M, 3/8 Bete Fog Nozzle Inc., Greenfield, MA), provided a drop-size distribution close to natural rainfall. Under a 5.7 L min^{-1} design nozzle discharge and a 56 kPa operating pressure, D_{10}, D_{50} and D_{90} (drop sizes cumulating 10, 50 and 90% of spray volume) values of 1.03, 2.06 and 3.47 mm, respectively, were measured. Below a droplet diameter of 2.5 mm, the vertical velocities of falling droplets were up to 10% above their theoretical terminal velocities, while larger droplets (>2.5 mm diameter) were up to 5% under their theoretical terminal velocities. The overall kinetic energy of the droplets issuing from nozzles set at a design height of 2.15 m was 0.201 MJ ha^{-1} mm-1, or 72% of the kinetic energy of a high-intensity (100 mm h^{-1}) rainstorm (Wischmeier and Smith, 1978).

A single test storm with a rainfall intensity of 150 mm h^{-1} was applied on a single plot consisting of paired hay/tilled subplots. Although intermittence in spray nozzles operation can produce a lower rainfall intensity, the rainfall simulator was used at maximum capacity in order to produce rapid and significant runoff. Test storm duration was based on the production of continuous runoff on the hay plot for a period of 15 minutes. Abundant crop canopy delayed onset of runoff on these plots, resulting in a variable runoff period duration on tilled plots. Test storm duration varied from 28 to 47 minutes, with a median duration of 37 minutes. The cumulative precipitation threshold for runoff generation (P_r) was calculated as the total precipitation volume sprayed on plots surface until runoff reached the trough. Runoff coefficient under saturated soil conditions (C_s) was calculated as the ratio of runoff volume to precipitation volume sprayed during the runoff period.

Prior to simulated rainfall events, each subplot was surrounded by sheet metal borders to isolate runoff and equipped with a downslope trough for runoff collection. Total runoff volume was estimated manually from sampling pits using 15 L pails, and the runoff subsequently stocked in 225 L barrels. Runoff subsamples were collected using a vertically integrated method following vigorous mixing of sampled runoff.

Runoff and Soil Analyses

Runoff samples were kept below 4°C until their analysis. Total suspended sediments (TSS) were determined by a filtration method (<0.45 µm). Sample pH was measured with a combined electrode Accumet meter, model 950. Reactive soluble phosphorus (DRP), bioavailable phosphorus (BioP) and total phosphorus (TP) concentrations were determined colorimetrically using the molybdenum-blue method of Murphy and Riley (1962), following filtration (<0.45 um), 0.1 N NaOH extraction (Sharpley et al., 1991) and persulfate digestion, respectively. Particulate P was calculated as TP minus DRP. Bioavailable PP was calculated as BioP minus DRP. Soil P concentrations were determined by extraction of 3 g soil subsamples using the Mehlich-3 extractant (Mehlich, 1984). Triplicate 0.1 m diameter core soil samples were collected on each experimental plot 48 hours after simulated rainfall experiment for determination of total porosity (Cully,1993), macroporosity (5 and 10 kpa suction; Topp et al., 1993) and saturated hydraulic conductivity (Reynols, 1993). Composite soil surface samples (0-0.15 m depth) were also collected for nutrient, organic carbon, and particle size distribution analyses (Sheldrick and Wang, 1993) and aggregate stability determination after simulated rainfall experiment (Kemper and Rosenau, 1986).

Statistical Analyses

Concentration data were shown to be independent of test storm duration and were thus used to document treatment effects and interactions on P exports rather than loadings estimates. Conceptually, concentration data are considered to reflect site′s potentially mobilized P under conditions of intense, non-transport limiting, hydrological activity. Soil and runoff data met acceptable normal distribution criteria, so statistical analysis were performed on untransformed data. The SAS package (SAS, 2000) was use for variance, correlation and regression analyses of runoff quality and independent site properties. Multiple comparisons of least squares means of treatment effects and interactions were adjusted using Tukey′s procedure to protect the overall experiment level of significance.

RESULTS AND DISCUSSION

Runoff

Simulated rainfall events produced runoff depths ranging from 8 to 53 mm, accounting for 9% to 52% of total simulated precipitation. The cumulative precipitation threshold for runoff generation

(P_r) and the runoff coefficient under saturated soil conditions (C_s) were significantly influenced by cropping treatment and soil type (Table 2). Mean P_r values of 67 and 39 mm were observed for hay and tilled subplots, respectively (Table 3). Following surface ponding, hay subplots also maintained lower runoff rates than tilled surfaces, resulting in significantly lower C_s values ($P< 0.001$).

Soil type had contrasting influences on P_r and C_s values. Mean cumulative rainfalls of 69 mm, 52 mm and 32 mm were required to induce runoff on the Bedford, Sainte-Rosalie and Saint-Sébastien soil series, respectively ($P< 0.05$). Although the Saint-Sébastien loam plots showed the earliest runoff, Sainte-Rosalie clay sites exhibited significantly higher C_s values ($p<0.05$). Among topsoil physical and chemical properties, saturated hydraulic conductivity (K_{sat}) best correlated with P_r ($r=0.53$, $P<0.001$), while clay content best correlated with the runoff coefficient, C_s ($r =0.51$, $P<0.05$). These correlations suggest that the onset of runoff during simulated rainfall runs was likely controlled by soil surface factors such as roughness and sealing. Soil crusting was particularly severe on the Saint-Sébastien loam, resulting in early runoff production and the lowest K_{sat} of core samples collected after the simulated runoff event. Following surface ponding and the onset of runoff, soil profile internal permeability more likely controlled runoff rate, as suggested by the significantly higher runoff depth on the clay-textured Sainte-Rosalie soil.

Values of P_r measured on the experimental sites were within the range of those observed over three years on the Castors Brook watershed, during the crop growth period: 30 to 75 mm of antecedent water infiltration was required to yield a 5 mm day^{-1} equivalent stream flow (Michaud et al., 2004). However, the P_r values of individual sites under rainfall simulation do not reflect the spatial pattern in hydrological activity at the watershed scale. Saint-Sébastien soil map units typically occupy higher altitude locations within the landscape, where depth to watertable, rapid internal drainage and porous schisty subsoil favour interflow pathways. In contrast, Sainte-Rosalie clay occupies the lower lying portion of the watershed. Convergent patterns of surface drains and interflow, shallow watertables and impervious subsoil provides this soil unit with a more intense hydrological surface activity. Bedford soil series occupy an intermediate elevation within the landscape and moderate hydrological activity.

Under simulated rainfall conditions, the onset of runoff was most likely controlled by the water infiltration rate at the soil surface. Under local climatic conditions, such infiltration-excess runoff is not the dominant form of runoff responsible for P mobility within the watershed. In fact, surface runoff is typically observed during the recharge period, under relatively low intensity rainfall (<15 mm hr^{-1}), in response to localized soil saturation developing in different portions of the landscape (Michaud et al., 2004). Episodic nutrient and sediment exports are particularly concentrated within saturation-excess runoff events from snowmelt and low-intensity precipitation on thawing or saturated soils in late-winter and early-spring. Contrasting observations on the relative hydrological activity of representative soil types, under watershed and runoff plot experimental set-ups, support the statements made by Gburek et al. (1996) and Gburek et al. (2000) that plot or field-scale processes alone are limited in their ability to explain the spatial variability in saturation-excess runoff and P export at the watershed scale.

Sediment Concentration in Runoff

At all sites, experimental conditions provided high-erosivity rainfall on a relatively short slope length, resulting primarily in interill erosion. Cropping treatment alone explained 49% of the variability observed in runoff TSS concentrations ($[TSS]_r$). Mean $[TSS]_r$ of 3.186 g L^{-1} and 0.685 g L^{-1} were measured in the runoff of tilled and hay plots, respectively. Soil type had distinct effects on $[TSS]_r$ from hay and tilled sites, as indicated by a significant Soil x Cropping interaction ($P<0.001$). The tilled Saint-Sébastien soil series yielded the highest $[TSS]_r$ ($P<0.001$), averaging

5.18 g L^{-1}, whereas $[TSS]_r$ from tilled Bedford and Sainte-Rosalie soil series averaged 2.12 and 2.36 g L^{-1}, respectively (NS; $P > 0.05$). Under the hay treatment, differences in $[TSS]_r$ among sites were no longer significant, reflecting the positive effect of canopy and dense root/rhizome system of the hay crop in preventing soil detachment and sediment transport. However, the mean soil loss from the Saint-Sébastien hay plots was two-fold greater than that from other soil series, though this difference was not significant under Tukey's multiple comparisons adjustment ($P > 0.05$). The relatively more abundant $[TSS]_r$ from the Saint-Sébastien site can be attributed to the nature of the hay cover: the two year-old alfalfa (*Medicago sativa* L.) stand at the Saint-Sébastien site presumably offered less protective cover than did the predominantly sod-forming grass cover at the other experimental sites. Zemenchik et al. (1996) reported significantly lower soil losses for smooth bromegrass [*Bromus inermis* Leyss.] than alfalfa. Higher $[TSS]_r$ from an alfalfa stand, as compared to one of bromegrass, was linked to increased export of BioP (Zemenchik et al., 2002).

Relatively higher runoff rates on Sainte-Rosalie tilled plots as compared to the other tilled soils did not yield higher $[TSS]_r$, contrasting with the direct proportionality generally reported between runoff rates and its transport/detachment capacity (Meyer, 1965). Meyer and Wischmeier's (1969) mathematical simulation of erosion processes supports the fact that for slope lengths < 7 m and gradients of <12%, sediment load theoretically corresponds to the transport capacity of rainfall and runoff. Under current experimental conditions, the relatively lower $[TSS]_r$ from the Sainte-Rosalie soil was associated with a relatively higher transport capacity of runoff, suggesting that $[TSS]_r$ variability among experimental sites was more likely detachment-controlled rather than transport-controlled. The relative resistance of the Saint-Rosalie to soil detachment is in agreement with the soil erodibility nomograph developed by Wischmeier et al. (1971), where elevated soil clay and organic matter contents were associated with lower vulnerability to erosion. The higher soil organic carbon content ($P < 0.001$) at the Sainte-Rosalie site (75 g kg^{-1}) compared to other sites (Table 1), likely promoted soil aggregate resistance to wetting and rain drop impacts (Imeson and Jungerius,1976). Greater soil aggregate stability has been related to reduction in sediment concentrations in runoff generated under simulated rainfall conditions at sites in southern Québec (Michaud, 1987), Western Canada (Luk, 1979), and in the United States (El-Swaify and Dangler, 1976; Young and Mutchler, 1977).

Total and Particulate Phosphorus

Mean total phosphorus concentrations in runoff, $[TP]_r$, ranged from a low of 1.17 mg L^{-1} on non-manured Bedford hay to 9.55 mg L^{-1} on manured and tilled Saint-Sébastien plots. An ANOVA of soil and cropping effects on $[TP]_r$ closely paralleled those for $[TSS]_r$ and PP concentration in runoff ($[PP]_r$) (Table 2). Overall, $[TP]_r$ was strongly correlated ($r=0.91$, $P<0.001$) with $[TSS]_r$ and $[PP]_r$, which in turn were linearly related to one another (Figure 2a) across various cropping x manure treatment combinations. The parallels in $[TP]_r$, $[PP]_r$, and $[TSS]_r$ strongly indicated that particulate transport was the primary vehicle for TP export under tilled plots. Indeed, PP constituted 77%, 81% and 97% of TP was exported from the Bedford, Sainte-Rosalie and Saint-Sébastien soil series, respectively (Table 2). Under the hay cropping treatment, $[PP]_r$ / $[TP]_r$ ratios were significantly lower ($P<0.05$), averaging 28%, 38% and 75% for the Bedford, Sainte-Rosalie and Saint-Sébastien soil series, respectively.

Based on the ANOVA, the significance of contributions of treatments effects and interactions in explaining $[TP]_r$ followed the order: Soil type > Cropping > Soil x Cropping > Manure effect. Saint-Sébastien experimental plots produced higher mean $[TP]_r$ (5.34 mg L^{-1}) than Sainte-Rosalie sites (2.93 mg L^{-1}) and Bedford sites (2.17 mg L^{-1}), reflecting the intrinsic soil erodibility and elevated soil P concentration ($[TP]_s$) at the Saint-Sébastien site. However, cropping treatment interacted strongly with soil type ($P<0.001$). Under the hay treatment, differences in $[TP]_r$ concentration among sites were not significant ($P>0.05$). According to multiple regression analysis and considering only the 18 tilled subplots, 67% of variability in $[TP]_r$ was explained by soil texture and $[TP]_s$:

$$[TP]_r = 5637 + 16.9\,[TP]_s - 177\,(\text{Clay}) \qquad R^2=0.67,\ P<0.0001 \qquad (1)$$

where $[TP]_r$, $[TP]_s$, and Clay are expressed in µg L^{-1}, kg ha^{-1}, and percent, respectively.

Conceptually, $[TP]_s$ expresses the quantity and reactivity of P near the soil surface that accounted for soluble and reactive P export. Under existing experimental conditions, $[TP]_s$ best predicted $[TP]_r$ ($R^2=0.41$, $p<0.05$), which is consistent with the well documented $[TP]_s$ control of dissolved P in runoff (Romkens and Nelson, 1974; Pote et al., 1996; Sharpley et al. 1996). Soil clay content seems to reflect the relative soil erodibility of experimental sites.

Manure treatment had a significant effect on $[TP]_r$, where plots receiving manure generated mean $[TP]_r$ 4.27 mg L^{-1}, whereas non-amended plots generated a mean $[TP]_r$ of 2.66 mg L^{-1} in runoff. Van Vliet et al. (2002) showed a similar (2-fold) relative difference in TP exports from natural runoff plots between those that did and did not receive fall manure applications. Under present experimental conditions, on both hay and tilled plots, the increase in $[TP]_r$ in response to swine manure application was related to nearly equivalent increases in particulate P and dissolved reactive P fractions.

Dissolved Reactive Phosphorus

An ANOVA regarding soil, cropping and manure effects on dissolved reactive phosphorus concentrations in runoff, $[DRP]_r$, differ markedly from those of $[TP]_r$ and $[PP]_r$. Manure effects accounted for 35% of overall $[DRP]_r$ data variance, while cropping and soil type effects accounted for 27% and 14% of variance, respectively. Considering the overall variability in $[DRP]_r$, manure treatment increased $[DRP]_r$ concentration significantly (P<0.0001), from 0.44 to 1.29 mg L^{-1}, a factor of three. The manure treatment effect on $[DRP]_r$ indicated that surface-applied manure served as a significant P source in runoff. Similarly, Kleinman et al. (2002) showed that in soils receiving surface application of P, the amendment, rather than the soil, served as the major source of P in runoff. They reported contrasting forms of P in runoff from simulated rainfall experiments, where DRP accounted for 64% of TP lost from manured plots, but only 9% of TP on non-amended plots. The predominant effect of surface-applied manure on the dissolved fraction of exported phosphorus is also consistent with the well documented increased mobility and solubility of P in manure-amended soils (Russell, 1973, Sharpley et al., 1984; Gangbazo et al., 1997; Haygarth and Jarvis, 1999; Sharpley et al., 2001). Reduced P sorption capacity of soils resulting from manure inputs could also favour the DRP fraction in runoff from manured plots. Higher concentrations of organic acids (not documented) resulting from addition of organic amendments has been shown to form complexes with P and limit the extent of P sorption (Sui and Thompson, 2000).

The $[DRP]_r$ was also significantly higher (P<0.0001) under hay cover (1.24 mg L^{-1}) than from tilled plots (0.49 mg L^{-1}) (Table 4). Higher average DRP concentration in runoff from hay plots and relatively higher DRP response to manure treatment on hay plots (Manure x Crop interaction, P<0.001) reflect the dominant soluble form of TP export generally documented for grassland, resulting from lower $[TSS]_r$ and $[PP]_r$ values (Young and Mutchler, 1977; Sharpley et al., 1993; Haygarth and Jarvis, 1999).

Soil type also significantly affected $[DRP]_r$ ($P<0.05$) as indicated by consistently lower $[DRP]_r$ at the Saint-Sébastien site (0.48 mg L^{-1}) than at the Bedford site (1.12 mg L^{-1}), despite nearly identical hydrologic responses to simulated rainfall, and an opposite gradient in $[TP]_s$. The soil type effect on $[DRP]_r$ also significantly interacted with cropping ($P<0.001$) and manure ($P<0.05$) treatments (Table 2). This effect of soil type and interacting factors on $[DRP]_r$ are presumably related to dynamics of dissolved P reaction with soil and suspended sediments in runoff. The influence of P sorption potential, $[TP]_s$ and soil erodibility of experimental sites on soluble/particulate P partitioning are best illustrated by contrasting P forms in runoff from manured hay treatments to those from tilled non-amended plots. Surface-applied manure was most likely the major P source for runoff on Bedford hay plots, where $[DRP]_r$ averaged 2.54 mg L^{-1}, or 80% of $[TP]_r$. On tilled non-amended plots, $[DRP]_r$ averaged 0.17 mg L^{-1}, or only 10% of $[TP]_r$. A similar gradient in $[DRP]_r$ / $[TP]_r$ ratio was observed on Sainte-Rosalie plots where $[DRP]_r$ accounted for 11% of $[TP]_r$ from tilled, non-amended plots, while 67% of $[TP]_r$ from manured hay plots was in the soluble (DRP) form. Finally, the Saint-Sébastien site demonstrated a lesser contrast in $[DRP]_r$ / $[TP]_r$ ratio, from 2% to 27% for similar treatment combinations.

Sorption mechanisms governing $[DRP]_r$ is further evidenced by $[DRP]_r$ being negatively correlated with $[PP]_r$ (r=-0.39, $P<0.05$) and $[TSS]_r$ (r=-0.50, $P<0.01$). Figure 2b depicts the relationship between $[DRP]_r$ and $[TSS]_r$. The DRP fraction remained dominant on Bedford and Sainte-Rosalie hay sites, where $[TSS]_r$ were relatively low. Above a $[TSS]_r$ threshold of 0.80 g L^{-1}, PP was the dominant form of P exported from all tilled sites, as well as from the Saint-Sébastien hay site. In fact, the Saint-Sébastien site had the lowest $[DRP]_r$ for all Manure x Cropping treatment combinations, despite having significantly higher $[TP]_s$ levels. The highest P fixation potential (2.54 g ha^{-1} Mehlich-3 Al; Table 1) and highest $[TSS]_r$ at the Saint-Sébastien experimental site seems to explain its lower $[DRP]_r$. Moreover, relative contributions of DRP to TP export on manured plots, whether tilled or in hay, followed the order Bedford > St-Rosalie > St-Sébastien, reflecting the P adsorptive potential of the soils, as indicated by their respective Al Mehlich-3 levels (Table 1), and conversely, their soil erodibility, as indicated by measured $[TSS]_r$.

Numerous studies have described the solubility, adsorption and fixation mechanisms of phosphorus in Québec soils (Laverdière and Karam, 1984; Tran et Giroux, 1985; Giroux et Tran, 1985; Tran et Giroux, 1990; Tran and Giroux, 1987; Tran et al., 1992; Giroux and Tran; 1996). The literature generally agrees that the disappearance of phosphate from soil solution results from a rapid initial sorption. Tran et al. (1988) demonstrated through an isotopic dilution ^{32}P method that soils having elevated P-adsorption capacity adsorbed over 90% of isotopically exchangeable P after 1 minute. The isotopic ratio was in turn significantly correlated with P adsorption and buffering capacities of soils. These studies of P dynamics in Québec soils support the idea that sorption mechanisms partly controlled $[DRP]_r$ under actual experimental conditions. From hay to tilled conditions, manured plots demonstrated a systematic decrease in $[DRP]_r$, contrasting with a rise in $[PP]_r$. The shallow (<50 mm) surface incorporation of swine slurry on tilled plots likely promoted sorption of largely inorganic soluble P within the topsoil. Rapid sorption by suspended sediments on ponded plot surfaces or in surface runoff was also favoured by elevated $[TSS]_r$, in response to the strong erosivity of simulated rainstorms.

Phosphorus Bioavailibility

Conceptually, bioavailable phosphorus concentration in runoff, $[BioP]_r$, quantifies the potential impact on aquatic ecosystems of TP exports. The BioP is the sum of reactive soluble phosphorus (DRP) and the bioavailable portion of particulate phosphorus (BioPP). Figure 3 illustrates the partitioning of these bioavailable P fractions together with non-reactive PP in runoff observed under various treatment and site combinations. Under the present experimental conditions, $[BioP]_r$ was closely correlated with $[TP]_r$ (r=0.96, $P<0.0001$) and with $[PP]_r$ (r=0.91, $P<0.0001$), but not with $[DRP]_r$. These relationships reflect the overall dominance of particulate P constituents in sampled runoff. Similar to the ANOVA for $[TP]_r$ the dominant explanation for $[BioP]_r$ variability resided in the Soil type effect and Cropping x Soil interaction. On hay sites, the Soil type effect did not show significant differences in $[BioP]_r$, which averaged 2.05 mg P L-1. On tilled plots, $[BioP]_r$ differed significantly among experimental sites and followed the order Saint-Sébastien > Sainte-Rosalie > Bedford with respective means of 6.49, 2.48 and 1.26 mg P L^{-1}.

Unlike $[TP]_r$, $[BioP]_r$ variability was more strongly influenced by manure than cropping treatment (Figure 2c). The $[BioP]_r$ averaged 3.46 mg P L^{-1} on the manured plots, and was significantly lower (1.99 mg P L^{-1}; $P<0.001$) on non-amended plots. The effect of manure treatment on the bioavailibility of runoff P is particularly evidenced on Sainte-Rosalie tilled plots. Manuring Sainte-Rosalie tilled sites resulted in a slight and non-significant ($P>0.05$) decrease in $[TP]_r$. However, the bioavailibility of runoff P ($[BioP]_r$ / $[TP]_r$) increase by 20% (from 59% to

79%) upon the application of manure, resulting in a net increase in $[\mathrm{BioP}]_r$. Such contrasting trends in $[\mathrm{TP}]_r$ *vs.* $[\mathrm{BioP}]_r$ responses to manure treatment on Sainte-Rosalie tilled plots is partly attributable to the effect of manure on soil physical properties. Under current experimental conditions, the surface incorporation and reaction of manure with the topsoil matrix in the two weeks preceding the rainfall simulations presumably promoted infiltration, aggregation and related resistance to detachment and physical transport of sediment during rainfall simulations. McDowell and Sharpley (2003) indicated that over the short term, surface application of manure may improve soil surface protection from raindrop impact and aggregate dispersion. Somewhat higher runoff coefficients and lower $[\mathrm{TSS}]_r$ (ns, $P>0.05$) observed on Sainte-Rosalie manured tilled plots (C_s: 35%; $[\mathrm{TSS}]_r$: 1.14 g L^{-1}), compared to non-amended plots (C_s: 40%; $[\mathrm{TSS}]_r$: 1.33 g L^{-1}), support this interpretation.

Opposite trends in $[\mathrm{TP}]_r$ and $[\mathrm{BioP}]_r$ in response to cropping treatment were also observed on the non-amended Bedford sites . While $[\mathrm{TP}]_r$ of tilled plots (1.64 mg L^{-1}) was higher than that of hay plots (1.17 mg L^{-1}), conversely, $[\mathrm{BioP}]_r$ was greater from hay plots (908 mg L^{-1}) than that of tilled plots (766 mg L^{-1}). Relatively high DRP content of hay plots runoff and relatively low bioavailibility of runoff PP on Bedford sites explain this overall contrast in P bioavailibility of runoff. On average, bioavailibility of runoff TP (BioP/PP) increased from 47% on tilled plots, to 79% on hay plots for non manured Bedford plots.

Conceptually, the wide variability in bioavailibility of runoff P observed among sites and treatment combinations is the resultant of fluctuations in $[\mathrm{DRP}]_r$ and the relative bioavailibility of particulate P in runoff. While DRP has been shown to be primarily influenced by manure and cropping treatments, in contrast, bioavailibility of particulate phosphorus was dominantly influenced by the site's characteristics. The ANOVA showed that 70% of the variability in particulate P bioavailibility ($[\mathrm{BioPP}]_r$ / $[\mathrm{PP}]_r$) could be explained by soil type alone, while cropping and manure treatments their interactions showed no significant effect on bioavailibility of PP (Table 4). Adjusted means of PP bioavailibility in runoff from Saint-Sébastien, Sainte-Rosalie and Bedford sites were 86%, 60% and 51%, respectively, all significantly different ($P<0.05$ level) from one another. When pooling the results from the 36 simulated rainfall plots, $[\mathrm{TP}]_s$ alone explained 66% of the variability in BioPP in runoff under simple linear regression:

$$\mathrm{BioPP} = 0.239 + 0.00145\,[\mathrm{TP}]_s \qquad R^2=0.66,\ P<0.001 \qquad (2)$$

where, BioPP and $[\mathrm{TP}]_s$ are expressed as a percentage and as kg Mehlich-3 extractable P ha^{-1}.

A practical implication of this runoff plot research for non-point P risk assessment is that an indication of PP bioavailibility is necessary to adequately assess the adverse impact of agricultural runoff on aquatic ecosystems.

CONCLUSION

The simulated runoff plot study demonstrated contrasting effects and interactions of soil type, cropping and manure treatments on total P export, on the relative contributions of soluble and particulate P in runoff, as well as on the bioavailibility of runoff particulate P. Cropping treatment and intrinsic soil erodibility provided dominant explanation of TP concentration variability in runoff, indicating that erosion and sediment delivery were the prime vectors of phosphorus export. This research also highlighted distinct effects and interactions of manure and soil P sources on concentration and reactivity of runoff P, indicating that unincorporated manure can serve as a major reactive P source for surface runoff, even under protective hay cover, and independently of soil P level. Experimental results suggest a rapid reorganisation of surface applied manure P into reactive particulate P, dependent on the site's erodibility and P sorption potential. Dissolved P concentration in runoff, alone, thus remained a poor indicator of runoff's adverse impact on aquatic ecosystems, due to the dominantly particulate nature of P in runoff. Experimental results also indicate that bioavailibility of particulate phosphorus varies considerably among experimental sites, but was found to be site specific and essentially explained by $[\mathrm{TP}]_s$ and soil clay content, independently of cropping and fertilization treatments.

The high level of interaction among cropping and manure treatments and the site-specific influence of soils physical and chemical properties on runoff P call for a holistic approach to non-point P risk assessment and management, focussed on timely, incorporated manure P inputs, long term control of soil P build-up and agricultural practices minimizing surface runoff.

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Table 1. Selected soil physico-chemical properties of experimental sites under cropping and manure treatments combinations.

Site/Treatment			Soil physical and chemical properties																	
Soil series	Crop	Manure	Porosity (%)				Sat. hydr. conduct. (cm min^{-1})		Aggregates Mean weight diameter (mm)		Organic carbon (g kg^{-1})		Mehlich-3					
			1.0 m Suction		Total								P (kg ha^{-1}) $[TP]_s$		Al (Mg ha^{-1})		P/Al (%)	
			Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Bedford	Hay	Manure	30.6	*14.9*	57.9	*2.2*	0.99	*0.73*	3.08	*0.44*	58.8	*23.0*	124	*75*	1.22	*0.08*	10.1	*5.6*
		None	20.8	*0.8*	57.2	*1.6*	0.97	*0.19*	3.23	*0.31*	43.7	*6.0*	102	*27*	1.16	*0.11*	8.8	*2.4*
	Tilled	Manure	27.4	*1.7*	62.5	*1.9*	1.09	*0.68*	3.02	*0.30*	53.0	*16.2*	110	*51*	1.14	*0.03*	9.7	*4.6*
		None	25.2	*1.8*	58.2	*0.5*	1.04	*0.38*	2.94	*0.13*	46.3	*15.1*	108	*27*	1.23	*0.10*	8.8	*2.4*
Ste-Rosalie	Hay	Manure	23.4	*0.4*	62.6	*0.9*	0.37	*0.13*	4.19	*0.21*	78.6	*7.2*	308	*14*	1.98	*0.08*	15.6	*1.2*
		None	22.3	*4.4*	62.9	*2.4*	0.64	*0.39*	4.35	*0.27*	73.0	*10.5*	310	*10*	1.78	*0.13*	17.4	*0.8*
	Tilled	Manure	23.4	*3.2*	63.7	*1.1*	0.46	*0.30*	4.05	*0.61*	73.4	*9.9*	328	*29*	1.84	*0.09*	17.9	*2.1*
		None	23.8	*4.9*	63.8	*3.6*	0.47	*0.17*	4.45	*0.42*	72.2	*12.0*	311	*14*	1.82	*0.13*	17.1	*1.0*
St-Sébastien	Hay	Manure	24.2	*0.7*	56.1	*1.9*	0.45	*0.09*	4.63	*0.34*	42.0	*5.6*	417	*19*	2.83	*0.24*	14.8	*1.2*
		None	24.4	*8.0*	56.4	*7.0*	0.20	*0.14*	5.00	*0.60*	42.3	*3.1*	378	*67*	2.61	*0.33*	14.4	*0.7*
	Tilled	Manure	30.1	*1.4*	61.1	*1.5*	0.40	*0.21*	4.26	*0.65*	43.9	*0.3*	376	*49*	2.42	*0.14*	15.6	*2.1*
		None	31.0	*4.3*	60.4	*1.5*	0.34	*0.19*	4.22	*0.25*	43.7	*4.5*	347	*60*	2.29	*0.28*	15.1	*1.0*

Table 2. Soil series, cropping and manure treatment effects and interactions (F-values) on runoff production, suspended solids and phosphorus concentration in runoff.

Source	Parameters tested							
	Threshold cumulative precipitation for runoff P_r	Saturation runoff coefficient C_s	Total suspended solids $[TSS]_r$	Phosphorus				
				Total $[TP]_r$	Particulate $[PP]_r$	Dissolved reactive $[DRP]_r$	Bioavailable $[BioP]_r$	Bioavailability of particulate P
Replicate	1.32	1.81	2.50	0.33	0.61	3.74	0.40	3.56
Soil[z]	20.58***	7.41**	17.17**	10.17*	20.49**	12.77*	47.23**	19.25**
Replicate*Soil	2.09	1.27	1.18	2.65	2.00	3.74	1.68	2.87
Manure[y]	0.00	2.95	0.19	16.82**	3.27	74.40***	57.72***	2.67
Manure*Soil[y]	0.09	0.83	1.48	2.72	3.99	6.47*	2.07	0.57
Replicate*Manure (Soil)	3.28	0.31	0.96	1.17	1.38	3.14	0.96	1.03
Crop	100.00***	11.87***	81.72***	36.97***	69.40***	176.67***	47.38***	0.33
Crop*Soil	1.20	0.21	7.51***	16.92***	13.38***	13.35***	50.48***	1.16
Crop*Manure	1.56	2.05	0.16	0.71	0.00	25.47***	2.71	0.30
Crop*Manure*Soil	1.08	1.57	0.21	2.02	1.50	4.77*	0.64	2.32
Model	9.71***	2.10*	6.79***	7.55***	9.32***	28.22***	16.68***	6.38***

[z] Tests of Hypothesis using the Type III MS for Replicate*Soil as an error term.

[y] Tests of Hypothesis using the Type III MS for Replicate*Manure (Soil) as an error term.

*,**,*** : significant at the 0.05, 0.01 and 0.001 levels, respectively.

Table 3. ANOVA model adjusted means for soil series, cropping and manure effects, as well as cropping x soil series interaction on precipitation prior to runoff, total runoff, event runoff coefficient, saturation runoff coefficient and total suspended solids (TSS) concentration in runoff.

Treatment effects and interactions	Hydrologic descriptors[z]			
	P_r (mm)	Q (mm)	C_s (mm mm^{-1})	Runoff [TSS] (g L^{-1})
Soil series				
Saint-Sébastien	31.8 a[y]	24.5 a	0.39 a	3.18 a
Sainte-Rosalie	51.9 b	33.8 b	0.56 b	1.40 b
Bedford	69.0 c	24.6 a	0.38 a	1.24 b
Cropping				
Tilled	39.1 a	37.8 a	0.51 a	3.19 a
Hay	66.7 b	17.5 b	0.38 b	0.70 b
Manure				
Manured	53.0 a	25.8 a	0.42 a	1.99 a
None	53.0 a	29.5 a	0.46 a	1.88 a
Cropping x soil				
Tilled-Saint-Sébastien	25.3 a	34.7 ab	0.47 ab	5.18 a
Tilled-Sainte-Rosalie	39.8 ab	44.5 a	0.63 a	2.36 b
Tilled-Bedford	52.2 bc	34.0 ab	0.43 ab	2.12 bc
Hay-Saint-Sébastien	50.1 bc	14.3 c	0.31 b	1.18 bc
Hay-Sainte-Rosalie	64.1 c	23.0 bc	0.49 ab	0.43 c
Hay-Bedford	85.8 d	15.2 c	0.33 b	0.45 c

[z] P_r, cumulative precipitation threshold for runoff; Q, total runoff; C_s, saturation runoff coefficient; [TSS], concentration of total suspended solids.

a-c Means with the same letter are not significantly different ($P < 0.05$), using Tukey's adjustment for multiple comparisons.

Table 4. ANOVA model adjusted means for soil series, cropping and manure effects, as well as cropping x soil series interaction on runoff concentration in total P (TP), particulate P (PP), dissolved reactive P (DRP) bioavailable P (BioP) and bioavailability of particulate P (BioP/PP).

Treatment effects and interactions	Phosphorus concentration (mg L^{-1})				$[BioP]_r/[PP]_r$ Bioavailability of particulate P (%)[z]
	$[TP]_r$ Total	$[PP]_r$ Particulate	$[DRP]_r$ Dissolved reactive	$[BioP]_r$ Bioavailable	
<u>Soil series</u>					
Saint-Sébastien	5.34 a[z]	4.82 a	0.48 b	4.45 a	0.86 a
Sainte-Rosalie	2.93 a	1.94 a	0.99 a	2.18 b	0.60 b
Bedford	2.17 b	1.05 b	1.12 a	1.56 c	0.51 c
<u>Cropping</u>					
Tilled	4.57 a	4.08 a	0.49 b	3.41 a	0.64 a
Hay	2.36 b	1.13 b	1.24 a	2.05 b	0.62 a
<u>Manure</u>					
Manured	4.27 a	2.98 a	1.29 a	3.46 a	0.65 a
None	2.66 b	2.23 a	0.44 b	1.99 b	0.60 a
<u>Cropping x Soil</u>					
Tilled-Saint-Sébastien	7.83 a	7.55 a	0.29 c	6.49 a	0.86 a
Tilled-Sainte-Rosalie	3.73 b	3.10 bc	0.63 b	2.48 bc	0.62 bc
Tilled-Bedford	2.16 b	1.60 bcd	0.56 bc	1.26 d	0.43 cd
Hay-Saint-Sébastien	2.78 b	2.09 bcd	0.68 b	2.41 bc	0.81 ab
Hay-Sainte-Rosalie	2.14 b	0.78 cd	1.36 a	1.88 bcd	0.67 ab
Hay-Bedford	2.18 b	0.51 d	1.67 a	1.86 bcd	0.37 d

[z] Means with the same letter are not significantly different ($P < 0.05$), using Tukey's adjustment for multiple comparisons.

Figure 1 : Experimental set-up for simulated rainfall runoff plot study on benchmark soils of Castors brook watershed.

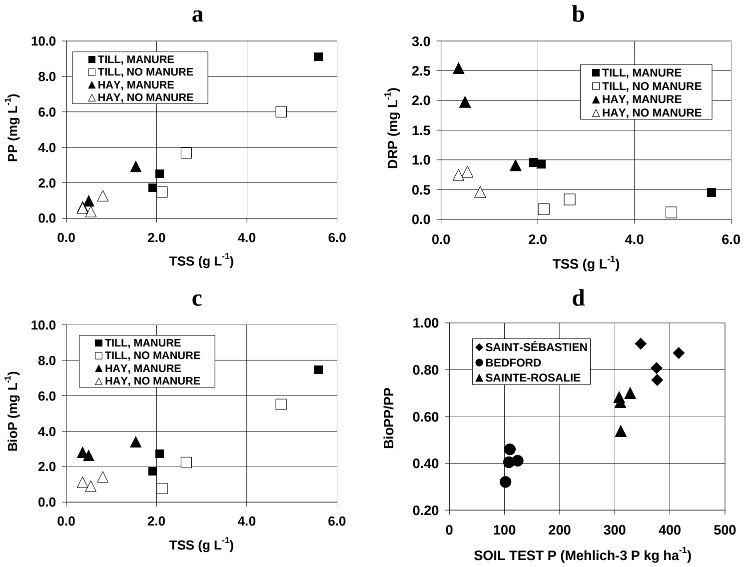

Figure 2. ANOVA model adjusted means (*n*’3) of particulate P (a), dissolved reactive P (b) and bioavailable P (c) for soil series, cropping and manure treatment combinations as a function of total suspended solids concentration in runoff and particulate phosphorus bioavaibility in runoff (d) in relation to soil test P levels.

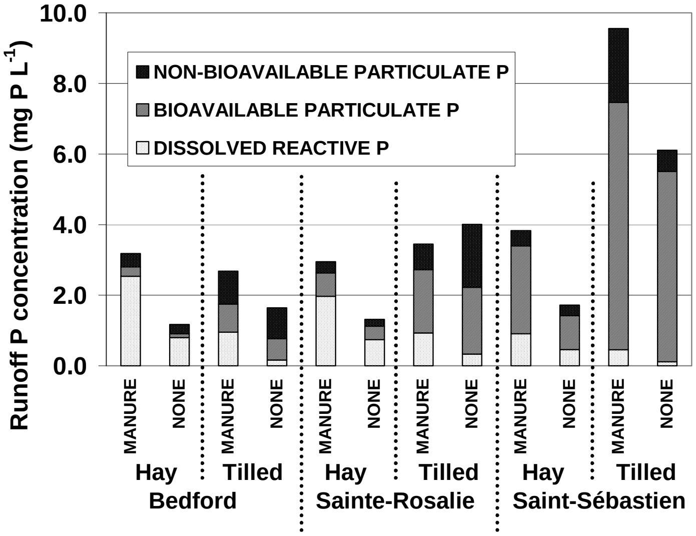

Figure 3. Phosphorus partitioning in runoff among soil series, cropping and manure treatment combinations.