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Speciation of riverine particulate phosphorus during rain events

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Abstract. Suspended sediments collected during rain events were analysed to assess the maximum potential bioavailability of particulate phosphorus (PP). Physical (separation by particle size) and chemical (sequential extraction) fractionation techniques were applied. Time differentiated sampling during rain events revealed that changes in the concentrations of soluble and particle bound phosphorus, and in the proportion of different PP phases, are due to the changing contribution of various sources of runoff and to flow related variations in particle size. Size fractionation and the extraction of PP phases, can help to distinguish resuspended sediments from sediments coming directly from outside the channel. In light of a former study, investigating PP sedimentation and transformations within the sediments of Lake Sempach, our results lead to the conclusion that, at least 25% (particulate inorganic and reductive soluble P) and at most 70% of the allochthonous PP supply transported during a single rain event, may become bioavailable after early diagenesis in the lake sediments. The uncertainty is due to the unknown time span necessary for the diagenesis, at the lake sediment surface, of particulate organic phosphorus of allochthonous origin.

Introduction

Bioavailability is related to the chemical quality of inputs and to the timing and magnitude of transport fluxes. Within an ecosystem, different compartments function alternately as sources or sinks, regulating nutrient supply to primary producers along with the succession of seasonal events. The potential impact of nutrient inputs cannot be established without obtaining detailed information about the magnitude of the nutrient flux and the biogeochemical reactivity of nutrients bound within different chemical compounds. The bioavailability of the phosphorus (P) supply to a lake can be assessed through the analysis of samples collected during rain events in tributary streams. Rain events are typically concentrated over short periods of time and runoff P contributes in major proportion to the annual supply. We recognize that it is hard to sample storm runoff adequately, but it is the most direct way to estimate the quantity and the chemical quality of the annual P load.

Potential P bioavailability in river sediments has been investigated by several authors using: adsorption/desorption isotherms and chemical extractions (Logan et al. 1979; Dorich et al. 1985; Dorioz et al. 1989; Mayer & Jarrell 1996) often in combination with biological assays (Chase & Sayles 1980; Dorich et al. 1980; De Pinto et al. 1981; Pionke & Kunishi 1992; Ekholm 1994; Fabre et al. 1996).

The aims of the present study are to:

- investigate the occurrence of different PP phases in suspended sediment samples identified by a widely recognized sequential extraction procedure;
- discuss mechanisms which may explain the changing concentrations of different PP phases during storm events;
- assess the contribution of suspended sediment transport during storm runoff to the annual bioavailable P load of Lake Sempach.

The Kleine Aa catchment

The Kleine Aa is a hardwater, first order stream, flowing into Lake Sempach in Central Switzerland. The 7 km^2 drainage basin consists of intensively managed grassland (60%), ploughed fields (15%), forests (15%), and urban areas (10%). Frequent manure applications (ca. 30 t P year^{-1}) constitute the dominant nutrient input with no significant point sources. The catchment is located at the foot of the northern rim of the Alps at 570 m a.s.l. Average yearly rainfall amounts to *ca.* 1200 mm; rain events are evenly distributed during the whole year but with significant peaks between May and July. The soils consist of shallow, loamy brown earths of low permeability. Forty percent of the catchment is artificially drained. At the river mouth the long-term average daily discharge amounts to *ca.* 0.12 m^3 s^{-1} while discharge peaks may reach 7–9 m^3 s^{-1} approximately once every ten years (Gächter et al. 1996). Rain intensities are high and the catchment exhibits a fast runoff response to rainfall with rapid increases in suspended sediments.

Methods

General sample treatment

Samples were collected either manually or by means of an automatic liquid sampler, Manning Ltd., U.S.A., model 4900, equipped with acid washed 1-L polyethylene bottles. Preliminary tests proved that the automatic sampler yielded representative samples of the dissolved and particulate nutrient concentration, in addition both sampling techniques, manual and automatic, produced similar results.

Between 50 and 300 ml were filtered within 0.5 to 8 hours after collection, either directly in the field or in the laboratory, using hot acid (10% HCl, 80 °C) leached, pre-dried, pre-weighed, 0.45 μm pore diameter, cellulose acetate filters. We avoided storing sediments separated from a water suspension since it has been shown that drying and wetting can mobilize P from solid phases (Twinch 1987; Baldwin 1996). Within 24 hours, unfiltered river samples kept at 4 °C in the dark, showed no significant concentration changes in soluble reactive phosphorus (SRP) or in the particulate phosphorus (PP) concentration. Suspended sediment dry weight was determined after drying the filters at 70 °C to constant weight; PP was determined after digestion in a microwave in the presence of H_2O_2 and concentrated HNO_3. Filtrates and digested samples were diluted and if necessary, neutralized, before orthophosphate analysis was carried out using standard analytical techniques adapted for an autoanalyser.

Selected samples were size-fractionated in the field immediately after manual collection by rapid settling through separation funnels. After 10 seconds, 10 minutes and 4 hours, aliquots (30 to 50 ml) of the suspension were removed from the funnel by releasing the outflow stopper; the remaining size fraction was represented by unsettled particles. During this operation no attempt was made to disperse natural sediment aggregates. Size distribution spectra were determined 1 day later (storage at 4 °C in the dark) with a Malvern Master Sizer (Weiner 1984) or immediately after collection, by means of a portable single-particle counter laser device (Particle Measuring Systems Inc.) described in Kobler and Boller (1997).

Sequential P extraction

To collect suspended particles, selected base flow and storm flow samples were filtered in the field and then processed through a 15-step sequential extraction procedure, modified from Psenner and Pucsko (1988) and Hupfer et al. (1995). To avoid possible changes in sediment chemistry, the extraction started in the field immediately after filtration. The filters, loaded with particles, were lacerated into small pieces using plastic forceps and incubated into acid leached, thoroughly rinsed, base-resistant, autoclavable, polysulfone centrifuge vials (50 ml). The capped vials were thoroughly shaken and transported to the laboratory. Here the extraction proceeded at 4 °C on a turning table. The extractants were applied in the following sequence:

- 1 M NH_4Cl (3–4 hours), (repeat for 1 hour), (H_2O wash);
- 0.11 M BD (Bicarbonate Dithionite, 2 hours), (repeat for 2 hours), (1 M NH_4Cl 20 min), (H_2O wash);

- 1 M NaOH (16–20 hours), (repeat for 2 hours), (1 M NH_4Cl 20 min) (H_2O wash);
- 0.5 M HCl (16–20 hours), (repeat for 2 hours), (1 M NH_4Cl 20 min) (H_2O wash).

The extractants were separated from the residues by centrifugation at 4000 g for 10 minutes. All extraction steps were carried out twice, the second incubation being limited to 1 or 2 hours. After the application of each extractant, the residue was washed for 20 minutes with 1 M NH_4Cl to prevent the underestimation of extracted P due to the secondary adsorption of the liberated P onto residual solid surfaces (Ruttenberg 1992). An additional H_2O wash was added to prevent the chemical interaction of the preceding extractant with the following extraction step. In each step, the ratio of the solid to the total extract volume was below 2 g l^{-1}, to avoid the risk of saturation of the solution with respect to the extracted P phase. All extracts were weighed to determine the amount of liquid carry-over from one extraction step to another; appropriate corrections were made. Not later than 8 hours after extraction, the extracts were diluted (all), neutralized (NaOH, HCl), or bubbled with moist air in presence of EDTA (BD). Digestion of the extracts and of the solid residue obtained after the last extraction step, was carried out by persulphate oxidation in the presence of 10% $K_2S_2O_8$ in an autoclave at 120 °C for 2 hours.

Standard molybdenum blue phosphate analysis was carried out by flow-through photometry, after appropriate dilution, on raw and on digested extracts. The first determination gave the reactive phosphorus extracted at each step (SRP-PP). The analysis of digested extracts gave the total PP extracted at each step, while nonreactive PP phases (NRP-PP) were defined as the difference between the two. Blanks and references were prepared by extracting leached filters with no sediment and by spiking known amounts of phosphate. Replicate P measurement in the extracts varied within 10% of the mean of 2 or 3 determinations. The interpretation of the PP phases represented by each different extract is based on Psenner and Pucsko (1988), Psenner et al. (1988) and Hupfer et al. (1995). Table 1 provides a general key.

Experiments were carried out to test the P extraction procedure; specifically we investigated the possible interference of filters with the P analysis and the speciation of PP after adsorption of SRP from solution. Superficial sediment was scooped from a pool in the streambed and gently elutriated in a bucket to separate the finer material from the rest. The suspension, containing silt and clay aggregates, was transported to the laboratory for centrifugation (4000 g, 20 minutes). An aliquot of the obtained wet sediment pellet, equivalent to 80 mg dry weight, was introduced into each of the 18 tubes to be sequentially extracted. Hot-acid leached cellulose acetate filters and a

Table 1. Key to the interpretation of the P extracts.

Extractant	Expected P forms	
	SRP	NRP
NH_4Cl (1 M)	Immediately available inorganic P P loosely adsorbed on surfaces (e.g. surfaces of $Fe_{(ox)}$, $CaCO_3$, clays)	Immediately available inorganic P P loosely adsorbed on surfaces (e.g. surfaces of $Fe_{(ox)}$, $CaCO_3$, clays)
BD (0.11 M) Bicarbonate Dithionite	Redox-sensitive P bound to Fe and Mn	Organic P
NaOH (1 M)	P bound to $Al_{(ox)}$ exchangeable against OH-, inorganic P compounds soluble in bases clay bound-P	Microorganism-P, polyphosphates, detritus organic-P, humic-P
HCl (0.5 M)	Carbonate and apatite bound-P	Organic P
$K_2S_2O_8$	Organic and mineral, non-extractable, refractory P	

Source: Hupfer and Gächter (1995)

phosphate spike (dipotassium hydrogen phosphate) were added to some of the tubes to obtain the following combinations: sediment only; sediment and filter; sediment and spike; sediment, filter and spike; filter and spike; spike only; filter only.

In a further experiment a suspension of superficial streambed sediment was divided into three parts: one subsample was immediately filtered to be extracted using the sequential extraction procedure while the other two subsamples were incubated at 4 °C in the dark on a rotary shaker to be extracted after 24 hours. One of the two subsamples was spiked with dipotassium hydrogen phosphate at the start of the incubation. The next day both subsamples were filtered and extracted.

Results

Effect of the filter

The sequential extraction of sediments collected on filters represents a methodological improvement as it allows to analyze samples with low sediment concentrations. In comparison to continuous flow centrifugation, filtration resulted in practice to be faster and more efficient in retaining fine sediment. Difficulties were however encountered at base flow when suspended sediments, constituted mainly of aggregates of <10 μm in diameter, caused rapid filter clogging. Under such conditions continuous flow centrifugation was employed to collect the particles.

Experiments to test whether the filter material interferes with the sequential extraction (Table 2), demonstrated that pre-cleansed cellulose acetate filters contain virtually no phosphorus, do not adsorb P during the extraction, nor alter otherwise the obtained results. During the 1 M NaOH extraction step, the filters dissolve completely and precipitate again, together with humic acids, during the acidification of the alkaline extract. Paludan and Jensen (1995) reported that organic matter, dissolved after NaOH extraction, is unlikely to bind P as it precipitates following acidification. Our experiments confirmed that the precipitation of the filter material does not affect the P concentration in solution.

Effect of phosphate adsorption

The NH_4Cl extraction step is designed to identify the adsorbed, exchangeable-P which is released as a result of an increase in salinity (Psenner et al. 1988). To test this assumption, a riverbed sediment suspension was split into three samples of equal sediment amounts. The first one was extracted

Table 2. Concentrations of SRP in the NaOH extracts of resuspended stream sediment with and without spikes and filters. Values are means of replicates expressed in $\mu g\ l^{-1}$.

Sediment	Filter	Spike	SRP	*n*
+	–	–	231	3
+	+	–	234	3
+	–	+	347	3
+	+	+	361	3
–	+	+	115	2
–	–	+	114	2
–	+	–	2	2

immediately after collection, the second one (control) after shaking it for 24 hours at 4 °C and the third one after spiking it with orthophosphate and equilibrating for 24 hours at 4 °C. Initially, most of the spike was in solution, bringing the concentration up from 30 μg SRP l^{-1} to almost 1030 μg SRP l^{-1} as expected if all of the spike remained in solution. Within a few hours, the SRP concentration in the spiked solution decreased to about 900 $\mu g\ l^{-1}$ as SRP was adsorbed (Figure 1(a)). After 24 hours the suspensions were filtered and replicate filters were sequentially extracted; the extraction revealed a significant increase in the NH_4Cl-PP phase (Figure 1(b)). An increase of a lesser extent was observed in the BD-PP phase indicating that possibly some of the orthophosphate taken up was associated with Fe(III). As Figure 1(b) shows, after 24 hours, other PP phases were not affected by the SRP sorbed to the solid matrix.

Streamwater and suspended sediment analysis

Analysis of baseflow samples revealed that the streamwater is naturally supersaturated in relation to calcite; the Ca concentration is often higher than 120 mg l^{-2}, the pH is between 7.5 and 8, and total alkalinity amounts to 6.0–6.5 meq l^{-1}. Solubility constant calculations proved that apatite may precipitate due to the high anthropogenic phosphorus loads. The clays are constituted primarily of illites and other Fe rich clays with virtually no kaolinite. Elemental Fe and Ca, measured by atomic adsorption spectroscopy on digested samples, constituted 2 and 8% of the suspended sediment respectively while organic carbon amounted to 10%. Three samples collected

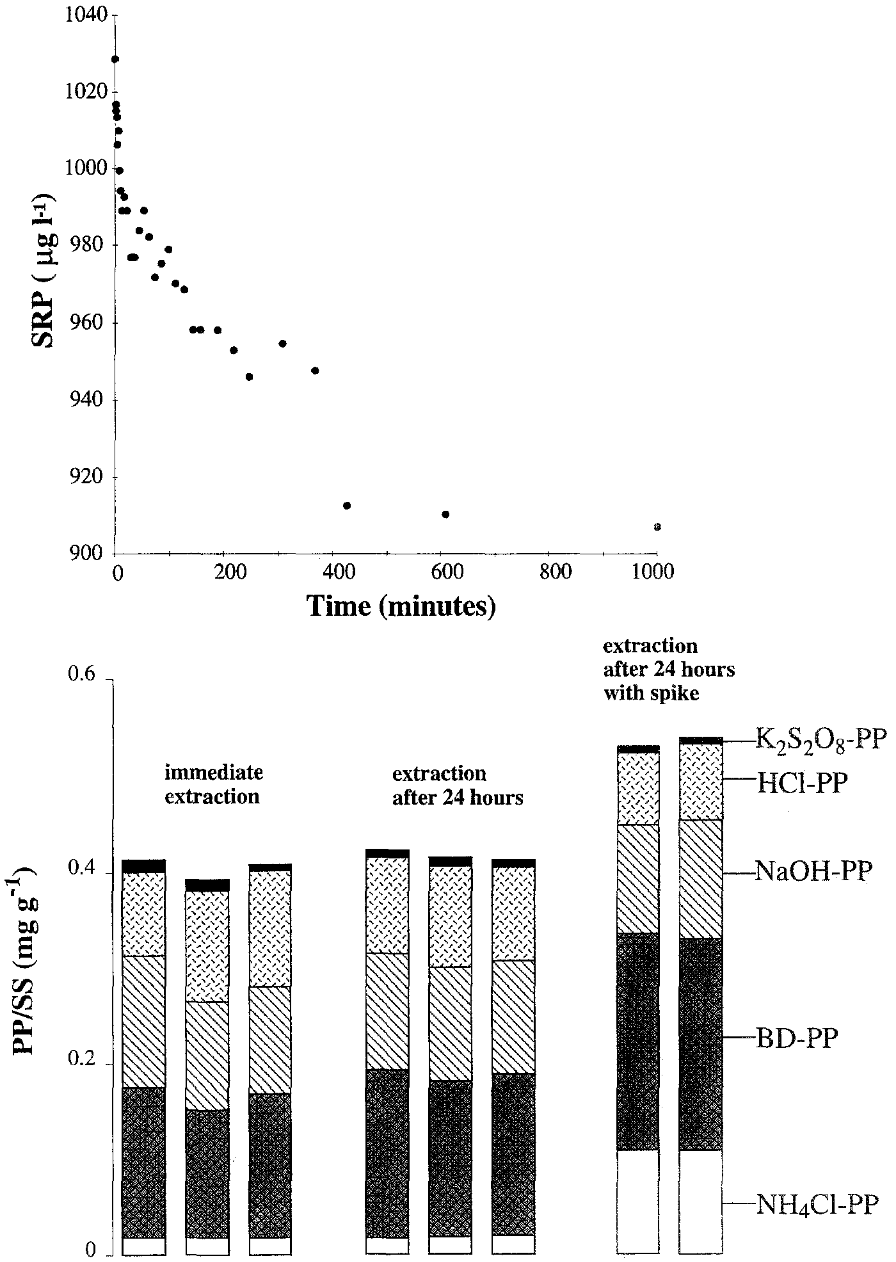

Figure 1. Sequential extraction of riverbed sediments before and after adsorption; (a) Observed reduction of soluble phosphate from solution during the adsorption, (b) PP extracts of the 3 different treatments.

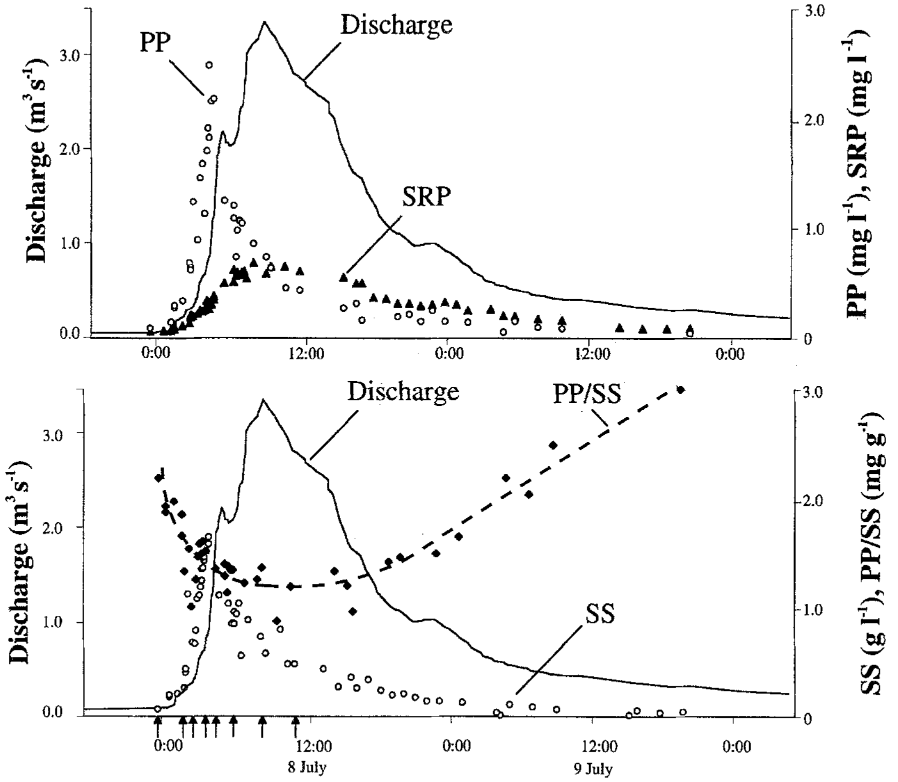

Figure 2. Changes in concentration recorded during the storm of the 7–8 July 1996; (a) particulate phosphorus (PP) and soluble reactive phosphate (SRP), (b) suspended sediments (SS) and phosphorus content of sediment (PP/SS), sequentially extracted sediment samples are indicated by arrows.

before, during and after the discharge peak did not significantly differ in mineralogical composition.

In the river SRP concentrations are usually 50–200 μg l^{-1} but may increase up to 1000 μg l^{-1} at higher discharge. Dissolved organic phosphate is negligible in comparison to SRP. Annual SRP losses are estimated to 1.15 kg P ha^{-1} a^{-1} (Gächter et al. 1996) while the maximum allowable SRP load for the recovery of Lake Sempach from eutrophication, has been set to 0.5–0.9 kg P ha^{-1} a^{-1} (Gächter & Stadelmann 1993). Particulate P may be as low as 3 μg l^{-1} during base flow but becomes the predominant form of transported P during intense storm events reaching concentrations of several mg l^{-1}.

The analysis of several storms between June 1996 and July 1997 revealed that, while there were significant inter-storm changes in the absolute concentration of SRP and PP, all events showed a consistent pattern of change in P transport. During a typical rain event in July 1996 (Figure 2(a, b)), as in all

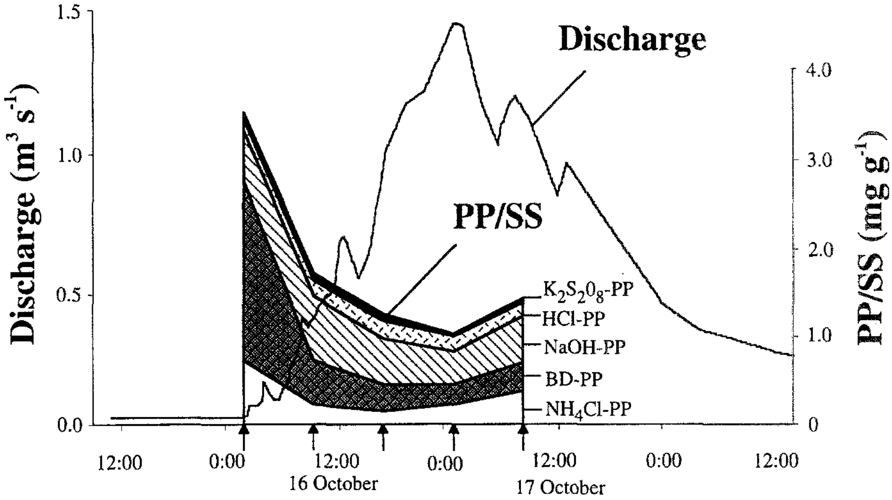

Figure 3. Changes in the concentrations of total PP phases during the course of the 16–17 October rain event. Five samples were extracted (indicated by arrows), the results are joined by a continuous trait for clarity.

other storms, PP increased in parallel with the increase in the concentration of suspended sediments (SS) and the increase in discharge. Suspended sediments and PP reached their maximum before the peak in discharge, while, in the majority of storm events, the SRP peak was delayed. During the storm the concentrations of total dissolved P (not shown), never exceeded that of SRP by more than 10%. The P concentration within the suspended sediment (PP/SS) was highest at baseflow (2.5–3.5 mg g^{-1}) and reached its minimum close to the peak in discharge (dashed line in Figure 2(b)).

Sequential extraction of PP during storms

Five samples were selected during the October 1996 storm and extracted in duplicate. Figure 3 illustrates the proportions of total PP extracted by each extractant; the proportions of reactive and nonreactive PP phases are reported in Table 3. The results indicate that the BD-SRP extract dominated among the reactive forms while NaOH-NRP prevailed among the nonreactive ones. In all extracts, except the NaOH, the SRP-PP exceeded the NRP-PP. Similar results were obtained in July 1996 when five samples were sequentially extracted. In this case the sum of reactive extractable P represented about half of the PP/SS in the samples. The decrease in PP/SS was accompanied by a progressive decrease in the proportion of the BD-SRP fraction, which was negatively related to discharge ($P < 0.005$) and a progressive increase in the proportion of HCl-SRP, which was positively related to it ($P < 0.005$).

Table 3. Relative proportions of reactive (SRP) and nonreactive (NRP) PP phases during the storm of October 1996.

	NH_4Cl-PP		BD-PP		NaOH-PP		HCl-PP			
Samples	SRP	NRP	SRP	NRP	SRP	NRP	SRP	NRP	Refractory-P	PP
1	11	9	45	12	5	12	3	1	2	100
2	7	6	29	1	7	35	10	0	5	100
3	8	4	23	1	9	33	17	0	5	100
4	14	7	20	4	4	32	14	2	4	100
5	16	9	18	4	1	37	13	0	4	100

Particle size of suspended sediment

Changes in particle size distribution during the progression of storm runoff, may explain the observed change in the P content of SS. The sediment P concentration is inversely related to the median particle diameter of size fractionated samples (Figure 4). The data show that fine clays (2μ) contain about 5 times the amount of PP contained in medium silt and more than 12 times the amount contained in sand ($>63\ \mu$m).

Moreover, the P content of SS can be related to particle diameter on the basis of a simple model (Figure 4) in which PP is subdivided into 2 components:

- matrix P, e.g., P contained within the particle matrix, assumed to be directly proportional to W (particle weight, [g]): $P_{mat} = \alpha * W$;
- adsorbed P defined as P bound to the particle surface: $P_{ads} = A * \beta$,

where A: particle surface [μm^2]; α and β are empirically derived constants [mg g^{-1}]. The division of the sum $P_{mat} + P_{ads}$ by the particle weight yields the particle P content (PP/SS):

$$PP/SS = \alpha + \beta * A/W.$$

Since the surface/volume ratio increases inversely to particle diameter, the PP/SS of fine particles is dominated by P_{ads} while the PP/SS of coarse sand grains, having a low surface/volume ratio, is dominated by P_{mat}. Hence, the constant α was approximated to 0.425 mg g^{-1}, the lowest PP/SS observed in our size-fractionated subsamples (median diameter: 192 μm). In order to fit the data shown in Figure 4, the constant β, defining surface bound-PP, was estimated by iteration, as $10^{-11.3}$ mg μm^{-2} (equivalent to 1.62^{-4} moles PO_4 m^{-2}). Since particle surface was estimated by means of optical methods (single particle counter laser measurements) which do not take

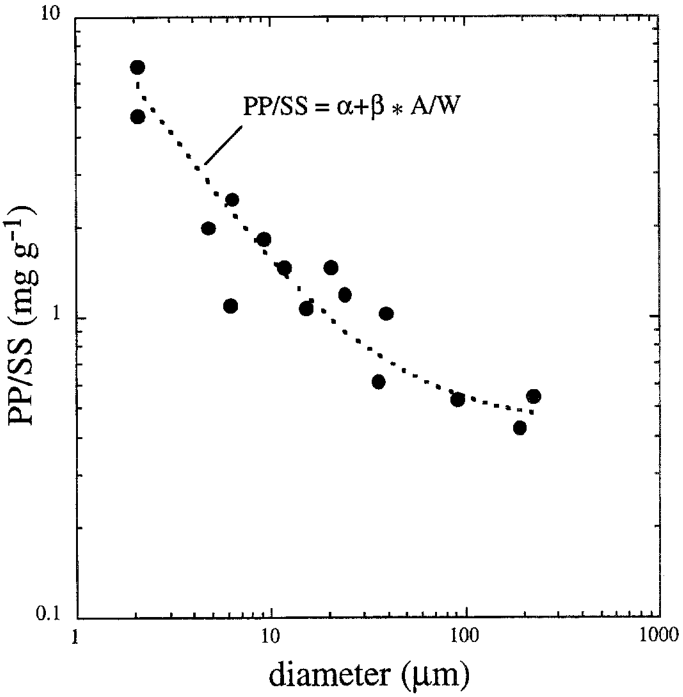

Figure 4. Relationship between the total phosphorus content of sediment (PP/SS) and sediment size arranged according to median diameter.

into account inner particle surfaces available for chemical exchange, it is considered that the value of β is likely to overestimate the true SS phosphate adsorption constant. Closer approximations might have been reached using particle surface estimates based on gas adsorption measurements.

Sediment size does not only influence the total P content, but also its speciation as can be seen in the analysis of a size fractionated sample collected during a rain event in June 1997 close to the peak in discharge (Figure 5). Small size particles (median diameter 6 μm) are relatively poor in reactive P but rich in NaOH extractable NRP, suggesting a high content in organic matter. They are also characterised by a relatively high proportion of NH_4Cl-PP reflecting their ability to carry sorption labile-P, which derives from their large specific surface. Large particles (>50 μ) contain instead 69% refractory PP, 17% HCl-PP, 7% NaOH-PP and only 7% between BD-PP plus NH_4Cl-PP. These particles consisted predominantly of mineral sand grains settling rapidly (within *ca.* 30 seconds) during size separation.

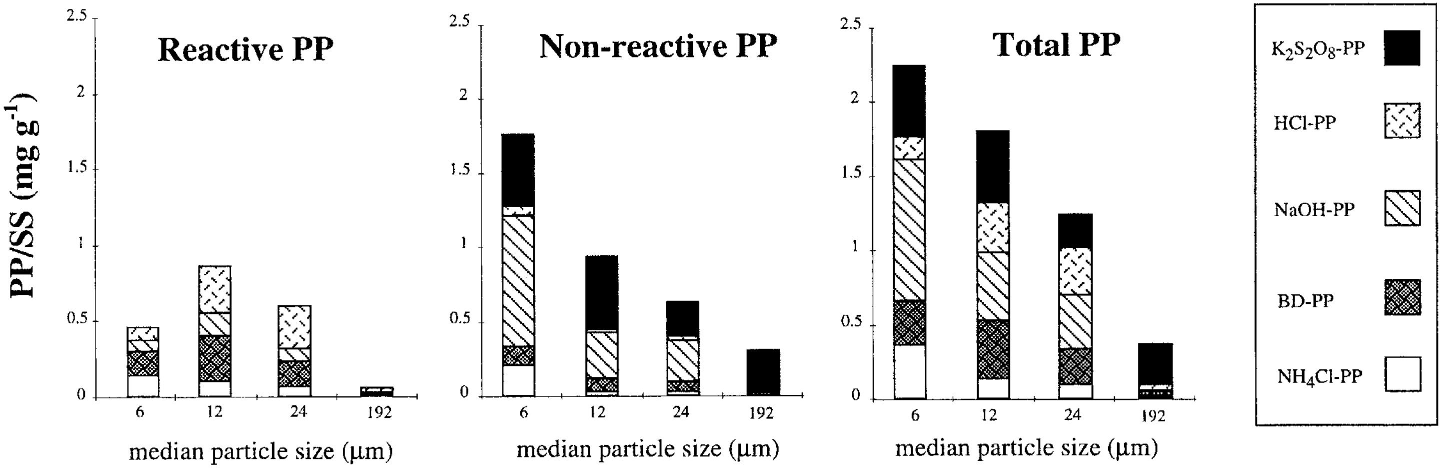

Figure 5. Sequential extraction of a size-fractionated sample collected during the rain event of 21 June 1997, just after the peak in discharge.

Fluxes

Fluxes of SRP, total PP and the various PP phases transported during storm events are presented in Table 4. The results indicate that the PP load can clearly exceed the load of dissolved P during rain events. Further, they show that about half of the PP is extractable inorganic P (SRP-PP), and half refractory and organic P (NRP-PP).

Discussion

Influence of particle size on P transport

It is often stated that changes in the sediment-P content during rain events are related to changes in the particle size distribution of SS (Horowitz 1991). Several studies have shown that PP increases with decreasing particle size and that this relationship is determined by particle surface and mineralogy (Viner 1982; Stone & Mudroch 1989). In addition to their size, small particles offer structural advantages: clays are weathered, laminated, secondary minerals offering large internal surfaces available for interactions with organic matter, metal oxo-hydroxides and nutrients. This surface expansion may increase the effective surface of a clay particle by more than two orders of magnitude in relation to a spherical particle of the same diameter (Jackson 1979; cited in Horowitz 1991). Stone and English (1993) showed that particle size correlated with the relative contribution of various PP phases to the P content of sediment. They related this to the observed increase in Fe and Al oxides with decreasing particle size. These phosphate scavengers are known to associate with surfaces and thus to become enriched in small sized particles (Brook & Moore 1988; Horowitz 1991). Consistently, in their sequential extraction of size-fractionated riverbed sediments, Stone and English (1993) showed that reducible solid P phases, extracted with BD, were most important in the smallest size class of sediment aggregates (2 μm median grain size). Results of our modeling exercise illustrated in Figure 4, show that the P content of SS can be understood as a function of particle size (surface/volume ratio) under the assumption that SS can be approximated to spherical particles and the geochemical composition is homogeneous among particles of different size.

As shown in Figure 2(b), the lowest PP/SS values were observed at the discharge peak. At that time the transport capacity of runoff is highest and may mobilise a larger amount of SS. Given the higher transport capacity we could intuitively assume that high flows transport a higher proportion of coarse particles than do base flows. Since PP/SS is inversely related to particle size (Figure 4) we could deduce that the decrease in PP/SS observed during

Table 4. Total mass fluxes of particulate and soluble phosphorus for a number of storms investigated between July 1996 and July 1997. The percent distribution of the single fractions is based on total particulate phosphorus (PP).

	8.7.96		16.10.96		3.6.97		8.6.97		21.6.97		5.7.97
Duration (hours)	54		72		24		18		48		48
Runoff (m^3)	185943		152890		3243		4475		303798		285945
SS (kg)	95356		42022		80		412		26105		1165041
SRP (g)	88415		59501		391		494		44720		115251
PP (g)	181558	100% PP	67128	100% PP	220	100% PP	920	100% PP	43177	100% PP	500892
SRP-PP (g)	89546	49% PP	33862	50% PP	79	36% PP	496	54% PP	18851	44% PP	
NRP-PP (g)	92011	51% PP	33265	50% PP	141	64% PP	424	46% PP	24326	56% PP	
NH_4Cl-PP (g)			10774	16% PP	25	11% PP	85	9% PP	4398	10% PP	
BD-PP (g)			16651	25% PP	105	48% PP	567	62% PP	8426	20% PP	
NaOH-PP (g)			26941	40% PP	59	27% PP	97	11% PP	12871	30% PP	
HCl-PP (g)			9752	15% PP	15	7% PP	130	14% PP	7795	18% PP	
Refractory-PP (g)			3009	4% PP	16	7% PP	104	11% PP	9685	22% PP	
MAX bioavailable PP (g)			46211	69% PP	161	73% PP	637	69% PP	21841	51% PP	
MIN bioavailable PP (g)			23312	35% PP	111	50% PP	554	60% PP	10900	25% PP	

MAX bioavailable PP = $0.85 * (NH_4Cl - PP + BD - PP + NaOH - PP)$
MIN bioavailable PP = $0.85 * (NH_4Cl - PP + BD - PP)$

rain events can be explained by an increasing proportion of large particles characterised by low P content. However, as shown in Figure 2(b), the SS concentration starts decreasing before the peak in discharge is reached, indicating that, transported sediment does not follow what would be predicted by the flow transport capacity (i.e. highest concentration at highest flow) because sediment sources become depleted. Furthermore, an analysis of SS aggregates by means of a laser single particle counter (Müller et al. submitted), revealed that large sediment aggregates ($>60\ \mu$) were transported during the early phase of the rising limb of the hydrograph, while discharge peaks were dominated by 1–20 μ aggregates without direct proportionality between median diameter and discharge. Measurements of particle size distributions conducted in several rivers in the United Kingdom show that, expectations of sediment transport, based on potential sediment transport capacities, are seldom realized, and that very soon, during an increase in discharge, the load and the median diameter of SS, are likely to depend on changes in sediment contributing areas within the basin (Walling 1996).

This argument is supported by the comparison of PP speciation of particles collected at baseflow (Figure 3) and at high discharge (Figure 5), showing clear differences in geochemical composition. Whereas at low flow PP is dominated by BD-PP, the predominant fraction at peak flow is NaOH-PP. From this we deduce that the changes in PP speciation and in PP/SS observed during rain events, could be influenced by changes in sediment sources and do not depend only on particle size. As discussed below, we suggest that BD-PP is enriched in river bed sediments due to processes taking place at the sediment-water interface, while NaOH-PP characterizes sediments originating from top-soil erosion.

The source of BD-P

During baseflow and during the very beginning of the rain event, BD is the prevailing phase of PP (Figure 3, Table 4). The occurrence of high BD-PP at low discharge was observed, with varying amplitude, in all baseflow samples and storm events analysed, and cannot be attributed to a seasonal effect. Due to the low transport capacity, SS transported during early runoff, consist primarily of fine sediments deposited transiently within the channel bed. Their contribution to sediment transport decreases with the progression of the storm as these sediments are washed out and sediments originating from river banks and from outside the stream channel start to make a significant contribution to SS transport. This change of sediment sources influences the phases of PP transported. Nevertheless, at elevated discharge rates, the contribution of different PP phases to the total P content of SS, is relatively constant (Figure 3), indicating that after reaching a certain discharge, the suspended matter does not change markedly in composition. The BD-PP enrichment of fine particles may occur at the oxic sediment/water interface. On the other hand, particles eroded from top soils and reaching the river at higher discharge, are likely to bear a higher content of organic matter and hence more organic PP (NaOH extractable) than sediment accumulated at the river bed during baseflow. This is consistent with the observed increase in NaOH-PP at high flow (Figure 3). Thus, even within the same catchment, sediments coming from different sources are characterised by a different geochemistry and hence, apart from particle size, the source of particles affects the proportion of different extractable PP phases. Tracing particle sources by their geochemical composition has been applied to a number of catchments in the United Kingdom to distinguish river bed sediments from bank material and from different top soils (Foster et al. 1996).

The "iron curtain"

The accumulation of BD-P phases at the river bed can be attributed to a process analogous to the mechanism that Chambers and Odum (1990) called the "iron curtain". These authors were able to extract amorphous iron and phosphate in tidal freshwater marshes and found that amorphous iron oxides and hydroxides removed dissolved phosphate from solution. The iron source was identified in advecting groundwater. Similarly in the Kleine Aa, influxes of poorly oxygenated groundwater, rich in dissolved iron, provide a continuous source of iron which precipitates in the oxygenated water forming fine deposits of colloidal aggregates at the sediment/water interface. On these surfaces phosphate is fixed and stripped from the water column. This internal source of BD-P accumulates during baseflow and becomes progressively eroded as the deposited sediment is transported during the first phase of the storm event.

A similar mechanism is likely to play a role in the "trapping processes" described by Dorioz et al. (1989) in the Redon, a tributary of Lake Geneva (Switzerland). During an extended period of baseflow, Dorioz et al. were able to measure a progressive increase in the P content of fine sediments deposited on the river bed. Comparing these data with SRP concentrations measured during periods of sediment erosion and deposition, they were able to calculate a theoretical SRP removal rate from the water column. However, they did not discuss explicitly SRP trapping in relation to Fe oxide and hydroxide formation in the riverbed. Our observation of the formation of redox sensitive P forms in riverbed sediments suggests that this mechanism could be of more general relevance than thought in the past. Mayer and Jarrel (1996) provided evidence of the formation of iron oxide colloids on the riverbed of the Tualatin River in Oregon. As in our study, the authors stated that colloidal

Fe associated with colloidal P was dominant in particles collected during baseflow, therefore originating from the riverbed, but would progressively loose importance as discharge increased.

Fluxes of PP during storm events

According to a study on SRP transport in the Kleine Aa, Gächter (1996) concluded that rain events and sustained high discharge periods were responsible for the major part of the annual SRP load, with baseflow playing a limited role. Estimates of average annual loads (1985–1996) based on continuous discharge measurements and a statistical relationship between daily P loads and daily discharge rates yield 860±173 kg P a^{-1} and 759±207 kg P a^{-1} for SRP and PP, respectively. Table 4 shows that the sum of the loads of the rain events sampled contributed nearly as much as the average annual load, indicating that the presented results are representative and that P transport in the Kleine Aa is concentrated in few intense storms. In agricultural plot-scale studies (Sharpley et al. 1981), most small watershed-scale studies (Miller et al. 1982; Johnson et al. 1976; Vaithiyanathan & Correll 1992; Pionke & Kunishi 1992) and particularly in studies with storm-based results (Pacini 1994; Hubbard et al. 1982; Johnson et al. 1976), PP fluxes greatly exceed those of dissolved P. In the Kleine Aa catchment, this was not always the case. Our observations indicate that PP transport reacts very promptly to increases in discharge but exceeded the SRP load only during some major rain events (Table 4). An important factor, likely to determine the amount of PP transported, is the length of the dry period preceding the storm. As shown by Dorioz et al. (1989), P storage during baseflow in the riverbed of the 15 km river Redon was estimated to be as much as 30 kg P $week^{-1}$.

Besides providing estimates of PP and SRP transport during storm events, our data give insight into the transport of different PP phases. The prevailing trend portrayed in Table 4 indicates that the proportion of SRP-PP:NRP-PP appears to be higher in less intense rain events, while rain storms causing top-soil erosion, are characterised by a low ratio as they transport higher fluxes of apatites and refractory PP. This observation can be explained by the higher selectivity of moderate storm events which primarily transport sediments which can be easily mobilized such as small-size particles and fine-textured aggregates of low bulk density, originating mainly from the riverbed and from areas near the river channel. By analogy, soil erosion studies showed that the P enrichment ratio of eroded sediments is negatively related to the erosive energy of storms, such as rainfall intensity and duration, and correlates positively with the clay content of the eroded sediment (Sharpley 1980).

This indicates that factors such as rain intensity, frequency and duration may determine the P availability of the exported suspended load by mobilizing different SS sources.

Bioavailability

Sequential sediment extractions allow us to distinguish different PP phases. Several authors have combined sequential extractions with incubations of sediments in the presence of P starved algal cultures (Golterman 1976; Dorich et al. 1985; Williams et al. 1980; De Pinto 1981; Fabre et al. 1996). Such experiments have shown that a significant proportion of PP, defined according to the different extraction procedures employed, is immediately available to algal cells. Pionke and Kunishi (1992) estimated that 42% of PP in riverine SS was bioavailable. Logan et al. (1979) set bioavailable PP between 30 and 80% of PP. The low estimate is based on the undigested NaOH extract, the higher estimate includes also the BD-PP which appears to be relatively stable in oxic sediments.

The results of sequential P extractions allow us to estimate fluxes of maximum potentially available PP. In doing this, it is important to distinguish this potentially bioavailable pool from the realized PP availability which supports primary production in the receiving system. The latter depends on factors which are not directly related to the quality of PP loaded to the lake; e.g., residence of particles in the euphotic zone, temperature, irradiation, stratification, redox conditions in the sediment and hence on trophic state.

Some recent evidence indicates that it is unlikely that PP discharged into a lake following a rain event may support primary production in the short term. Studies conducted in Lake Constance (Stabel & Geiger 1985), Lake Sempach (Hupfer et al. 1995), Lake Lugano (Mattenberger, unpublished), tropical reservoirs (Pacini et al. 1993; Pacini 1994) and experiments conducted with the artificial introduction of sediments to limnocorrals (Cuker et al. 1990), indicate that rain events may, in the short term, actually depress primary production. This apparent paradox is due to increases in turbidity and in mixing depth, to the physical disruption of compact algal blooms, and to loss of P from the water column by fixation onto the surface of sedimenting particles during their settling.

Eutrophication models are designed to guide management actions to control nutrient transport over medium temporal scenarios at the catchment scale. To investigate the supply of bioavailable P, the study of actual sediment diagenesis in the receiving lake, may provide more reliable information than short term algal assays conducted in the laboratory. While NH_4Cl-PP represents a fully exchangeable and therefore bioavailable phase (Figure 1(a)), the bioavailability of other phases will depend on geochemical transformation and on the time allowed for diagenesis. The release of BD-PP is likely to occur at the end of the summer season when the decomposition of the summer primary production becomes intense and deep waters in the lake become anoxic (Hupfer et al. 1995). High diffusive fluxes of SRP from lake sediments have been measured towards the end of the summer stratification period and attributed to the dissolution of solid redox sensitive PP species (Gonsiorczyk et al. 1997; Belzille et al. 1996). Notwithstanding artificial aeration and oxygenation, in Lake Sempach, redox sensitive forms of P do get released from bottom sediments even in the oxic hypolimnion and therefore should be considered as part of the short-term (annual) bioavailable P pool.

Hupfer et al. (1995) estimated that most of the BD-PP and NaOH-PP in the sediments of Lake Sempach is released after reduction of Fe(III) and mineralization of organic matter. Within 5 to 6 years only 30% of the sedimented PP remained in the sediment. While HCl-PP and refractory PP accumulated entirely, about 85% of NH_4Cl-PP, BD-PP and NaOH-PP were released and can be considered as representative of the maximum potentially bioavailable PP. If these findings are applied to riverine sediments (Table 4), then it can be deduced that between 50 and 70% of the PP supply may become bioavailable (see MAX bioavailable PP in Table 4). This estimate, based on comparing riverine material and lake sediments, suffers from the uncertainty related to differences in geochemical composition of the two types of sediment. The bioavailability of riverine PP may be overestimated since allochthonous sediments are by nature richer in refractory organic matter than lake sediments, consisting of settled planktonic material. We should consider that NaOH-extractable PP obtained from riverine SS may represent a pool which decomposes less readily than the NaOH-PP extracted by Hupfer et al. (1995) from lake sediments. Thus, we distinguish between a maximum estimate of PP bioavailability, which, following the results of Hupfer et al. (1995), considers a large proportion of non-apatite PP phases to be bioavailable, and a minimum (conservative) estimate, which considers allochthonous NaOH-PP as totally refractory. By these estimates, bioavailable PP is comprised between about 25 and 70% of the PP transported during rain events (Table 4). The realized PP bioavailability is probably more closely related to early diagenesis processes at the sediment-water boundary than to rapid P releases during particle delivery into the receiving system. Restoration plans designed for the sole control of SRP inputs which do not take into account lake sediments as internal P sources, are likely to underestimate the time needed for restoration (Sas 1989).

Conclusions and recommendations

- To characterise P transport it is important to study SS rather than rely on the collection of material deposited on the river bed, as these may differ significantly in respect of P content and availability.
- The relative contribution of different P phases to PP is affected by the geochemical environment the suspended particle experiences. This is especially true for small size particles which are more readily affected by changes in the surrounding environment.
- Sequential P extraction can be used to trace sediment sources. The extraction of different sediment size classes does significantly improve the interpretation of results.
- Changes in the P content of sediment and in the proportion of different solid P phases observed during rain events cannot be explained simply by sediment grain size. The high amount of BD-P observed at low discharges is probably due to the coating of sediment particles with iron oxides and hydroxides and bound P.
- The contribution of SS to the P transport in the Kleine Aa cannot be neglected in the estimate of the annual P export flux. All the non-apatite PP (NH_4Cl-PP, BD-PP and NaOH-PP) may be considered potentially bioavailable. Uncertainties reside in the estimation of the actual release of phosphate from allochthonous particles over longer time scales due to lack of information about their further diagenetic evolution in the bottom sediments.

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