Dissolved reactive phosphorus in runoff assessed by soil extraction with an acetate buffer

Risto Uusitalo and Håkan Jansson

MTT Agrifood Research Finland, Environmental Research, FIN-31600 Jokioinen, Finland,
e-mail: risto.uusitalo@mtt.fi

Agronomic soil test phosphorus (STP) data is, in addition to fertility studies, increasingly utilised in environmental risk assessment. We compared relationships between soil P extracted by acid ammonium acetate (AAAc-P) and water-soluble P (Pw) in laboratory, and AAAc-P and dissolved molybdate-reactive P (DRP) in field runoff. The laboratory study suggested a close relationship ($R^2 = 0.87$, $n = 64$) between AAAc-P and soluble P concentration in 1:100 (w/v) soil-to-water extracts, described by a linear equation: $Pw (mg l^{-1}) = 0.021 \times AAAc-P (mg l^{-1} soil) - 0.015 (mg l^{-1})$. In Lake Rehtijärvi catchment, dominated by clayey soils, the AAAc-P content of field Ap horizon in a similar manner influenced the flow-weighted DRP concentration in surface runoff and drainflow: a 1 mg l$^{-1}$ increase in soil AAAc-P corresponded to 0.015 and 0.018 mg l$^{-1}$ increase in surface runoff and drainflow DRP, respectively. When the AAAc-P vs. Pw relationship obtained in the laboratory test was used to predict the average DRP concentration in edge-of-field runoff, the precision of the DRP estimates inferred from STP data was in 95% of the cases ± 0.10 mg l$^{-1}$. In the L. Rehtijärvi catchment, 50% of the diffuse DRP loading risk was assigned to an area that corresponded to less than 20% of the fields and the situation may be similar in the national scale.

Key words: eutrophication, phosphorus, runoff, soil testing, catchment studies

Introduction

Even though agronomic soil P tests have not been designed for an assessment of P loss capacity of a soil, soil test P (STP) data have been found to serve as an indicator for elevated P loss risk (Heckrath et al. 1995, McDowell and Sharpley 2001). Likely being the most accessible and economic means for this purpose, STP is a convenient input parameter to be included in models aiming to predict – not only elevated P loss risks (Lemunyon and Gilbert 1993, Jokela et al. 1998, Gburek et al. 2000) – but also P concentration in runoff and P losses to surface waters (Tattari et al. 2001, Daly et al. 2002).

The agronomic soil test in use in Finland is based on extraction with an acidic ammonium acetate buffer (AAAc; 0.5 M ammonium acetate and 0.5 M acetic acid, pH 4.65; Vuorinen and
Mäkitie 1955), an extractant quite similar to those used in the republic of Ireland (Morgan’s test) and in some north-eastern states of the USA (Vermont I test). The acetate tests are related to the size of the easily soluble P pool in soil and they sensitively respond to soil P buffering (see Lee and Bartlett 1977, Kuo 1990). Because the most easily desorbable part of surface-adsorbed soil P likely determines the concentration of dissolved molybdate-reactive P (DRP) in runoff, acetate soil tests may be a theoretically sound option as environmental soil tests when DRP losses are concerned (see Magdoff et al. 1999). This is not necessarily the case with all soil tests, as many of them (e.g., Bray, Mehlich) are designed for estimation of (long-term) P supplying capacity of soils and lack sensitivity to P buffering by soils (see Holford 1980); therefore, the P pool extracted by these tests may rather refer to the potential for P release from eroded soil material.

When different soil tests have been compared, the acetate tests have been found superior to the stronger extractants when predicting water- or CaCl₂-extractable P in soils from north-eastern USA and Ireland (Magdoff et al. 1999, Maguire et al. 2001). Also in a field study, Turtola and Yli-Halla (1999) showed that average DRP concentration in surface runoff from a Spodosol amended with different amounts of slurry and mineral fertilisers very sensitively followed the changes in soil AAAC-P, more so than the changes in bicarbonate-extractable P, the estimate of P saturation (ratio of the sum of NH₄F-P and NaOH-P to the sum of oxalate-extractable Al and Fe), or anion exchange resin-extractable P.

Were we able to reliably estimate DRP concentration in runoff by using soil AAAC-P content, the data from a limited number of experimental fields could possibly be complemented by more geographically representative data, e.g., when the impacts of different management practises to DRP losses from agricultural fields are studied. In Finland, all of the farmers that are committed to the Agri-Environmental Programme (AEP; for an overview of the Finnish AEP, see Valpasvuo-Jaatinen et al. 1997) have to test their soils for P every fifth year to avoid excessive P fertilization. As a result of the commitment to the AEP, up-to-date AAAC-P data exist for about 90% of the fields of the country. Whether it is possible to utilise this data in directing different management options in a cost-effective manner to control eutrophication is one question to be evaluated.

We studied the relationship between AAAC-extractable P and the concentration of soluble P in a water extract (Pw, according to Yli-Halla et al. 1995 suited for approximation of average DRP concentration in surface runoff) in laboratory using 64 soils sampled from the Kokemäenjoki river basin, southern Finland. Then, we tested the feasibility of this relationship as a predictor for DRP concentration of surface and sub-surface runoff at Lake Rehtijärvi catchment (south-western Finland). We also assessed the frequency of the fields with high P loss potential in the L. Rehtijärvi catchment, and made a remark on the situation in the scale of whole Finland.

Material and methods

Study sites and soil analyses

For the laboratory study, mineral soil samples weighing about 5 kg each were taken from catchments of five lakes within a 10,000 km² area of the upper Kokemäenjoki river basin at the Häme region, southern Finland (Fig. 1). The samples represented a variety of textural classes, soil pH and organic matter content (Table 1). Of the total of 64 samples taken, 59 were from agricultural land (arable fields and pastures), and five from non-cultivated areas (forest floor and set-aside areas). At the sites where the depth of the latest primary tillage was visible, the sampling depth was the depth of cultivation (mostly 0–20 cm, because sampling was mostly done on ploughed soil); at the other sites, the sampling depth was 0–5 cm.
The site of the field survey was the Lake Rehtijärvi catchment (Fig. 1) at Jokioinen community, south-western Finland. Soils of this area have been classified and detailed by Yli-Halla and Mokma (2001). The agronomic soils of the catchment, 225 ha in total, were mostly tile-drained Typic Cryaquepts, with some Aquic Dystrochrepts according to the US Soil Taxonomy (Soil Survey Staff 1998). The soils were predominantly clayey in texture (Table 2) and the fields were mostly used for growing cereals, especially barley (*Hordeum vulgare*). All of the fields of the catchment were sampled by taking 10–12 subsamples at the depth of the latest cultivation (mostly 0–20 cm, as almost all of the fields were annually ploughed at about 20 cm) which were combined to make one representative 0.5-litre soil sample for each field hectare.

The soil samples were dried at 35–40°C, ground to pass through a 2-mm sieve, and homogenised. Concentration of total C was determined using a LECO (St. Joseph, MI, USA) CN-2000 analyser. Soil pH was measured in 1:2.5 (v/v) soil-water suspension and soil texture was assessed by fingers.

In the AAAc extraction (Vuorinen and Mäki-tie 1955), 25 ml air-dry soil was shaken end-over-end (37 rpm) with 250 ml of AAAc solution (0.5 M CH₃COONH₄ and 0.5 M CH₃COOH, pH 4.65) for 30 min, whereafter the suspension was passed through a S&S 5893 blue ribbon paper (Schleicher & Schuell, Dassel, Germany), and the filtrate analysed for P using stannous chloride reduction of the phospho-molybdate complex. The 64 Kokemäenjoki basin soils were extracted with duplicates, whereas the soils sampled from the L. Rehtijärvi catchment were ana-

![Fig. 1. The shaded areas represent the catchments of the lakes where the soils for this study were sampled.](image)

Table 1. Properties of the Kokemäenjoki basin soils studied, grouped according to texture. Numbers are median values, followed by the range in parentheses.

<table>
<thead>
<tr>
<th>Soil group</th>
<th>n</th>
<th>Texture</th>
<th>pH(H₂O)</th>
<th>Org. C</th>
<th>Olsen-P</th>
<th>Pw₁:100</th>
<th>AAAc-P</th>
<th>Mehlich 3-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine-textured</td>
<td>18</td>
<td>c, sic</td>
<td>6.0</td>
<td>3.8</td>
<td>41</td>
<td>13.4</td>
<td>7</td>
<td>61</td>
</tr>
<tr>
<td>Medium-textured</td>
<td>25</td>
<td>scl, cl, sicl</td>
<td>5.8</td>
<td>3.7</td>
<td>32</td>
<td>11.3</td>
<td>6</td>
<td>63</td>
</tr>
<tr>
<td>Coarse-textured</td>
<td>21</td>
<td>ls, sl, scl, l, sil</td>
<td>5.7</td>
<td>3.1</td>
<td>34</td>
<td>12.5</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td>All soils</td>
<td>64</td>
<td></td>
<td>5.8</td>
<td>3.6</td>
<td>34</td>
<td>12.6</td>
<td>7</td>
<td>61</td>
</tr>
</tbody>
</table>

Textural classes: c, clay; sic, silty clay; scl, sandy clay loam; cl, clay loam; sicl, silty clay loam; ls, loamy sand; sl, sandy loam; scl, sandy clay loam; l, loam; sil, silt loam

Olsen-P: P extracted by 0.5 M NaHCO₃, pH 8.5 (Kuo 1996)

Pw: water-extractable P

AAAc-P: P extracted by ammonium acetate buffer

Mehlich 3-P: P extracted by Mehlich 3 extractant (Mehlich 1984)
lysed without replicates, as is done in routine soil testing. For quality control, every tenth sample was extracted with a duplicate and the results of the duplicate determinations were allowed to differ from each other 20% at maximum, or the batch in question reanalysed. Previously analysed samples were included in all test series, and the whole test series were reanalysed in case the difference of the results exceeded 20%.

For 1:100 (w/v) water extraction of the 64 Kokemäenjoki basin soil samples, 1 g of air-dry soil was shaken end-over-end (37 rpm) in 100 ml deionised water for 18 h, whereafter the suspension was passed through a 0.2-µm Nuclepore (Whatman International, Maidstone, UK) polycarbonate filter. The phosphorus concentration in the filtrate was determined colorimetrically by the molybdate blue-ascorbic acid method (Murphy and Riley 1962). The water extraction was performed with triplicates.

**Runoff sampling and analyses**

At the L. Rehtijärvi catchment, sampling from field drains and open ditches was conducted at 90 sampling points during 1994–1996 (a part of the results obtained from this campaign has been published by Jansson et al. 2000). For the present study, the study area and the analyses results were later re-examined and all of the drains and ditches that were possibly influenced by household wastewater or leakage from manure storage, i.e., non-diffuse P sources, were carefully excluded. After the first selection, that excluded the sampling points located downstreams of cowsheds and piggeries, or that were known to receive septic tank effluents, further selection was done on the basis of chemical analyses. It was found (Jansson, unpublished data) that the concentrations of Na and B in filtered runoff samples were, especially at low-flow periods, higher in the wastewater-affected ditches than in those ditches that were known to carry only field and forest runoff. Presence of B as an indication of wastewater in field drains has earlier been used by Gardner et al. (2002). In the field runoff at the L. Rehtijärvi catchment, typically less than 6 mg Na l⁻¹ and less than 0.03 mg B l⁻¹ was measured. A drain or a ditch that could possibly be connected to a point-source (e.g., septic tank) was not taken into our comparison in case the concentrations of these tracers in any of the samplings exceeded 15 mg Na l⁻¹ or 0.1 mg B l⁻¹; maximum values measured in our original data set were 50 mg Na l⁻¹ and 0.5 mg B l⁻¹. Finally, data from 54 sampling points were found suitable for the present study.

Surface runoff samples (0.5 l) were taken during two or three calendar years (1–7 samples per each ditch and year) as grab samples from 18 open ditches running along the fields studied. Water flow in the ditches at the time of samplings was approximated by calculating from flow velocity and water cross section. As well, water discharging from 36 subsurface drainage pipes was sampled (1–9 samples per each drain

<table>
<thead>
<tr>
<th>Field area, ha</th>
<th>Fields of the Lake Rehtijärvi catchment</th>
<th>Surface runoff source area</th>
<th>Drainflow source area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>225</td>
<td>69</td>
<td>137</td>
</tr>
<tr>
<td>Fields with more than 30 % clay</td>
<td>88 %</td>
<td>89 %</td>
<td>93 %</td>
</tr>
<tr>
<td>Ammonium acetate-extractable P, mg l⁻¹ soil</td>
<td>3.6 (1.3–66)</td>
<td>3.1 (1.3–19.8)</td>
<td>4.4 (1.4–19.8)</td>
</tr>
<tr>
<td>pH</td>
<td>5.9 (5.3–7.0)</td>
<td>5.8 (5.3–6.8)</td>
<td>6.0 (5.5–6.7)</td>
</tr>
<tr>
<td>Organic C, %</td>
<td>3.4 (1.0–10.3)</td>
<td>3.5 (1.0–5.9)</td>
<td>3.4 (2.0–4.9)</td>
</tr>
<tr>
<td>Electrical conductivity, mS cm⁻¹</td>
<td>0.46 (0.26–2.10)</td>
<td>0.43 (0.26–1.67)</td>
<td>0.53 (0.31–1.67)</td>
</tr>
</tbody>
</table>
and year, sample size 0.5 l); the flow was then assessed by measuring the discharge volume per second.

Concentrations of DRP and TP in runoff were analysed with the method of Murphy and Riley (1962) after filtration through a 0.4 μm Nuclepore for DRP, and after peroxidisulphate-sulphuric acid digestion of an unfiltered subsample in an autoclave (120°C, 30 min.) for TP. Particulate P (PP) was taken as the difference between TP and DRP. Total suspended solids (TSS) concentration was estimated by weighing the evaporation residue of a 50–100 ml subsample. The concentrations of individual samples were pooled to get an estimate of the mean flow-weighted concentration in runoff within a calendar year. The flow-weighted annual concentrations of the (two or three) study years were then averaged over the years to be compared with the arithmetic mean AAAc-P of the source. The AAAc-P test value for which the comparison was made represented 1–13 field hectares, the median field size being 3.8 ha.

**Results**

For the 64 Kokemännenjoki basin soils, with variable physical and chemical properties (see Table 1) and soil P status ranging from ‘poor’ to ‘high’ according to the agronomic interpretation, the P concentration of the water extracts clearly increased with the AAAc-P concentration of the soils (Fig. 2). The relationship could be described by a linear equation where a 1 mg l⁻¹ increase in soil AAAc-P concentration corresponded to a 21 μg l⁻¹ (with a standard error, SE, of 1.0 μg l⁻¹ and a probability-value less than 0.0001) increase in P concentration in the water phase and a constant term (y-axis intercept) having a value of −15 μg l⁻¹ (with a SE of 11 μg l⁻¹ and a probability-value of 0.1863). This equation accounted for 87% of the variation in water-soluble P for these soils. Whether this pattern could be observed in field runoff, was then tested at the L. Rehtijärvi catchment.

The L. Rehtijärvi catchment soils containing the highest concentrations of AAAc-extractable P in the Ap horizon tended to produce runoff with the highest mean DRP concentrations in surface runoff (viz. water sampled from open ditches; Fig. 3) and drainflow (Fig. 4). The slope estimates of the least squares lines drawn in Fig. 3 and 4 were somewhat smaller than in the laboratory study, and similar to each other: a unit increase in soil AAAc-P corresponded to 15 and 18 μg l⁻¹ (with standard errors, SE, of 1.5 and 2.7 μg l⁻¹, respectively; probability-values less than 0.0001) increase in DRP for surface runoff.

![Fig. 2. Relationship between soil test P (AAAc-P) concentration and water-extractable P (Pw) for the 64 soils sampled in the Kokemännenjoki basin. The x-axis error bars represent the range in duplicate AAAC-P determinations and the y-axis error bars represent standard deviation of the P concentration of the water extracts (n = 3).](image-url)
The DRP concentrations measured in surface and subsurface runoff at the L. Rehtijärvi catchment had a wide within-site variation, as well as, variation between different sites with comparable STP values. For the individual samples collected during 1994–1996, a typical within-site variation in DRP concentration was 10-fold, almost 80-fold variation (0.002–0.158 mg l⁻¹) being the maximum. The variation in average flow-weighted DRP concentration in runoff between all study sites was about 30-fold (0.015–0.452 mg l⁻¹) and for the sites associated with AAAc-P concentrations of 2–5 mg l⁻¹ (these STP corresponded to 65% of the fields of this study) average flow-weighted DRP varied 10-fold (0.015–0.145 mg l⁻¹). Given such a large variation in DRP concentrations, certainly owing to a number of factors, a question arises how confident would the soil test-based estimates of typical DRP concentration be, even in a small and a relatively uniform catchment as studied here.

For the purpose of studying how the STP-inferred DRP estimates corresponded to the observed (long-term average) DRP concentrations, we used the Pw concentrations calculated for the
Kokemäenjoki basin soils \([P_w (\text{mg} \ l^{-1}) = 0.021 \times \text{AAAc-P} (\text{mg} \ l^{-1} \ \text{soil}) - 0.015 \ (\text{mg} \ l^{-1})]\) as a proxy for the predicted DRP concentration. This was considered possible because the \(t\)-test suggested that the slope estimate of the combined data (AAAc-P vs. surface and subsurface DRP) did not differ from that obtained for the Kokemäenjoki basin soils (AAAc-P vs. Pw). In addition, all of the slope estimates were fairly close to each other and, after all, there are no other independent (AAAc-P vs. DRP) data sets available for this purpose.

In Fig. 5, the observed flow-weighted mean DRP concentrations (both surface and subsurface runoff) that were subtracted from the predicted \((P_w)\) values are plotted against the prediction. The deviation between the predicted values and the measured flow-weighted average DRP concentrations in runoff was \(0.144 \ \text{mg} \ l^{-1}\) at maximum. In all but three sites, thus in about 95% of the cases, the deviation fitted into a prediction envelope of \(\pm 0.10 \ \text{mg} \ l^{-1}\). Averaged over all of the 54 Rehtijärvi ditches and drains, the prediction deviated about 20% from the measured average DRP concentrations. There was, however, a clear tendency for the deviation to increase with predicted DRP concentration and a trendline fitted to the data plotted in Fig. 5 (Deviation = \(0.21 \times \text{DRP} - 0.003; \ r^2 = 0.11\)) had a slope with a probability-value of 0.0147.

For the 397 individual runoff samples studied, particulate P (PP) was the major P form in runoff, with an average share of 76% of TP (range 8–99%, median 81%). Because this dominant P form was clearly dependent on the TSS concentration in runoff (Fig. 6), a comparison between AAAc-P and runoff TP concentration was not considered meaningful. For turbid runoff samples, Uusitalo et al. (2000) suggested that TP vs. TSS relationship, instead of TP concen-
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The laboratory data suggested that a linear model could be used to describe the relationship be-
tween AAAc-P and water-soluble P. The Kokemäenjoki basin soils of the laboratory study had widely variable chemical and physical properties, and were partly sampled from non-cultivated areas. There didn’t seem to be any soil property (textural class, pH, organic C) that would have caused deviation from the general trend in AAAc-P vs. Pw relationship. Approximately linear relationships between Morgan’s P (Maguire et al. 2001) and Vermont 1-P (Jokela et al. 1998, Magdoff et al. 1999) vs. P soluble in water or dilute CaCl₂ solution have been described over a wide range of soils and STP concentrations, suggesting that all of these acetate tests are closely related to P intensity characteristics of soils.

At the predominantly clayey L. Rehtijärvi area, the measured average DRP concentrations in runoff had a surprisingly good match to those predicted by the equation obtained from the laboratory data, i.e., AAAc-P vs. Pw relationship, despite the wide within-site variation in DRP. The success in predicting flow-weighted DRP concentrations supports the view that AAAc-P can be used to estimate the DRP loss potential of soils (Turtola and Yli-Halla 1999). In addition, our results support the view that extraction of soil using wide water-to-soil ratio may be used to approximate DRP concentration in runoff from clayey soils of southern Finland (Yli-Halla et al. 1995), even though the predicted DRP concentrations in our data were somewhat higher than the observed ones.

Our data showed that runoff from a given area may in different samplings show very variable DRP concentrations, and it is evident that runoff sampling has to be intensive and extended over long periods if we wish to establish STP vs. DRP relationships in such a relatively narrow STP range as was measured in the L. Rehtijärvi catchment. We believe that in our case, when the average DRP concentrations were based on grab samples, additional indicators of water chemistry – for example based on applications such as ion exchangers to monitor water chemistry (Edwards et al. 1993) or chemical P analysis of ditch sediment that equilibrates with runoff (Jansson et al. 2000) – would have provided useful supporting information on the typical DRP levels.

The paramount importance of soil sampling that matches the soil layer interacting with runoff, discussed by several authors (e.g., Sharpley and Withers 1994, Nash and Murdoch 1997), is also to be stressed. As shown by Haygarth et al. (1998), the P concentration may in grassland soils decrease very sharply within a few centimetres depth. Consequently, the mismatch of the sampled soil depth and that actually being in contact with runoff may lead to very different DRP concentrations in runoff than would be predicted by soil analyses (see Turtola and Yli-Halla 1999). In the Ap horizon of annually ploughed soils, the P distribution is, however, more homogenous as compared to grassland soils. Based on the fact that almost all of the Rehtijärvi fields were annually ploughed, and supported by the reasonably good fit between the observed and predicted DRP, sampling the whole depth of the latest primary cultivation seemed to be satisfactory in our case.

Assuming a linear STP vs. DRP relationship, a unit’s decrease at any STP level would result in as big a reduction in average DRP concentration and, hence, DRP losses. On the other hand, the labile P pool tends to decrease more rapidly in the high STP concentrations than in the low ones (Saarela et al. 1995, Yli-Halla et al. 2002). Thereby, when a P test that responds to soil P buffering is used, the most effective strategy for DRP loss reduction at the Rehtijärvi catchment would likely be based on measures that decrease the AAAc-P concentrations of the 20% of the fields testing higher than 8 mg AAAc-P l⁻¹. A similar strategy could also be used in a national scale, based on the similar AAAc-P frequency distribution in the L. Rehtijärvi catchment and the Viljavuuspalvelu data.

In conclusion, we suggest that soil AAA-P concentration serves as an indicator for a soil’s potential to contribute to DRP losses from agricultural fields to the water environment. The DRP losses may be especially important in areas where erosion is not a major concern. How-
ever, as a measure of easily desorbable P, AAAC-P does not relate to P losses associated with eroded soil particles that may be the major P form in runoff (Jokela et al. 1998). For that purpose, other types of soil tests may be suitable.

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References


SELOSTUS

Viljavuustutkimuksen fosforianalyysin valumavesiin liuenneen fosforin pitoisuuden kuvaajana

Risto Uusitalo ja Håkan Jansson

MTT (Maa- ja elintarviketalouden tutkimuskeskus)
