

Phosphate adsorption by mineral weathering particles in oligotrophic waters of high particle content

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[1] We investigated the interactions of dissolved reactive phosphorus (DRP) and dissolved nonreactive phosphorus (DNRP) with suspended and settled aquatic particles. The sorption to minerogenic particles from an alpine catchment collected in rivers, hydropower reservoirs, and a downstream ultraoligotrophic lake was modeled using Langmuir-type isotherms. DRP and DNRP exhibited about equal affinities to particle surfaces. The sorption of dissolved species to surfaces alters the fate of P in water bodies. In spite of the small surface-binding constants, high particle concentrations enhance the sorption of P to surfaces, and, consequently, chemical analysis of DRP can substantially underestimate the potentially bioavailable P. In unpolluted rivers with high content of suspended mineral particles, e.g., triggered by heavy rain events (2 μg DRP/L, 1.3 g/L suspended particles), P loads solely based on DRP measurements underestimate the true load of potentially bioavailable P by more than a factor of two. Modeling P sorption equilibria with a single type of surface site generates a management tool for water quality in P-limited oligotrophic systems.

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1. Introduction

[2] The productivity of most freshwater lakes is phosphorus (P)-limited [Schindler, 1977]. Phosphate that can readily be taken up by algae is defined operationally as the dissolved reactive P (DRP) that during filtration, passes a 0.45 μm pore size membrane [Wenzel, 2001]. Additionally, part of the nonreactive P (DNRP) (passing the filter but not being reactive with molybdenum) may become bioavailable after appropriate chemical transformations. Analytically, the DNRP consisting mainly of dissolved organic P (DOP) and colloidal P is the difference between the total dissolved P (TDP) analyzed after oxidative digestion of the filtrate minus DRP. As part of these dissolved P species may reversibly sorb to particle surfaces ($\equiv\text{SP}$), also this particulate P fraction may contribute to the potentially bioavailable P pool.

[3] While sorption of P to synthetic Fe(III) minerals is well characterized [Dzombak and Morel, 1990], its sorption to natural particles is usually neglected due to the low affinity at ambient pH values [Baldwin *et al.*, 2000], the low particle content (<50 mg/L suspended particulates) and their small specific surface area (<10 m^2/g). However, at low concentrations of free phosphate and high particle loads, the scavenging of dissolved P may significantly affect the physicochemical speciation and thus the fate of P within the aquatic environment. Input of riverine P to lakes is substantial during periods of high water discharge [Pacini and Gächter, 1999; Gächter *et al.*, 2004], when concentrations of suspended particles can reach several g/L and

TDP is increased 10 to 20 fold compared to low flow. In principle, if particles are small and settling is slow, sorbed P can be remobilized within the productive zone. Thus, as routine monitoring programs generally determine only the DRP and/or the TDP load but do not consider the fraction of reversibly sorbed P, they may significantly underestimate the true load with P potentially available to their biota. Scavenged P may desorb during particle and/or TDP dilution or due to TDP consumption by primary producers. However, settling particles may also remove TDP from layers with elevated TDP concentrations, e.g., in an anoxic hypolimnion. In conclusion, the physicochemical speciation may be particularly important for surface waters poor in P such as high alpine streams, lakes and reservoirs [Ashley *et al.*, 1997; Stockner and Macisaac, 1996] heavily loaded with mineral particles.

[4] An important prerequisite for physicochemical speciation is the availability of quantitative adsorption-desorption data applicable to natural particles at ambient pH values. Müller and Duffek [2001] suggested conditional adsorption parameters for several trace metal cations to natural aquatic particles and found them remarkably independent from particle composition. Surface sorption properties of anions to natural particles are, however, scarce. Sigg and Stumm [1981] described the adsorption of DRP to goethite, applying a detailed model of surface species including binding constants and pH and allowing the extrapolation to natural waters. Goldberg [1985] modeled sorption competition between DRP, selenite and silicate on goethite. However, quantitative information on P sorption with particle surfaces other than iron or aluminum oxides is scarce. Ioannou and Dimirkou [1997] published surface-binding constants for DRP with kaolinite, a layer silicate. Millero *et al.* [2001]

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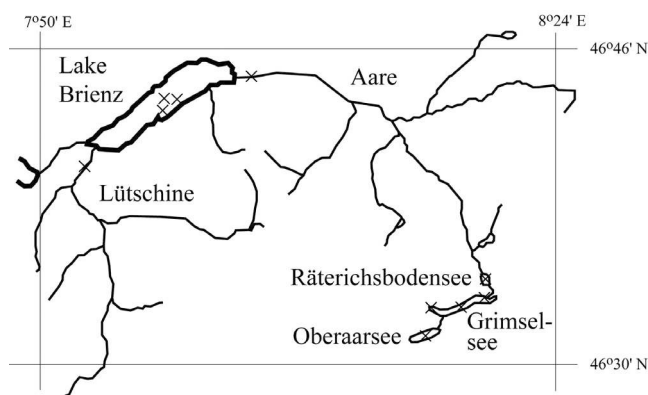


Figure 1. Map of the catchment of Lake Brienz (Switzerland) with the two main contributing rivers Aare and Lütschine. Oberaarsee, Grimselsee, and Räterichsbodensee are reservoirs built for hydropower production. Crosses indicate sampling sites.

provided very detailed data on P sorption onto calcite and aragonite.

[5] As it is questionable whether sorption constants derived from experiments with synthetic mineral phases are applicable to natural systems [Gustafsson, 2001], we determined the P sorption properties of a variety of natural suspended particles and sediment material in a concentration range where these inorganic surfaces may significantly compete with algae for bioavailable P. Sorption parameters resulting from our chemical equilibrium model and the experimental data are applied in discussing the P loads of the nutrient-poor and turbid rivers Aare and Lütschine, the main tributaries to Lake Brienz. This lake was subjected to distinct reoligotrophication due to P load reduction as well as to changes in the load of mineral particles as a consequence of the construction of reservoirs built for hydropower production (B. Müller et al., Past and present bio-available phosphorus budget in the ultra-oligotrophic Lake Brienz, submitted to *Aquatic Science*, 2006; A. Wüest et al., Quantifying non-inert phosphorus fluxes in particle-laden ultraoligotrophic lakes, manuscript in preparation, 2006, hereinafter referred to as manuscript in preparation).

[6] The aim of our investigation was (1) to provide conditional sorption constants and surface-binding capacities describing the interaction of DRP with crystalline weathering particles encountered in rivers and lakes, (2) to relate the physicochemical parameters responsible for the sorption of phosphate to particle composition and specific surface area, (3) to estimate the fractions of dissolved and reversibly adsorbed P in particle loaded rivers, and (4) to discuss practical consequences for the estimation of loads and P budgets of ultraoligotrophic lakes.

[7] Our experimental attempt was twofold: (1) P desorption was measured from gradually diluted suspensions of 16 particle samples from lotic and lentic sites within the same watershed. Applying a chemical mass action law, the amount of reversibly bound P was obtained from this “mild” desorption procedure (by mere dilution and without using other ions to displace P) together with a conditional surface-binding constant. (2) In adsorption experiments, suspended particles were “titrated” with increasing amounts of P, resulting in a maximum surface-binding

capacity and a conditional surface-binding constant for the situation of high surface coverage. The layout of the paper follows the order of the four aims of this investigation.

2. Materials and Methods

2.1. Sampling Sites

[8] Lake Brienz is an ultraoligotrophic ($<4 \mu\text{g P/L}$ [Organisation for Economic Co-operation and Development, 1982]), deep perialpine lake in Switzerland (Figure 1). It has a surface area of 29.8 km^2 , a volume of 5.17 km^3 , maximum depth of 260 m and average hydrological load of $62.3 \text{ m}^3/\text{s}$ (variability $\pm 50.4 \text{ m}^3/\text{s}$). While the Lütschine, one of the two major contributing rivers, drains a partly calcareous catchment of an unaltered hydrological regime, the Aare flows from a crystalline catchment whose flow is heavily altered by several reservoirs built for hydropower generation. The annual particle load is typically in the range of 250–350 kt (average 302 kt) and has decreased by approximately 232 kt/yr due to sedimentation in the reservoirs Grimselsee, Räterichsbodensee, and Oberaarsee [Finger et al., 2006; Anselmetti et al., 2006]. Grimselsee is a reservoir at 1904 m altitude with a small catchment of glaciers and rocks. Räterichsbodensee and Oberaarsee are in similar environments and are located down gradient and up gradient of Grimselsee, respectively. Corresponding to the different geology of the catchments, the pH in the reservoirs was around 7; in the Aare, Lütschine and Lake Brienz it was between 7.5 and 8.6. The sediment consists of clastic minerogenic particles. The composition of settling particles shows little seasonal variations. Thus P dissolution is precluded, and the repartitioning of P is constrained to adsorption and desorption reactions.

2.2. Field Measurements

[9] Discharge measurements in the Aare and Lütschine with a time resolution of 10 min were obtained from the Swiss Hydrological Survey of the Federal Office for Water and Geology (BWG/LHG) for 2003. Corresponding particle concentrations were used from Finger et al. [2006]. DRP concentrations were measured in two campaigns with high temporal resolution (1/h during floodwaters) and several month of occasional sampling (1/d). The continuous courses of DRP for 2003 were calculated in the same time resolution as discharge with a rating curve [Cohn, 1995; Moosmann et al., 2005] expressing the concentration as a function of discharge, as determined from monitoring data ($a + bQ^c$, where $a = 1.75$, $b = 0.13$, $c = 0.66$ for the Aare, $a = 0$, $b = 0.36$, $c = 0.44$ for the Lütschine), where concentrations are in $[\mu\text{g P/L}]$ and Q in $[\text{m}^3/\text{s}]$. Although sediments were sampled only once per year, the interannual variability in sediment composition is considered negligible for these lakes, because particles consist almost entirely of geogenic weathering material (consistently low organic content) that change over multiple timescales in concentration, but not in composition.

2.3. Sampling, Sample Treatment, and Analysis

[10] Samples of particulate matter were collected from various locations to obtain a representative set of particle compositions (Table 1). Settling particles were collected with cylindrical traps of 9.2 cm diameter and 75 cm length

Table 1. Codes, Location, Date, Depth, and Positions of Sampling of Particulate Material Used for Sorption Experiments With Phosphate

Code	Description	Date/Exposition/Position
Grimsel inflow	Grimsel sediment, 3 m depth, inflow	8 Oct 2003
Grimsel center	Grimsel sediment, 80 m depth, center	8 Oct 2003
Grimsel outflow	Grimsel sediment, 45 m depth, outflow	8 Oct 2003
Räterichsboden	Räterichsboden sediment	27 May 2004
Oberaarsee	Oberaarsee sediment	8 Oct 2003
BR03-1 50 m	Lake Brienz, particle trap, 50 m	20 Jun to 21 Aug 2003
BR03-2 50 m	Lake Brienz, particle trap, 50 m	25 Aug.–21 Oct 2003
BR03-1 255 m	Lake Brienz, particle trap, 255 m	12 May to 21 Aug 2003
BR03-2 255 m	Lake Brienz, particle trap, 255 m	25 Aug to 21 Oct 2003
BR04 20 m (0–0.5)	Lake Brienz, sediment 20 m, 0–0.5 cm	6 May 2004/Pos. 640895/173967 ^a
BR04 20 m (9–10)	Lake Brienz, sediment 20 m, 9–10 cm	6 May 2004/Pos. 640895/173967 ^a
BR04 212 m (0–0.5)	Lake Brienz, sediment 212 m, 0–0.5 cm	6 May 2004/Pos. 641150/174850 ^a
BR04 212 m (9–10)	Lake Brienz, sediment 212 m, 9–10 cm	6 May 2004/Pos. 641150/174850 ^a
Aare	Particles from floodwater	May 2005
Lütschine	Particles from floodwater	May 2005
Lütschine	Particles from floodwater	July 2005

^aPositions in Swiss Grid coordinates

exposed at depths of 50 m and 255 m in Lake Brienz. Sediment cores were collected with a gravity corer [Kelts *et al.*, 1986] at 20 m and 212 m depth of Lake Brienz on 6 May 2004. Sediments from the reservoirs Grimselsee, Räterichsbodensee and Oberaarsee were grab sampled. Suspended particles from the Aare and Lütschine were collected during two storm events (May and July 2005). Coarse particles that settled within minutes were ignored, and suspended particles were subsequently harvested by filtration of 10 l of floodwater using cellulose acetate membrane filters of 0.45 μm pore size. Phosphate was determined photometrically with the molybdenum blue method following EN 1189:1996 [Deutsche Einheitsverfahren zur Wasseruntersuchung, 1996]. A 5 cm quartz cuvette was used, and the span of the calibration curve was 0.5–20 $\mu\text{g P/L}$, yielding a detection limit of approximately $0.3 \pm 0.2 \mu\text{g P/L}$. Chemical analysis of TDP, TP and TN was performed after extraction of 25 mL of filtered water sample or about 50 mg freeze-dried particulate sample with sodium hydroxide and potassium persulfate in an autoclave (1 h, 120 °C). Molybdate-reactive phosphorus was then determined as described above. According to Lambert and Mahler [1995], the digestion procedure gives good recoveries up to 100 $\mu\text{g P/L}$. It is under discussion, however, whether mineral phases in the sample remain partly intact and retain P [Nollet, 2000]. TN was oxidized and present as NO_3^- in the same extraction solution. NO_3^- was determined photometrically at 540 nm with an autoanalyzer as nitrite (NO_2^-) after passing a Cd-Cu reductor and following the procedure EN 26777:1993 [Deutsche Einheitsverfahren zur Wasseruntersuchung, 1996]. The fractions of P and N that cannot be mineralized with this treatment may be irrelevant with respect of their bioavailability in the aquatic environment; however, one has to be aware that values for TP and TN depend on the analytical methods applied and on the quality of particles. Sediment was freeze-dried and the water content was determined from weight loss. A limited number of sorption experiments were performed with particles that were not freeze-dried to investigate the possible changes of particle properties, and results were within the range of parameters obtained with dried particles. The specific surface area of several samples was determined by BET- N_2 adsorption at 77 K. Mass density was calculated from dry weight and

volume (determined by the displacement of water in a volumetric flask). Fe, Mn and Ca were determined with inductively coupled plasma and optical emission spectroscopy (ICP-OES, Spectro Ciros, Spectro Analytik) after acid digestion with 4 mL of concentrated, suprapure HNO_3 (Merck) and 1 mL H_2O_2 in a microwave oven. Accuracy levels based on rock standard samples were 10% for Fe and between 2% and 8% for Mn and Ca, respectively. Total carbon (TC) and total organic carbon (TOC) were determined by combustion in an oxygen stream with a Heraeus elemental vario EL without treatment and after acidification with 5M HCl, respectively. Total inorganic carbon (TIC) was calculated as the difference between TC and TOC. The accuracy and reproducibility of the TC analysis were 5% and 1.6%, respectively.

2.4. Phosphate Desorption Experiments

[11] Stock suspensions of 100 g/L were prepared by ultrasonification of freeze-dried particles for 15 min in 1 mM NaHCO_3 solution to disperse conglomerates. Desorption was determined in 1 mM NaHCO_3 solutions at a pH of 8.6 containing particles at concentrations from 6 g/L to 0.5 g/L. Suspensions were shaken for 40 to 70 h in the dark at 8 °C. Samples were then 0.45 μm membrane filtered, and DRP and TDP were determined as described above. The experiments were repeated up to three times; however, only the experiment where the titration curve fitted best to the model was used for evaluation.

[12] Surface-binding constants and maximum sorption capacities were determined from adsorption and desorption experiments for each of the 16 particle samples. Adsorption experiments reached high surface coverage (ratios phosphate/particles = 0.8 to 8 mmol/kg), while desorption experiments covered a range of low phosphate/particle ratios (0.1 to 0.9 mmol/kg). The sorption processes were described with Langmuir adsorption isotherms, where a distinct amount of surface-binding sites Γ of the sorbent is occupied by the adsorbate P with a constant stoichiometry [Stumm and Morgan, 1996]. Pairs of parameters characterizing surface sorption (surface-binding constants K_n and surface concentrations Γ_n) obtained from desorption experiments revealed the actual surface concentration of DRP (K_{DRP} , Γ_{DRP}) and DNRP (K_{DNRP} , Γ_{DNRP}).

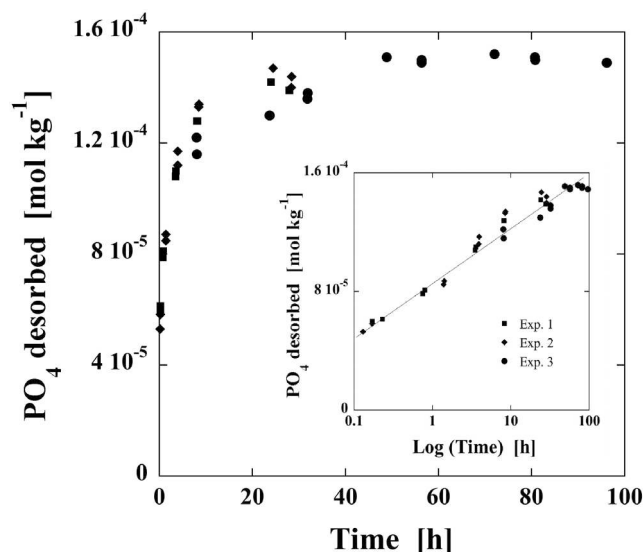


Figure 2. Three identical kinetic desorption experiments suspending 4 g/L of sediment trap particles (BR03-2 255 m) in a solution of 1 mM HCO_3^- . The inset depicts the logarithmic relation of the desorption process with time.

[13] The desorption process is formulated as a chemical mass action law with one type of adsorbent site (as an initial test of the hypothesis that adsorption on natural particles within this watershed can be adequately modeled by a single adsorbent):



$$K_n = \frac{[\equiv SP]}{[\equiv S][P]} \quad (2)$$

[14] The sorption constant, K_n , is conditional for the type of particles, the chemical composition of the solution in which the experiments were performed, and the range of

phosphate concentrations. $\equiv S$ depicts a surface sorption site, and $\equiv SP$ a phosphate ion or complex adsorbed to the particle surface. P as well as the index n stand for DRP or DNRP. TP_n of the experimental suspension consists of the sum of P and $\equiv SP$:

$$TP_n = [P] + [\equiv SP], \quad (3)$$

and the sum of surface sites $A\Gamma_n$ is

$$A\Gamma_n = [\equiv S] + [\equiv SP] \quad (4)$$

where A is the particle concentration in g/L and Γ is in mol/g.

[15] In order to determine the present surface concentration, the total occupied surface sites are set equal to the total remobilizable (reversibly adsorbed) P:

$$A\Gamma_n = TP_n \quad (5)$$

[16] Equations (2) –(5) were combined and rearranged to obtain the linear relationship (equation (6)) that was used to estimate values for K_n and Γ_n from desorption experiments:

$$\frac{A}{[P]} = \frac{1}{\Gamma_n} + \frac{K_n[P]}{\Gamma_n} \quad (6)$$

2.5. Phosphate Adsorption Experiments

[17] Adsorption experiments contained a set of 12 samples of decreasing particle additions (5–2.25 g/L) and simultaneously increasing P concentrations (2.5–17 $\mu\text{mol/L}$) from a stock solution made of equivalent proportions of NaH_2PO_4 and Na_2HPO_4 . The resulting pH of the suspensions was 8.5–8.6. These experiments provide the maximum sorption capacity Γ_{max} , and the binding constant K_{max} at high TP_n concentrations.

$$A\Gamma_{\text{max}} = [\equiv S] + [\equiv SP] \quad (7)$$

Table 2. Chemical and Physical Composition of Samples of Particulate Matter Used for P Sorption Experiments^a

Sample	Density, g/cm ³	BET, m ² /g	TP, mmol/kg	TN, mmol/kg	TOC, mmol/kg	TIC, mmol/kg	TC, mmol/kg	Fe, mmol/kg	Mn, mmol/kg	Ca, Mmol/kg
Reservoir sediments										
Grimselsee inflow	nd	nd	26	1.3	41	19	60	408	6.9	244
Grimselsee center	nd	nd	22	2.0	65	15	80	673	12	193
Grimselsee outlet	2.64	2.09	18	4.6	125	31	156	694	15	232
Räterichsbodensee	nd	2.86	19	6.7	178	73	251	647	14	268
Oberaarsee	nd	nd	21	25	120	570	690	694	16	238
Lake Brienz suspended particles										
BR03-1 50 m	nd	10.22	14	16	258	1417	1676	936	16	1502
BR03-2 50 m	nd	nd	15	14	256	1334	1591	897	15	1538
BR03-1 255 m	2.58	6.68	16	20	nd	nd	2761	726	13	2400
BR03-2 255 m	nd	nd	16	8.1	253	1801	2054	729	13	2378
Lake Brienz sediments										
BR04 20 m (0–0.5 cm)	nd	nd	18	39	334	1743	2077	897	15	1898
BR04 20 m (9–10 cm)	nd	nd	21	34	33	1746	2076	843	15	1982
BR04 212 m (0–0.5 cm)	nd	9.57	16	33	328	1361	1688	699	18	2498
BR04 212 m (9–10 cm)	nd	8.16	17	35	338	1596	1934	690	13	3165
River suspended particles										
Aare May 2005	nd	nd	nd	nd	nd	nd	nd	587	11	3000
Lütschine May 2005	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Lütschine July 2005	nd	nd	nd	nd	nd	nd	nd	640	11	2850

^aHere nd indicates not determined.

Table 3. Surface-Binding Constants and Actual Surface Concentrations of DRP ($\log K_{\text{DRP}}$, Γ_{DRP}), DNRP ($\log K_{\text{DNRP}}$, Γ_{DNRP}), and TP ($\log K_{\text{TP}}$, Γ_{TP}) as Determined by Desorption Experiments^a

Sample Quality and Origin	Desorption Experiments						Adsorption Experiments	
	$\log K_{\text{DRP}}$	Γ_{DRP} , mmol/kg	$\log K_{\text{DNRP}}$	Γ_{DNRP} , mmol/kg	$\log K_{\text{TDP}}$	Γ_{TDP} , mmol/kg	$\log K_{\text{max}}$	Γ_{max} , mmol/kg
Reservoir sediments								
Grimselsee inflow	7.21	0.16	6.89	0.02	7.11	0.21	6.16	0.23
Grimselsee center	6.83	0.24	7.51	0.08	6.64	0.28	6.28	0.42
Grimselsee outlet	6.57	0.33	6.97	0.09	6.54	0.49	6.24	0.81
Räterichsbodensee	6.2	0.22	6.44	0.12	6.16	0.38	6.69	0.6
Oberaarsee	6.37	0.3	6.98	0.29	6.25	0.51	6.27	0.61
Average \pm SD	6.49 \pm 0.27	0.27 \pm 0.05	6.98 \pm 0.44	0.15 \pm 0.09	6.40 \pm 0.23	0.41 \pm 0.11	6.37 \pm 0.22	0.61 \pm 0.16
Surface sediments and settling particles from Lake Brienz and suspended particles collected in its tributaries								
BR03-1 50 m	6.39	0.39	5.97	0.18	5.93	0.54	5.65	1.4
BR03-2 50 m	6.12	0.31	5.55	0.16	5.55	0.43	5.81	1.2
BR03-1 255 m	6.55	0.38	6.44	0.23	6.02	0.47	5.74	1.7
BR03-2 255 m	6.41	0.31	5.96	0.12	5.93	0.39	5.75	1.6
BR04 20 m (0–0.5 cm)	5.77	0.4	5.57	0.25	5.4	0.65	5.61	1.1
BR04 212 m (0–0.5 cm)	6.01	0.41	5.84	0.18	5.79	0.63	5.7	1.2
Aare May 2005	6.56	0.88	nd	nd	nd	nd	6.06	1.3
Lütschine May 2005	7.05	0.41	7.17	0.32	6.83	0.76	5.68	1.3
Lütschine July 2005	6.19	0.91	7.22	0.1	6.09	0.93	nd	nd
Averages \pm SD	6.34 \pm 0.37	0.49 \pm 0.23	6.22 \pm 0.67	0.19 \pm 0.07	5.82 \pm 0.25	0.60 \pm 0.18	5.75 \pm 0.14	1.35 \pm 0.21
Subsurface sediments of Lake Brienz								
BR04 20 m (9–10 cm)	5.83	1.03	6.83	0.25	5.55	1.04	5.72	1.2
BR04 212 m (9–10 cm)	5.63	0.98	6.14	0.22	5.5	1.16	5.61	1.2
Averages \pm SD	5.73 \pm 0.14	1.01 \pm 0.04	6.48 \pm 0.49	0.23 \pm 0.03	5.53 \pm 0.04	1.10 \pm 0.08	5.66 \pm 0.08	1.21 \pm 0.06

^a Adsorption experiments represent surface sorption constants for high surface coverage and maximum sorption capacities ($\log K_{\text{max}}$, Γ_{max}). Numbers in italics were omitted for the calculation of averages. Here nd indicates not determined. For sample identification, see Table 1.

Insertion in equation (2) and rearrangement lead to

$$\frac{A[P]}{[\equiv SP]} = \frac{1}{K_{\text{max}}\Gamma_{\text{max}}} + \frac{[P]}{\Gamma_{\text{max}}} \quad (8)$$

If this linear relation between measured DRP and the term on the left hand side of the equation is fitted to experimental data, Γ_{max} and K_{max} result from the slope and the intercept with the y axes, respectively.

[18] The kinetics of P desorption from particulate surfaces was investigated by incubation of a 4 g/L suspension of trap material (BR03-1 255 m) at 5°C in the dark for 100 h. Desorption of phosphate reached 95% of the long-term equilibrium after 20 h (Figure 2).

[19] The program ChemEQL [Müller, 2004] was applied to assess chemical equilibria and to model surface sorption.

3. Results

3.1. Physical and Chemical Particle Characterization

[20] Table 2 characterizes the particle composition. Most obvious is the much lower Ca, TN, TOC and TIC content and BET surface of the particles from the crystalline Grimselsee catchment area compared to those collected in Lake Brienz and its direct tributaries. In contrast, the extractable TP content of all particles was very similar.

3.2. Surface Sorption Parameters

[21] Desorption and adsorption experiments were clustered in three groups of surface-binding constants describing the interaction of particle surfaces with (1) dissolved reactive P (DRP), (2) dissolved nonreactive P (DNRP), and (3) total dissolved P (TDP). In addition, the adsorption experiments provided the maximum DRP sorption capacity of the investigated particles and the associated complexation constants at high surface coverage (Table 3). Interestingly,

binding constants ($\log K$) of both, sorption and desorption experiments, were very similar despite different amounts of sorbed inorganic P. As the binding constant expresses the inner sphere interaction between the surface ligand site and the sorbing inorganic phosphate anion, these similarities indicate that the chemical structure of the surface-binding sites were quite uniform within the three groups of investigated particles. The maximum sorption capacities that resulted from adsorption experiments were only about 50–100% higher than the actual surface concentrations found by the desorption experiments, indicating that even in these low dissolved P environments a substantial fraction of the available P-binding sites was already occupied. Surprisingly, adsorption constants for DRP and DNRP were similar, suggesting a similar type of chemical interaction of organically bound P or poly P with the particulate surface as for the inorganic phosphate ion.

[22] Sorption constants and surface-binding capacities from desorption experiments classify the investigated particle samples in three categories, namely, (1) settling particles and surface sediments of Lake Brienz and riverine particles, (2) lake sediments from 9 to 10 cm depth, and (3) sediments from the high alpine reservoirs (Table 3).

[23] Comparison of the contents of total P (Table 2) and total desorbable P (Table 3) indicates that only about 2%, 3 to 4% and 5 to 7% of the particles' total P was readily desorbable in the sediment of the reservoirs, the surface sediment and settling particles of Lake Brienz, and its subsurface sediment, respectively. 60 to 80% of the total desorbable P consisted of DRP, while 20 to 40% was DNRP (Table 3).

3.3. Surface Sorption and Particle Composition

[24] BET measurements suggest that particle surfaces of reservoir sediments were 3–5 times per mass unit smaller than Lake Brienz particles (Table 2). The same trend is also

expressed in the maximum adsorption capacities, Γ_{\max} (Table 3), which were all clearly larger for Lake Brienz particles (1.1–1.7 mmol/kg) than for the samples from the reservoirs (0.23–0.81 mmol/kg). The high density and low TOC content especially of the reservoir particles confirm their predominantly mineral nature. Quartz, mica, feldspars and calcite are the main mineral constituents of the suspended particles and sediments of Lake Brienz. All these minerals, except calcite, which dominates preferentially in Lütischine, adsorb P poorly [Stone and Mudroch, 1989].

[25] The narrow concentration range of desorbable P (Table 3) and of other constituents (Table 2) observed in settling particles obtained from different depths indicates that little mineralization occurred during settling across the hypolimnion. This is plausible as the average residence time of particles in the water column of Lake Brienz was estimated at only 14 d (Wüest et al., manuscript in preparation, 2006). Surprisingly, the TOC content of sediment samples (333 ± 4 mmol/kg) exceeded that of settling particles (256 ± 3 mmol/kg) by about 30%. The amount of desorbable P did not change significantly between the upper (0.49 mmol/kg) and lower (0.43 mmol/kg) sediment traps, which is in line with the small changes of dissolved phosphate concentrations measured in the water column (Wüest et al., manuscript in preparation, 2006). However, the older sediment collected in the zone between 9 and 10 cm depth contained almost twice as much desorbable P as the settling particles and the surface sediment. This suggests that early diagenesis resulted in P transformations that increased the amount of desorbable P. The lowest desorbable P content was found for the Grimsensee sediment. The contents were clearly graded, as the sample near the glacier meltwater inflow gave the lowest value and the particles sampled at the dam the highest. The content of both TOC and TIC were low and the density of the material very high, thus confirming the mineral nature of the particulate matter (Table 2).

3.4. Kinetics of Adsorption and Desorption Processes

[26] Kinetic experiments revealed a fast initial step of desorption (50% of the equilibrium is reached within less than 1 h) and a subsequent slower phase, with a τ_{95} (time when 95% of the final equilibrium concentration is attained) of 20 h (example shown in Figure 2). The temporal desorption isotherm fits a logarithmic function (inset in Figure 2). In the adsorption process, an initially fast phase followed by a slower phase was always observed [Fox and Malati, 1993; Millero et al., 2001]. Moreover, desorption processes were found to be much slower than adsorption processes [Goldberg and Sposito, 1985]. Colombo et al. [1994] suggested that slow adsorption and desorption processes (hours to days) occur preferentially at surface-binding sites with lower affinity toward phosphate. As the timescale of the adsorption/desorption processes determined in laboratory experiments (hours) is shorter than the timescale of floodwaters or rain events where settled river particles are resuspended and transported to the lake or settle through its water column (days), we assume sorption/desorption equilibria to be established in the rivers and lake, with minimal changes in chemical composition and no water column redox gradients observed in the lakes (Wüest et al., manuscript in preparation, 2006).

3.5. DRP Concentrations in Lake Brienz and Its Tributaries

[27] DRP concentrations varied between 0.3–2.3 $\mu\text{g P/L}$ in the water column of Lake Brienz. Vertical concentration profiles of DRP and TP are given by Wüest et al. (manuscript in preparation, 2006). Measurement campaigns in the Aare and Lütischine with high temporal resolution (one sample per hour) exhibited DRP concentrations of 1 to 5 $\mu\text{g/L}$ with exceptional peaks not higher than 9 $\mu\text{g/L}$ in both rivers. In 2003, the Aare transported 65 kt of particles in 1.13 km³ of water containing 3.95 t DRP. An additional 0.19 t P were reversibly sorbed to particles. The Lütischine transported 242 kt of particles in 0.60 km³ of water with 1.11 t DRP and 0.43 t P sorbed to particles. Average DRP and suspended matter concentrations were 3.4 $\mu\text{g P/L}$ and 57 mg/L (Aare) and 1.5 $\mu\text{g P/L}$ and 400 mg/L (Lütischine).

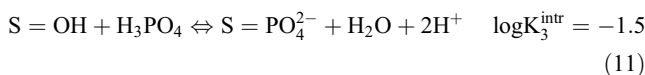
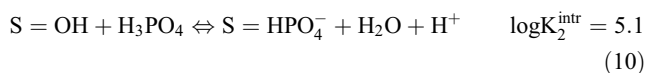
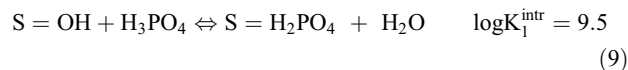
4. Discussion

4.1. Surface Binding Capacities of Various Particles for Phosphate

[28] Maximum P adsorption capacities Γ_{\max} published in the literature vary over multiple orders of magnitude. They are higher for pure metal oxides and smaller for mixed minerals or organic adsorbents such as soils [Goldberg and Sposito, 1985]. The sorption tendency of HPO_4^{2-} at pH > 7 is rather low. Gomez et al. [1999] observed a transition from Fe-sorbed phosphate to organically bound phosphate when pH increased from 7 to 8. Experiments of Ioannou and Dimirkou [1997] and Dimirkou et al. [2002] show that the dependence of P sorption on the suspension pH is weak for hematite and kaolinite. The same results from estimations of Sigg and Stumm [1981] for goethite. Sakadevan and Bavor [1998] reported maximum adsorption capacities (Γ_{\max}) of 1430 mmol/kg for blast furnace slag, 140–170 mmol/kg for soil samples, and 69 mmol/kg for zeolite. Fontes and Weed [1996] determined a Γ_{\max} range of 70–160 mmol/kg for soil clays with particle sizes <2 μm and a (BET) area of 45–110 m²/g. For aragonite a sorption capacity of 20 mmol/kg was calculated by Millero et al. [2001]. Our values of 0.2–1.7 mmol/kg (Table 3) extend this range to particulate matter from natural surface waters with significantly smaller surface areas (2.1–10.2 m²/g) in a pH range important for hardwater lakes and rivers (pH 7.5–9).

4.2. Comparison of Surface Sorption Constants

[29] Sigg and Stumm [1981] suggest surface sorption constants for the sorption of phosphate to goethite of:



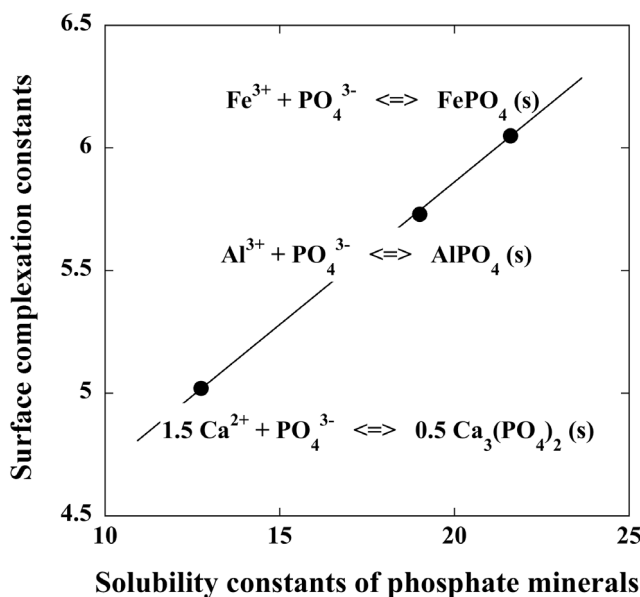


Figure 3. Correlation between complexation constants of phosphate on goethite, kaolinite, and calcite, and the solubility constants of FePO_4 (amorphous [Krauskopf, 1979]), AlPO_4 (berlinite [Lindsay, 1979]), and $\text{Ca}_3(\text{PO}_4)_2$ (alpha [Lindsay, 1979]).

[30] The constants are intrinsic (intr), indicating their validity for zero surface charge. Previous researchers have applied these model assumptions to experiments with different particulate surfaces, which allow direct comparison of the binding constants. Dzombak and Morel [1990] critically selected the $\log K^{\text{intr}}$ values of 9.59, 3.69, and -3.98 for the surface sorption to hydrous ferric oxide. Ioannou and Dimirkou [1997] introduced a model for the sorption of phosphate to kaolinite with $\log K_1^{\text{intr}} = 9.96$, $\log K_2^{\text{intr}} = 4.78$ and $\log K_3^{\text{intr}} = -0.87$. These parameters suggest a weak dependence of P sorption on the pH of the suspension.

[31] In natural waters of pH 7.2 and higher, HPO_4^{2-} is the dominating DRP species. In order to compare the intrinsic constant given in equation (10) with the sorption constants observed in this study ($\log K_{\text{DRP}} = 5.6$ to 7.1), 'conditional' constants for natural pH values had to be derived. Including the pH in equation (10) and using the appropriate species instead of H_3PO_4 , we obtained constants that are comparable to the sorption constants observed in our experiments. At a pH of 8.4 the conditional constants $\log K^{\text{cond}}$ for phosphate adsorption to goethite and kaolinite are 6.05 and 5.73, respectively. Millero *et al.* [2001] determined a $\log K^{\text{cond}}$ of 5.02 for the adsorption of phosphate to aragonite at 15°C and zero salinity. These values follow the general trend of the affinity of phosphate toward the complexing cation or the series of solubility constants. A correlation between the adsorption of cations to a specific particulate surface, and the logarithm of their first hydrolysis constant is well known [Schindler and Stumm, 1987]. The correlation between the logarithms of surface-binding constants and minerals of phosphate with the corresponding cation (Figure 3) is a consequence of the inner sphere character of the adsorbed phosphate. The agreement of our modeling results, derived from field data, with theoretical descriptions

of phosphate sorption generates a management tool for water quality in phosphate-limited oligotrophic systems.

[32] The somewhat higher $\log K$ values observed in our experiments may originate from the low fraction of potentially possible surface coverage with phosphate, thus not occupying a representative area of the whole mineral but instead preferentially those surface sites with the highest binding energies (where kinks and steps in the lattice may be more reactive than face sites [see Stumm, 1992]). Also, other Fe- PO_4 minerals with higher solubility products than amorphous FePO_4 (e.g., strengite, $\log K_{s0} = 26.4$ [Krauskopf, 1979]) continue the correlation with our surface-binding constants of Figure 3 and may indicate the presence of Fe minerals that allow more preferable steric and/or electrostatic conditions for the adsorption of phosphate. However, we did not observe correlations between the surface sorption capacities and the Fe content in our set of particle samples. This is likely because the sorption of phosphate is related to the concentrations of iron oxyhydroxides and only a small fraction of the particulate iron is accessible for surface complexation.

4.3. Sorption of Phosphate to Aquatic Particles in Natural Waters

[33] Because of the tendency of dissolved P (DP) to sorb to solids, the DP present in the water column is not necessarily identical with the DP available to the biota, as, depending on the concentration and quality of suspended particles, a significant fraction of potentially available P may be sorbed to the particle surfaces. The adsorption isotherms presented in Figure 4 show for selected TDP concentrations ($1\text{--}300\ \mu\text{g P/L}$) how the fraction of dissolved P decreases

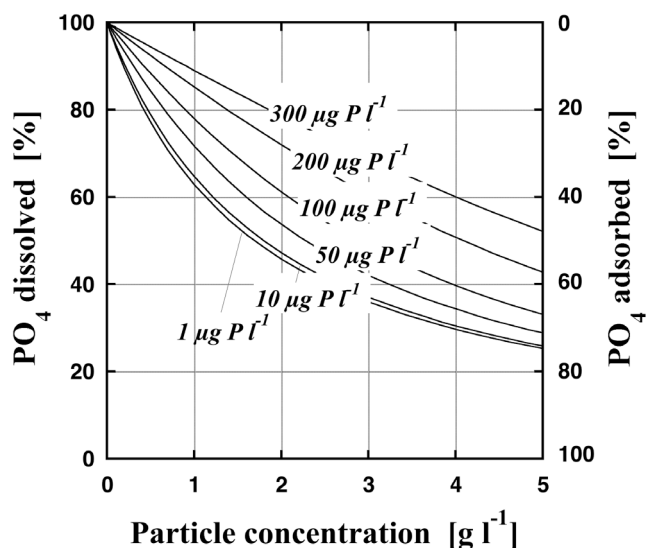


Figure 4. Model calculation of the distribution of phosphate between particulate surfaces and solution. Dissolved fractions of phosphate in percent (available to direct analysis) were calculated for total phosphate concentrations of 1, 10, 50, 100, 200, and $300\ \mu\text{g P/L}$ at pH 8.4, 1 mmol/L alkalinity, and 0.5 mmol/L Ca^{2+} for increasing particle concentrations. Sorption parameters from river particles ($\log K_{\text{TDP}} = 5.82$, $\Gamma_{\text{max}} = 1.35\ \text{mmol/kg}$) were used as presented in Table 3. Electrostatic effects on the sorption process were not considered.

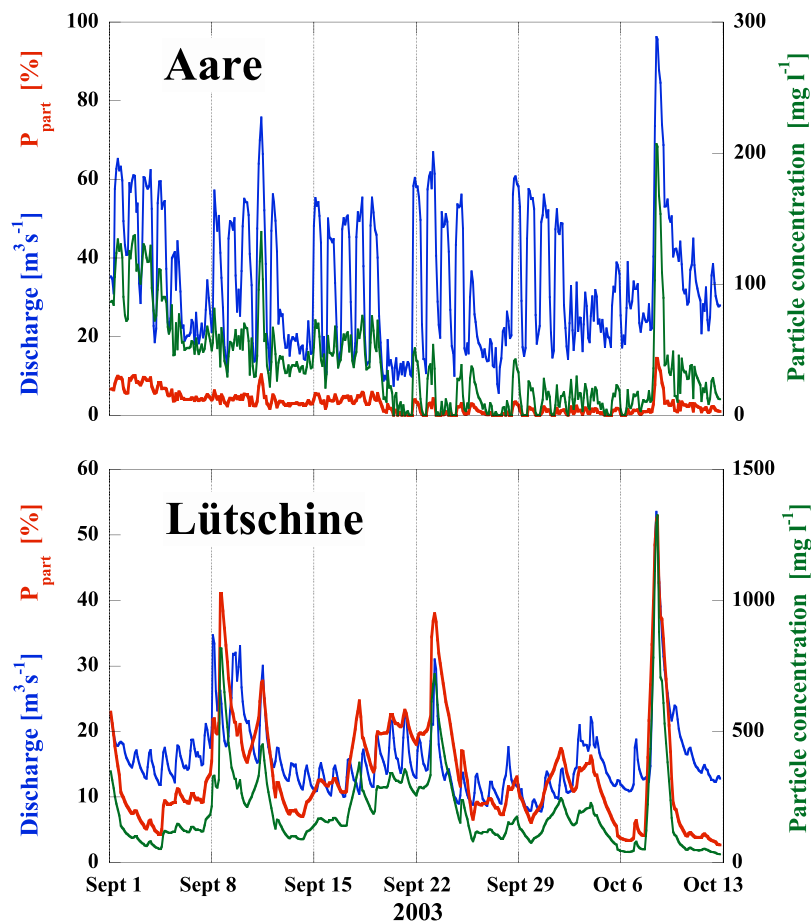


Figure 5. Transported bioavailable P (calculated) in Aare and Lüttschine, which is sorbed to particulate surfaces in percent of the total bioavailable P (red line). Model assumptions were $\log K_{\text{DRP}} = 5.82$, $\Gamma_{\text{max}} = 1.34 \text{ mmol/kg}$, $[\text{Ca}^{2+}] = 0.5 \text{ mmol/L}$, $[\text{HCO}_3^-] = 1 \text{ mmol/L}$ and $\text{pH} = 8.4$. The blue line depicts the monitored hydrological discharge Q [m^3/s], and the green line shows the particle concentration (right scale), as calculated from Q using the rating curve relation between Q and particle concentration [Finger *et al.*, 2006]. (top) River Aare. (bottom) River Lüttschine.

when the particle concentration increases. Figure 4 depicts the fractions of sorbed and dissolved P as a percentage of the total P potentially available to biota. It is applicable to natural surface waters containing particles low in organic carbon and Fe-(oxy)hydroxides.

4.4. Consequences for the P Budget of Downstream Waters

[34] In 2003, the two major contributors Aare and Lüttschine carried an annual load of 307 kt of mineral particulate matter to Lake Brienz. In such situations, the conventional DRP or TDP analyses may severely underestimate the lake's load with bioavailable P, as in the river water a significant fraction may be overlooked by neglecting reversible surface sorption. However, while the rivers enter the lake and distribute their particle load, due to the sudden particle dilution part of the reversibly sorbed P will desorb from the particles, as can be derived from Figure 4.

[35] For illustration, Figure 5 presents water discharge and particle concentration observed in the Aare and Lüttschine during a period of six weeks in 2003. For an estimation of P speciation, i.e., the distribution of potentially bioavailable P between solution and particles, we applied the constants from Table 3 ($\log K_{\text{TDP}} = 5.82$, $\Gamma_{\text{max}} = 1.34 \text{ mmol/kg}$)

and include 0.5 mM Ca^{2+} , 1 mM HCO_3^- . In the Aare, because of hydropower peaking, the regular daily fluctuations in water discharge often reached or even exceeded $40 \text{ m}^3/\text{s}$, whereas in the Lüttschine, because of snowmelt periodicity, they only amounted to about $5 \text{ m}^3/\text{s}$. Whereas within the drainage area of the Aare on average 232 kt of particulate matter is trapped annually in the various reservoirs while no such reservoirs exist in the catchment of the Lüttschine, the average particle concentration of the Lüttschine exceeded that of the Aare by a factor of 1.9 (note the different scales for particle concentration and water discharge in Figures 5, top, and 5, bottom).

[36] In the Aare, where particle concentrations were $0\text{--}50 \text{ mg/L}$ and DRP concentrations were around $2 \text{ }\mu\text{g/L}$, less than 10% of the potentially bioavailable P was sorbed to particle surfaces except during a short rain event on October 9 when the particle concentration increased to over 200 mg/L and the sorbed fraction of bioavailable P exceeded 10% during a limited period of time (Figure 5, top). In the Lüttschine the particle concentration always exceeding 50 mg/L , was 400 mg/L on average [Finger *et al.*, 2006] and regularly exceeded 1500 mg/L during flood events. As a consequence, 50% or more of the potentially bioavailable P was sorbed to particles during peak flow.

[37] For 2003 we calculated averages of 7.4% and 24.8% of the total bioavailable P that were transported reversibly sorbed to particles in the Aare and Lüttschine. As the percentage of bioavailable P that is transported associated with particles increases with decreasing DRP and with increasing particle concentration, the conventionally determined DRP load may substantially underestimate the effective load with bioavailable P in unpolluted but turbid rivers. As shown in Table 3, each kg of mineral particles collected from unpolluted reservoirs contained 0.41 mmol of desorbable P. Thus, taking into account that the reservoir annually trapped 232 kt of particulate matter [Finger *et al.*, 2006] and that an estimated 2/3 of it has a grain size comparable to the material we investigated, they also retained 2.0 t/yr of potentially bioavailable P that otherwise would have been loaded to Lake Brienz.

5. Conclusions

[38] In summary we conclude the following.

[39] 1. In unpolluted rivers with a high content of suspended mineral particles (>50 mg/L) P loads solely based on DRP measurements may substantially underestimate their true loads with bioavailable P to downgradient lentic environments.

[40] 2. For the P-limited, oligotrophic lakes considered in this study, modeling P sorption onto a single type of surface site adequately described trends in the field data. The maximum sorption capacity and conditional sorption constants of mineral particles for phosphate are in the order of $\Gamma = 1$ mmol/kg and $\log K = 6$, respectively, and are nearly independent of the particles' organic carbon (0.1–0.34 mol/kg) and iron (0.6–0.9 mol/kg) content.

[41] 3. The parameters given may generally be applied for mineral weathering suspended matter. However, sorption experiments should be extended to particulate matter from a larger variety of aquatic systems in order to gain a more systematic view of the sorption behavior of phosphate toward natural aquatic particles.

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