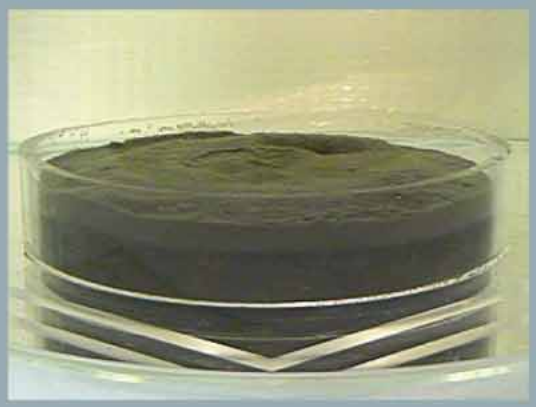
Prepared in cooperation with the Bureau of Reclamation

Effect of Water-Column pH on Sediment-Phosphorus Release Rates in Upper Klamath Lake, Oregon



Water-Resources Investigations Report 03-4271

U.S. Department of the Interior
U.S. Geological Survey

Cover photographs, clockwise from lower left:

Laboratory apparatus used to determine phosphorus release rates from Upper Klamath Lake sediments

Sediment sample from Upper Klamath Lake

Closeup of acrylic column used in phosphorus-release-rate experiments

U.S. Department of the Interior
U.S. Geological Survey

Effect of Water-Column pH on Sediment-Phosphorus Release Rates in Upper Klamath Lake, Oregon, 2001

By LAWRENCE H. FISHER and TAMARA M. WOOD

Water-Resources Investigations Report 03–4271

Prepared in cooperation with
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U.S. DEPARTMENT OF THE INTERIOR
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CONVERSION FACTORS

[SI = International System of units, a modernized metric system of measurement]

Factors for converting SI metric units to inch/pound units

Multiply	By	To obtain
	Length	
micrometer (μm)	0.00003937	inch (in)
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937008	inch
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square centimeters (cm^2)	0.1550003	square inch (in^2)
square meters (m^2)	10.76391	square foot (ft^2)
square kilometers (km^2)	0.386	square miles (mi^2)
	Mass	
microgram (μg)	0.00000003527	ounce (oz avoirdupois)
milligram (mg)	0.00003527	ounce
gram (g)	0.03527	ounce
kilogram (kg)	2.205	pound (lb)
	Temperature	
degrees Celsius (°C)	(1)	degree Fahrenheit (°F)
	Concentration, By Volume	
micrograms per liter (μg/L)	1	parts per billion (ppb)
milligrams per liter (mg/L)	1	parts per million (ppm)
	Concentration, By Mass	
milligrams per kilogram (mg/kg)	1	parts per million (ppm)
	Concentration, By Area	
milligrams per square meter (mg/m^2)	0.000003277	ounce per square foot (oz/ft^2)
	Specific Conductance	
microsiemens per centimeter (μS/cm)	0.00254	micromho per inch (μmho/in)
	Rate	
kilometer per hour (km/hr)	0.6213712	mile per hour (mi/hr statute)
micrograms per liter per day (μg/L/day)	1	parts per billion per day (ppb/day)
milligrams per square meter per day (mg/m2/day)	0.000003277	ounce per square foot per day (oz/ft^2/day)

[1]Temperature °F = 1.8 (Temperature °C) + 32

MISCELLANEOUS ABBREVIATIONS

A. flos-aquae	*Aphanizomenon flos-aquae*
BOR	Bureau of Reclamation
BQA	branch of quality assurance
CO_2	carbon dioxide
CRA	CO_2-reduced air
DAHP	dissolved acid-hydrolyzable phosphorus
DMA	designated management agency
DOP	dissolved organic phosphorus
DUP	dissolved unreactive phosphorus
HP	horsepower
K	cell constant
KH_2PO_4	potassium dihydrogen phosphate
MDL	method detection limit
N	normality
NaOH	sodium hydroxide
NaOH-nrP	nonreactive fraction of NaOH extractable phosphorus
NaOH-rP	reactive fraction of NaOH extractable phosphorus
P	phosphorus
PPM	parts per million
QA/QC	quality assurance/quality control
SRP	soluble reactive phosphorus
SRS	standard reference sample
TDP	total dissolved phosphorus
TP	total phosphorus
TSP	total suspended phosphorus
USGS	U.S. Geological Survey

Effect of Water-Column pH on Sediment-Phosphorus Release Rates in Upper Klamath Lake, Oregon, 2001

By Lawrence H. Fisher *and* Tamara M. Wood

Abstract

Sediment-phosphorus release rates as a function of pH were determined in laboratory experiments for sediment and water samples collected from Shoalwater Bay in Upper Klamath Lake, Oregon, in 2001. Aerial release rates for a stable sediment/water interface that is representative of the sediment surface area to water column volume ratio (1:3) observed in the lake and volumetric release rates for resuspended sediment events were determined at three different pH values (8.1, 9.2, 10.2). Ambient water column pH (8.1) was maintained by sparging study columns with atmospheric air. Elevation of the water column pH to 9.2 was achieved through the removal of dissolved carbon dioxide by sparging with carbon dioxide-reduced air, partially simulating water chemistry changes that occur during algal photosynthesis. Further elevation of the pH to 10.2 was achieved by the addition of sodium hydroxide, which doubled average alkalinities in the study columns from about 1 to 2 milliequivalents per liter. Upper Klamath Lake sediments collected from the lake bottom and then placed in contact with lake water, either at a stable sediment/water interface or by resuspension, exhibited an initial capacity to take up soluble reactive phosphorus (SRP) from the water column rather than release phosphorus to the water column. At a higher pH this initial uptake of phosphorus was slowed, but not stopped. This initial phase was followed by a reversal in which the sediments began to release SRP back into the water column. The release rate of phosphorus 30 to 40 days after suspension of sediments in the columns was 0.5 μg/L/day (micrograms per liter per day) at pH 8, and 0.9 μg/L/day at pH 10, indicating that the higher pH increased the rate of phosphorus release by a factor of about two. The highest determined rate of release was approximately 10% (percent) of the rate required to explain the annual internal loading to Upper Klamath Lake from the sediments as calculated from a lake-wide mass balance and observed in total phosphorus data collected at individual locations.

INTRODUCTION

Upper Klamath Lake (fig. 1) is a large, shallow lake in south central Oregon with a surface area of about 208 km^2 (square kilometers) and a mean depth of about 3 m (meters) when the lake is at full pool. The lake receives drainage from 9,800 km^2 of phosphorus-rich volcanic soils. A paleolimnological study has shown that nutrient and sediment loading to the lake has increased over the last century and that recent bottom sediments have become enriched with phosphorus (Eilers et al., 2001). Activities in the basin, including logging, grazing, and agriculture, can mobilize phosphorus-rich soils. In addition, over 120 km^2 of wetlands in the basin have been drained, allowing organic soils to decompose and act as a large external source of phosphorus to Upper Klamath Lake (Snyder and Morace, 1997).

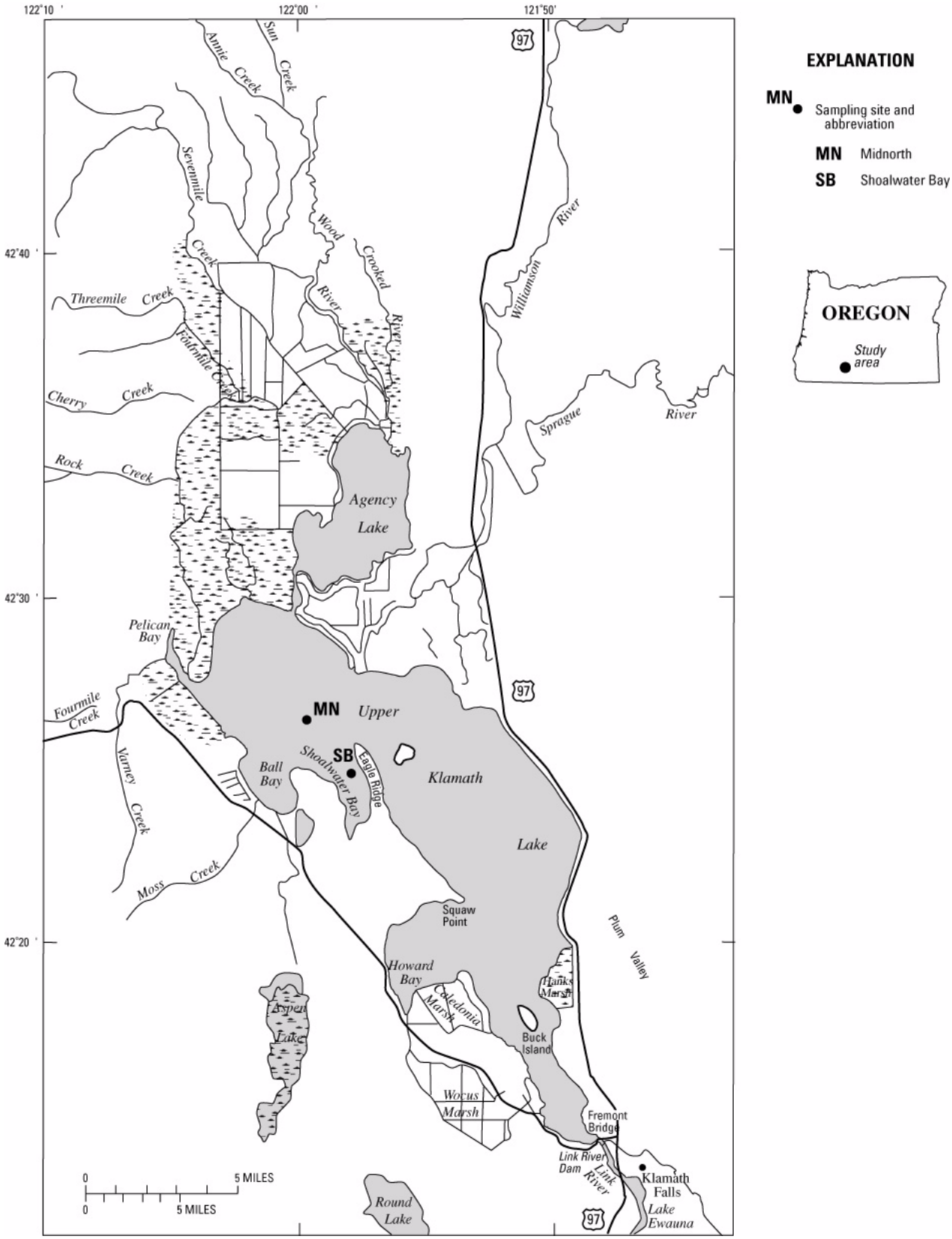

Figure 1. Upper Klamath Lake with sampling site identification and location.

As a result of these changes, Upper Klamath Lake, which had been a highly productive, eutrophic lake for at least the last 1,000 years (Eilers et al., 2001), has become hypereutrophic, and now experiences annual occurrences of near-monoculture blooms of the blue-green alga *Aphanizomenon flos-aquae (A. flos-aquae)*. This algal bloom corresponds to a large seasonal increase in total phosphorus (TP) in the lake each spring that cannot be accounted for by external loading estimates (Kann and Walker, 1999). Figure 2 shows spring increases in TP, chlorophyll *a*, and pH, as well as changes in soluble reactive phosphorus (SRP), that were measured in grab samples collected by the Klamath Tribes at Shoalwater Bay in 2001 (data obtained from Lawrence Dunsmoor of Klamath Tribes Natural Resources, Chiloquin, Oregon, 2001). Internal loading of phosphorus from lake sediment, occurring on seasonal cycles, can drive the increase in TP and feed the algal blooms. During this TP increase SRP is released but concentrations remain low due to algal uptake. SRP concentrations begin to climb as the algal biomass decreases, seen in figure 2 as a decrease in chlorophyll *a* concentration.

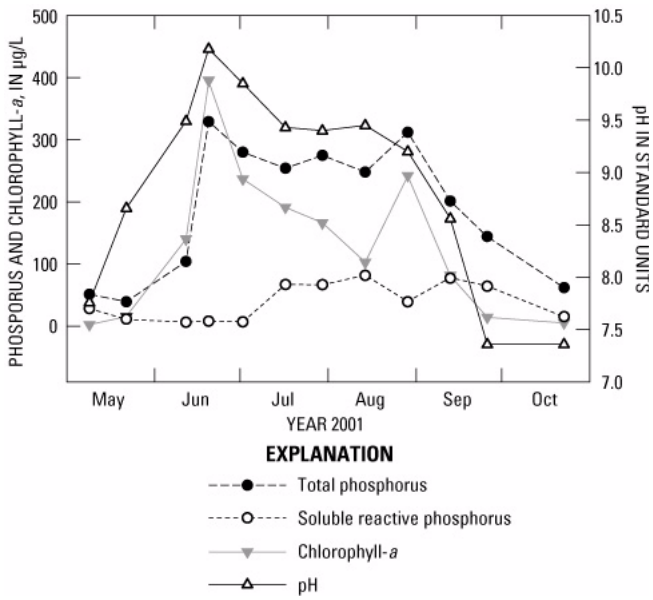

Figure 2. Total phosphorus, soluble reactive phosphorus, chlorophyll *a*, and pH as measured in biweekly samples collected at Shoalwater Bay, Upper Klamath Lake, Oregon, in 2001 by the Klamath Tribes.

Because the lake is relatively shallow and rarely becomes anaerobic near the bottom sediments, this seasonal internal loading process appears to occur under primarily aerobic conditions. High pH values observed in Upper Klamath Lake have been associated with algal photosynthesis during the rapid early growth phase of the *A. flos-aquae* blooms; median June pH values are often greater than 9.5 (Wood, et al. 1996). Under aerobic conditions, internal phosphorus loading in the lake has been described primarily as a geochemical phenomenon in which phosphorus is mobilized from bottom sediments into a water column under high pH conditions. Kann (1998) postulated that under high pH, hydroxide ions compete with phosphate ions for sorption sites on iron hydroxides, thereby releasing phosphorus into the water column. Additional support for this release mechanism in Upper Klamath Lake is provided by a correlation between pH and whole-lake mass balance calculations of internal phosphorus loading (Walker, 2001; Welch and Burke, 2001). Whole-lake mass balance calculations for the years 1991–99 have shown that the rate of internal loading required to account for measured increases in TP concentration peaks between 15 and 25 mg/m^2/day (milligrams per square meter per day) (Walker, 2001).

Several laboratory studies have demonstrated the efficacy of this high pH mechanism in releasing phosphate ions from bottom sediments. However, the interpretation of some studies is confounded by the fact that pH was increased with the addition of strong base, which increased the ionic strength and alkalinity of the water markedly (Andersen, 1975; Jacoby et al., 1982; Drake and Heaney, 1987; Appan and Ting, 1996). In natural lake systems, the photosynthetic removal of dissolved CO_2 raises the pH but does not increase the alkalinity. In many hard water lakes, alkalinity decreases with the precipitation of calcite during algal photosynthesis. Boers (1991) concluded that enhanced phosphate release when NaOH was used to raise pH was an artifact of increasing the alkalinity in the water column from 6.1 to 19.4 meq/L (milliequivalents per liter) with the addition of enough NaOH to reach pH 9.5.

In addition to pH considerations, it has been reported that resuspension of lake sediment can increase the internal phosphorus loading in lakes. Resuspension of lake sediments in the wind-exposed Lake Arreso, Denmark, resulted in phosphorus loading 20–30 times greater than loading from undisturbed lake sediment (Sondergaard et al., 1992; Reddy, et al., 1996). Laenen and LeTourneau (1996) estimated that the suspended sediment concentration in Upper Klamath Lake could be as high as 200 mg/L (milligrams per liter) as a result of a 16 km/hr (kilometers per hour) wind out of the northwest lasting 2 hours. Estimates of the TP concentration associated with resuspended sediments during this wind event

ranged from 360 to 2,000 μg/L (micrograms per liter). Thus, a wind event strong enough to resuspend sediments has the potential to enhance mechanisms for mobilizing phosphorus in the bottom sediments by virtue of both the increased sediment surface for phosphorus desorption processes and the large mass of phosphorus that bottom sediments can carry into the water column.

This report presents data on phosphorus uptake and release from stable and suspended Upper Klamath Lake sediments under varying pH regimes. The study was funded by the Bureau of Reclamation in Klamath Falls, Oregon. Sample and data collection began in April of 2001 and continued through January of 2002.

Objectives

The intent of the investigation was to determine whether the phosphorus release from Upper Klamath Lake sediments, at the photosynthetically elevated pH values measured in the lake, could account for the rapid increase in total phosphorus concentration observed each spring. The study was designed to investigate both the areal phosphorus release rates from sediments at a stable sediment-water interface and the desorption of phosphorus from suspended sediments that would occur during a wind-induced sediment resuspension event. The former investigation is referred to as the Stable Interface Study; the latter is referred to as the Resuspended Sediment Study.

An additional objective incorporated into the experimental design was to elevate pH in a manner that would simulate the water chemistry changes that occur during algal photosynthesis. This was then followed by the addition of a small amount of strong base to elevate the pH in the column further for comparison.

Additional experimental design objectives were to incorporate a ratio of sediment surface area to water column volume that is characteristic of the lake into the Stable Interface Study, and to use a sediment concentration representative of an extreme, but not rare, wind event in the Resuspended Sediment Study. Because of the nature of column studies in the laboratory, many study designs incorporate an unrealistically large sediment surface area to water column volume ratio when investigating processes at the sediment/water interface and an unrealistically high sediment concentration when investigating resuspension events.

Acknowledgments

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METHODS AND MATERIALS

Sample Collection

Sediment samples and water samples were collected twice in the spring of 2001. The first samples were collected on May 25, 2001, for preliminary experiments at the established monitoring site, Midnorth (fig. 1). Preliminary experiments were conducted to establish methods and protocols for the study, and are not presented here. A second set of samples were collected June 21, 2001, from the established monitoring site in Shoalwater Bay in the northeastern part of Upper Klamath Lake (fig. 1). Review of historical Shoalwater Bay data indicates that samples collected in June would typically represent conditions prior to the TP peak. However, the samples used in this study were collected after the 2001 spring increase in TP, chlorophyll *a*, and pH (fig. 2).

All sample water was collected from the surface of the lake and filtered in the field through a 353 μm (micrometers) mesh sieve. Bottom sediment samples were collected at the same site at a lake depth of 3 m (meters) with an Eckman dredge. The top layer of sediment from three dredge samples was collected, avoiding the deeper, anoxic sediments, and then combined and homogenized into a single sample to be used in the laboratory study. All samples were iced

during transport to the laboratory where they were stored at 4ºC (degrees Celsius) until used in the experiments.

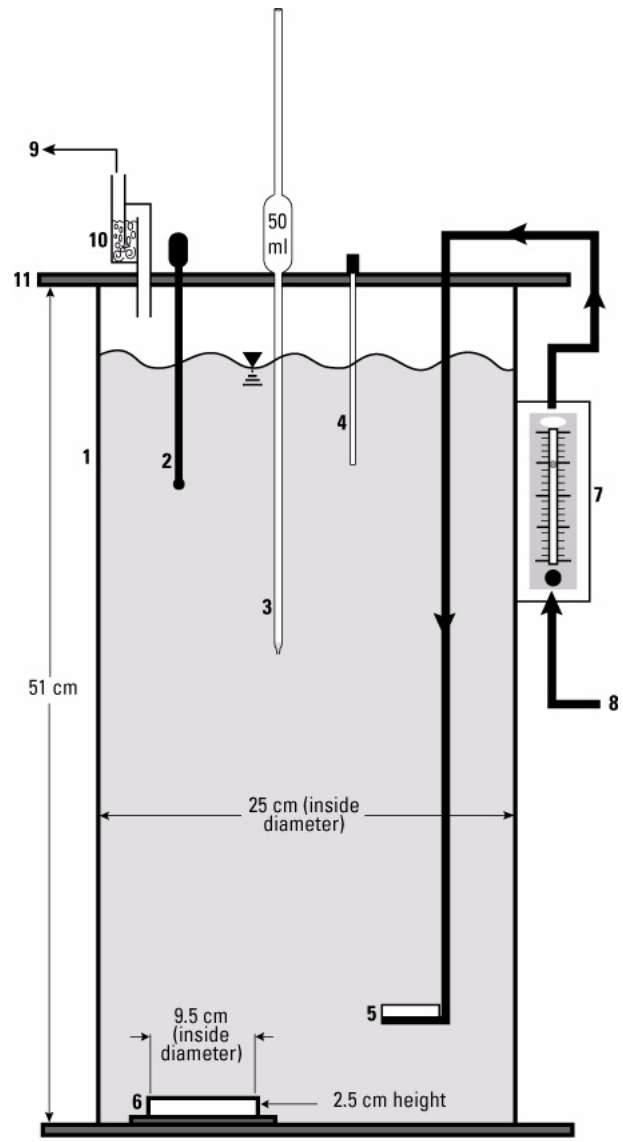
Experimental Design

Both the Stable Interface Study and the Resuspended Sediment Study were conducted in the USGS Oregon District Laboratory with four identical acrylic columns 51 cm (centimeters) tall with a 25 cm inside diameter (fig. 2). When filled to approximately 48 cm, the column contained a sample volume of 23 L. Each column was constructed with a sealed bottom and a removable airtight lid. The lid was constructed with ports that allowed for a deep vessel pH probe, a temperature probe, a sampling tube (or pipette), some tubing for the sparging gas, and a one-way bubble-type exhaust valve. All ports were kept sealed between sampling, which allowed all exhaust gases to exit through the one-way exhaust valve. Sparge gas flow rates for each column were set using a Dwyer Rotameter ball-type flow gauge with a flow-metering valve. During the experiments, the columns were kept dark with aluminum foil to minimize algal growth.

Stable Interface Study

For the Stable Interface Study, acrylic cups 2.5 cm tall with an inside diameter of 9.5 cm were constructed to hold a sediment sample at the bottom of each study column (fig. 3). The dimensions of the cup were such that sediment within the cup had a surface area of 71 cm^2 (square centimeters), resulting in a sediment surface area to volume ratio in the column of 3.1 cm^2/L. This is the same ratio that would be found in a water column 3.1 m in depth with a 1 m^2 (square meter) sediment surface area. Sample withdrawals over the course of the experiment increased the sediment surface area to water volume ratio by about 10% (percent).

The experiment was conducted in triplicate in columns denoted A, B, and C; the fourth column (denoted D) was the study control. Prior to filling the columns with lake water, three sediment cups were filled with approximately 182 g (grams) of wet sediment and one cup was placed in the bottom of each of A, B, and C; an empty cup was placed in column D (control). A subsample of the sediment was analyzed for moisture content, which was determined gravi-



EXPLANATION

1	Column
2	pH probe
3	Sample collection pipette
4	Temperature probe
5	Glass sparge frit
6	Sediment cup
7	Flow meter with valve
8	Sparge gas input (silicon tubing)
9	To atmosphere
10	Air-lock
11	Removable lid

Figure 3. A column used in the Stable Interface Study designed to have the same sediment surface area to water column volume ratio that is observed in the lake. The same column design was used for the Resuspended Sediment Study, except that, the sediment cup was removed and a large stir magnet was placed in the bottom, which was spun with a heavy duty stir plate situated under the column. The schematic shown is not to scale.

metrically to be 89.4%. The lake water was filtered through a 0.45 µm filter and slowly added to each column, taking care to minimize disturbance of the sediment. As the filtered lake water crested the top of the sediment cups, a small amount of sediment was entrained into the water column. After the column was filled with 23 L of filtered lake water, the sediment was allowed to settle to the bottom of the column. The displaced sediment was removed with a glass tube connected to a peristaltic pump with silicon tubing. This left no visible "loose" sediment around the sediment cup.

The Stable Interface Study was conducted in three phases. During phase I, the columns were maintained at ambient pH for 2 weeks by sparging with atmospheric air (approximately 350 ppm [parts per million] carbon dioxide [CO_2]) supplied by a Dayton Speedaire 1 HP diaphragm pump. During phase II the pH was first elevated to approximately 9.1 by sparging with "synthetic" compressed air that was manufactured by mixing relatively pure nitrogen with oxygen in appropriate concentrations to obtain 20.9% oxygen. The columns were maintained at pH 9.1 for 2 weeks. After 2 weeks, the synthetic compressed air gas stream, which had a CO_2 concentration of 1–2 ppm, was passed though a "scrubber train" that consisted of two flasks of 1N NaOH, a column of soda lime CO_2 absorbent, and a column of Ascarite II CO_2 absorbent. The "scrubbing" delivered a CO_2-reduced air (CRA) for sparging that elevated the pH by an additional 0.1–0.2 units. Delivery of the CRA to the columns continued for another 2 weeks, which completed phase II. A pH of 9.2–9.3 was the maximum achievable in the columns with CO_2 removal alone. At the beginning of phase III approximately 25 mL of 1N NaOH was added to each column to raise the pH to 10.2. Prior to titration, the alkalinity averaged 1.0 meq/L. The addition of strong base increased the alkalinity by 1.1 meq/L and the specific conductance by 168 µS/cm (microsiemens per centimeter). Phase III lasted for 2 weeks, during which the columns continued to be sparged with CRA.

Resuspended Sediment Study

The Resuspended Sediment Study was designed to investigate the desorption of phosphorus from suspended sediment during simulated wind-induced resuspension events. During such an event, any limitation on the rate of phosphorus release from sediments that would be in effect at a stable sediment-water interface would be removed. The columns previously described were used without the sediment cups. Each column was placed on a Corning model 611 heavy-duty stir plate and resuspension of the sediment was achieved by means of a magnetic stir bar inside the column. In order to avoid overheating the motor, each stir plate's power cord was connected to a digital time controller programmed to turn the stir plates on for 3 hours followed by 1 hour of shutdown. This was repeated throughout the duration of the study. During the 1-hour periods of no stirring, the only mechanism for mixing was the scrubber-gas stream. Under these conditions, some of the sediment settled, but the finer sediment particles remained suspended, leaving a turbid water column. While the stir plate was operating, the sediment was mixed well throughout the column. Each column (except controls) received approximately 33 g of wet sediment with a moisture content of 89.4%, resulting in a suspended sediment concentration of approximately 150 mg/L.

During the Resuspended Sediment Study, each treatment column was used to investigate desorption from the sediments under differing conditions (summarized in table 1). Column A was used to investigate desorption at photosynthetically elevated pH and received filtered lake water, sediment addition, and pH adjustments. Initial pH adjustments were made by sparging with CRA for approximately 7 days until a pH of 9.1 was reached. This was followed by the addition of 33 g of wet sediment, after which the column was sparged with CRA for another 19 days (phase I). The pH of the column was then adjusted to pH >10 with 26.8 mL of 1N NaOH, and the column was sparged with CRA for an additional 21 days (phase II). The immediate increase in alkalinity after titration was 1.0 meq/L; specific conductance increased by 123 µS/cm.

Table 1. Column pH adjustments, sediment additions, and other treatments for the Resuspended Sediment Study

Column	pH adjustment[a]	Sediment addition[b]	Other
A	yes	yes	-
B	yes	yes	preconditioning phase added
C	no	yes	-
D	yes	yes	titrated to pH 10.2 prior to sediment addition
E	yes	no	-

[a] Column pH was incrementally adjusted to 9.1 and >10 following phosphorus release assessments at ambient pH.

[b] Addition of 33 grams (wet weight) of Klamath Lake sediment.

Column B was used to determine if an SRP concentration gradient was inhibiting sediment-phosphorus release. The column underwent a preconditioning phase that removed SRP from the water column prior to raising the pH while undergoing the usual resuspension events. Column B was filled with 23.2 L of unfiltered Upper Klamath Lake water, then received 33 g of wet sediment while sparging with ambient air for about 6 days and maintaining a pH of 7.9 ± 0.1. The column was then filtered through a 0.45 µm filter to remove the sediment, followed by another addition of 33 g of wet sediment. The column was again sparged with ambient air for 8 days maintaining a pH of 7.9 ± 0.0 before filtering again as before. During this preconditioning, SRP was monitored daily (with the exception of some weekends). At the end of this preconditioning the SRP concentration in the column was less than 2 µg/L. The column was then sparged with CRA for 7 days until a pH of 9.1 was reached. At that point 33 g of wet sediment was added, and the column continued to be stirred and sparged with CRA for another 15 days (phase I). The pH in Column C was then titrated to pH>10 with 20.0 mL of 1N NaOH and the column was sparged with CRA for another 17 days (phase II). The immediate increase in alkalinity after titration was 0.9 meq/L; specific conductance increased by 144 µS/cm. An additional 3.5 mL 1N NaOH was added 9 days into phase II to keep the pH greater than 10.

Column C was used to investigate the effect of photosynthetically elevated pH on the desorption and received filtered lake water and sediment addition, but had no pH adjustments. The column was first sparged with ambient air for approximately 7 days. Then 33 g of wet sediment were added to the column, after which it was stirred and sparged with ambient air for another 40 days, corresponding to phases I and II in the other columns.

Column D was used to provide a comparison with previous lab studies that have raised the pH by the addition of strong base. Due to a limited supply of sample lake water, three-fourths of the column was filled with 0.45 µm filtered Upper Klamath Lake water, while the remaining one-fourth was filled with deionized water. The column received 33 g of wet sediment and was titrated immediately to pH >10 with 11.5 mL of 3N NaOH. The column was then sparged with ambient air for 10 days. During this time, a total of 20.0 mL of 6 N NaOH was needed to maintain the pH above 10. The alkalinity after all strong base was added was 6.6 meq/L; specific conductance was 668.8 µS/cm. This is a change in alkalinity of approximately 5.5 meq/L; specific conductance increased by about 558 µS/cm.

Column E was a control column that received no sediment, but it received filtered lake water and the same pH adjustments as Column A. During phase II, the pH was adjusted to greater than 10 with 21.1 mL of 1N NaOH. The immediate increase in alkalinity after titration was 1.0 meq/L; specific conductance increased by 140 µS/cm.

Phosphorus Fractionation Study

After the Resuspended Sediment Study was in progress, additional data was collected to determine if SRP was the dominant form of phosphorus in the water column. These samples were collected from columns A, C, and D at the beginning of phase III of the Resuspended Sediment Study, and from column B just prior to and just after the start of phase III of the same study. Figure 4 shows a flow chart that helps explain how the phosphorus fractions were determined. Unfiltered samples were analyzed for TP. Additional samples were collected and filtered through a 0.45 µm filter. Colorimetric analysis of this filtrate yields the biologically available SRP in the sample, plus a small amount of condensed phosphates that are unavoidably hydrolyzed during the analysis. Hydrolysis of the filtrate with hot acid yields the SRP fraction plus the acid-hydrolyzable fraction. By subtracting the SRP concentration, the dissolved acid-hydrolyzable phosphorus (DAHP) fraction can be determined. The DAHP fraction consists mostly of condensed inorganic phosphates that did not react to direct colorimetric analysis. Ammonium persulfate digestion of the filtrate followed by colorimetric analysis yields total dissolved phosphorus (TDP). TDP minus the SRP and DAHP fractions yields the dissolved organic phosphorus (DOP) fraction. The difference between TP measured on the unfiltered water sample and TDP is the total suspended phosphorus (TSP) fraction. This fraction of phosphorus is associated with organic and inorganic particles that are removed during the 0.45 µm filtration process.

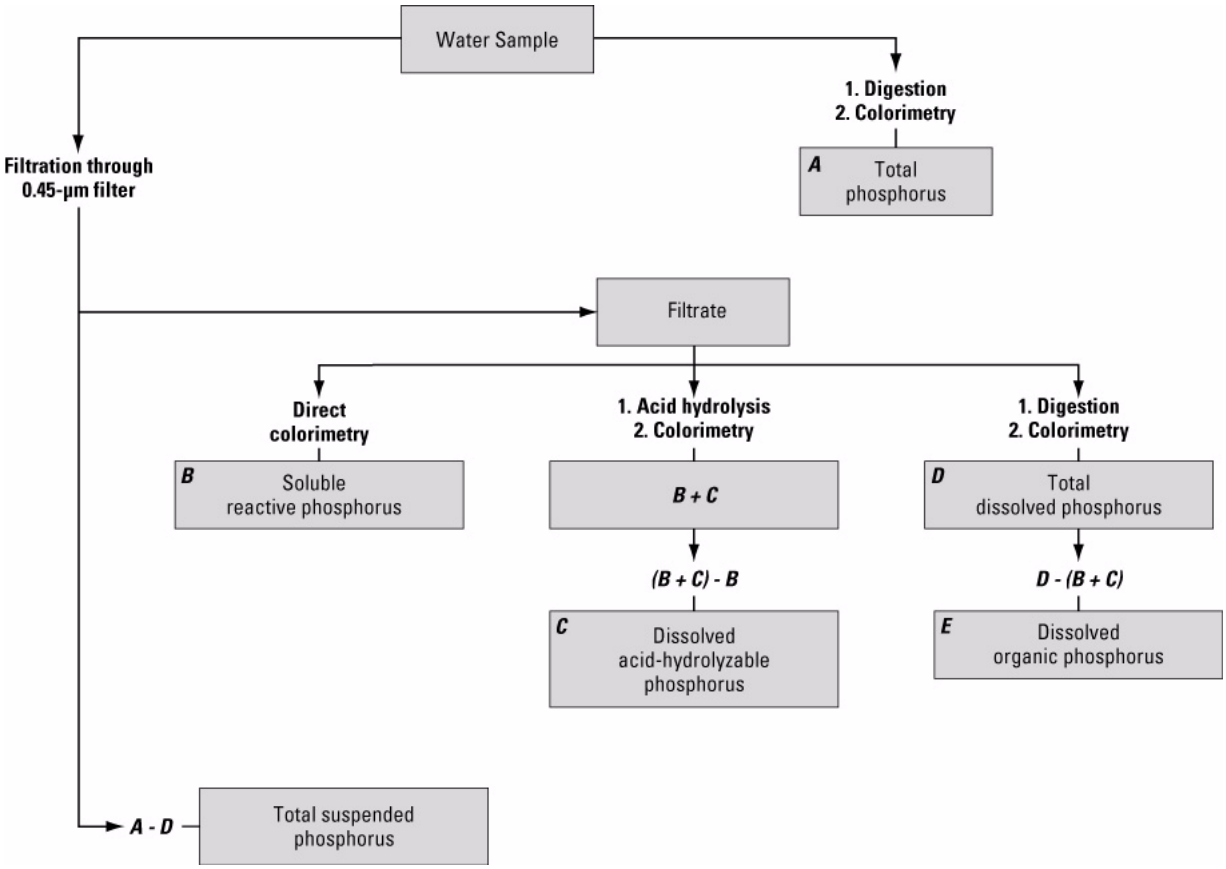


Figure 4. Steps followed for analysis of phosphorus fractions.

Analytical Methods

An ammonium bicarbonate extraction (schedule 515 for benthic phosphorus) was conducted on a subsample of the collected sediment by the USGS National Water Quality Laboratory in Denver, Colorado, in order to determine phosphorus content. This resulted in a sediment-phosphorus content of 1,027 mg/kg of dry sediment. Therefore, 33 g of wet sediment added to columns during the Resuspended Sediment Study had the potential to contribute about 155 µg/L of P to the water column.

Water samples were taken from the center of each column, 27 cm above the bottom. Water samples for TP were collected using a 50-ml glass pipette. Water samples for SRP (50 ml) were collected using a section of 8 mm diameter glass tubing attached to a 60 ml disposable syringe via silicon tubing. During the Stable Interface Study, SRP and TP samples were collected during each sample event. During the Resuspended Sediment Study, phosphorus samples were collected while the stir plate was engaged in order to maintain a homogeneous mixture during sample collection. For this study, SRP was collected during each sample event, and occasional samples were collected for TP in order to check the assumption of constant TP concentration. The sample collection interval was as short as 12 hours at the beginning of each phase, and as long as 6 days when column pH was stable and no rapid changes in concentration were expected. Samples for alkalinity and conductivity were collected prior to, and after, addition of strong base to the water column for phase III.

Samples collected for SRP determinations were filtered through a 0.45 µm filter prior to analysis. Samples collected for TP analyses were digested using the persulfate digestion method as outlined in 4500-P, B5 in Standard Methods (Clesceri et al., 1998). Samples for DAHP were treated with nitric and sulfuric acid and heated to boiling. Phosphorus analysis was conducted by the ascorbic acid method as detailed in 4500-P, E in Standard Methods (Clesceri, et al. 1998). Absorbance readings were made on a Milton Roy

Spectronic 401 spectrophotometer using a 10 cm cylindrical cuvette cell. A summary of the data quality is presented in Appendix A, and includes results from preliminary column tests, determinations of method detection limits, and data quality assurance/quality control.

Temperature, pH, and sparge gas flow rates were recorded during each subsample collection. Measurements of pH were obtained using an Orion Research model SA250 digital pH meter equipped with a Corning deep vessel pH probe and temperature probe for temperature compensation. Alkalinity was measured on filtered samples by digital count titration with 0.1600N H_2SO_4. Alkalinity was calculated using the inflection point method. Determinations of conductivity were corrected for temperature and measured with a YSI model 32 bench top conductivity meter (K=1).

RESULTS

Stable Interface Study

Patterns of both SRP and TP in replicate columns A, B, and C are nearly identical (fig. 5). In each column, the SRP concentration declined rapidly from the initial concentration of about 20 µg/L to between 1 and 3 µg/L 4 days after the initial filling of the column. The trend in concentration then reversed and over the next 10 days the concentration increased in all three columns back up to about 15 µg/L. During phase I of the study, therefore, SRP was largely removed from the water column and then replaced, while pH was maintained between 8 and 8.2.

At the beginning of phase II, pH in the three columns increased by about 1 pH unit within 24 hours with no apparent affect on SRP concentration (fig. 5). During phase II of the study pH was maintained between 8.9 and 9.3 by sparging with CRA. SRP concentrations in all three columns showed small and consistent oscillations around a linear trend line that indicated an average (of the three replicates) SRP release rate of 1.4 mg/m^2/day (milligrams SRP per square meter of sediment surface area per day) (table 2) during this 28-day phase.

At the beginning of phase III, pH in the three columns increased by 1.1 to 1.2 pH units within 14 hours with no apparent immediate effect on SRP concentration (fig. 4). During phase III of the study pH was maintained between 10.1 and 10.4 by sparging with CRA. After a single addition of NaOH, SRP concentrations in all three columns showed small and consistent oscillations around a linear trend line that indicated an average (of the three replicates) SRP release rate of 1.8 mg/m^2/day (table 2) during this 14-day phase.

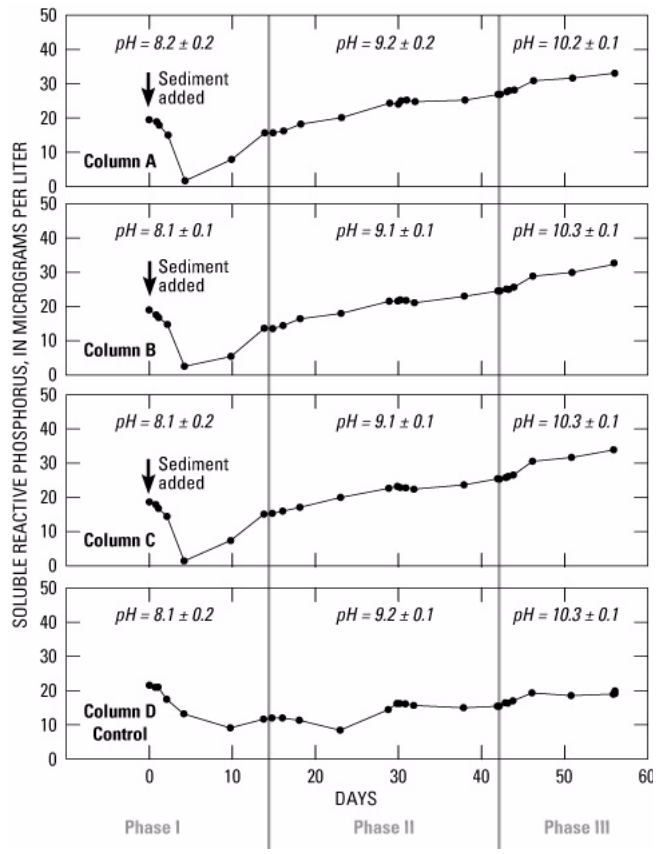


Figure 5. Soluble reactive phosphorus (SRP) concentrations divided into three phases for each column during the Stable Interface Study. During phase I, all columns were sparged with ambient air. During phase II, all columns were sparged witn CO_2-reduced air (CRA). At the beginning of phase III, all columns were titrated to a pH of 10.2 or 10.3. Columns A, B, and C were treated identically, and column D had no sediment in the sediment cup.

SRP concentration in the control column D initially decreased as in the treatment columns, but at a slower rate and did not reach as low a minimum (fig. 5). This trend appears to have reversed prior to beginning phase II of the study, but the column did not regain as much of the lost SRP as did the treatment columns. The result was that the overall decrease in SRP concentration by the end of phase I was greater in the control column than in the treatment columns.

Table 2. Column pH, and soluble reactive and total phosphorus release rates by phase for the Stable Interface Study
[µg/L, micrograms per liter; mg/m^2, milligrams per square meter]

Phase	Column	Median pH	Soluble reactive phosphorus release rate		Total Phosphorus Release Rate	
			µg/L/day[A]	mg/m^2/day[B]	µg/L/day[A]	mg/m^2/day[B]
I	A, B, C averaged	8.1 ± 0.2	-0.3 ± 0.1	-1.0 ± 0.2	-0.5 ± 0.2	-1.7 ± 0.7
	D	8.1 ± 0.2	-0.7	-2.4	-0.3[C]	-0.9
	A, B, C corrected[E]	-	0.4	1.4	-0.2	-0.8
II	A, B, C averaged	9.2 ± 0.1	0.4 ± 0.0	1.4 ± 0.1	0.3 ± 0.1	1.0 ± 0.3
	D	9.2 ± 0.1	0.1	0.4	-0.3	-0.9
	A, B, C corrected[E]	-	0.3	1.0	0.6	1.9
III	A, B, C averaged	10.3 ± 0.1	0.6 ± 0.1	1.8 ± 0.3	0.6 ± 0.1	2.0 ± 0.3
	D	10.3 ± 0.1	0.3	1.1	0.2[D]	0.7
	A, B, C corrected[E]	-	0.3	0.7	0.4	1.3

[A] Release rates were derived from the difference between the beginning and the ending phosphorus concentration divided by the number of days.

[B] Release rates were derived from the difference between the beginning and the ending phosphorus concentration divided by the cross sectional area of the sediment cup and the number of days.

[C] The initial TP concentration was 38.5 µg/L and increased to 46.7 µg/L in 25.5 hours. It is believed that the increase was due to contamination of the column. The release rate was calculated from data after this initial contamination.

[D] At the end of the Stable Sediment Interface Study Column D had flocculate that was resuspended and sampled for SRP and TP. The release rate was calculated from data prior to this resuspension of flocculate.

[E] The rate for the control column (no sediment) was subtracted from the average of columns A, B, and C.

Like the treatment columns, the control column oscillated around a linear trend line through phases II and III, and overall gained SRP through the rest of the experiment. When the control column rates are normalized to the same sediment area used with the treatment columns, the increase in SRP in the control column can be expressed in terms of a "release rate" equal to -2.4, 0.4, and 1.1 mg/m^2/day for phases I, II, and III, respectively (table 2). When these calculated release rates in the control column were subtracted from the treatment columns, the average release rates of SRP were 1.4, 1.0, and 0.7 mg/m^2/day for phases I, II, and III, respectively (table 2).

TP in the treatment columns decreased during phase I, then increased during phases II and III, but with a different magnitude from the SRP release rates (fig. 6). TP declined by an average of 1.7 mg/m^2/day during phase I, increased by an average of 1.0 mg/m^2/day during phase II, and increased by an average of 2.0 mg/m^2/day during phase III (table 2). In the control column D, TP concentration decreased through phase I and phase II. When the control column rates are normalized to the same sediment area used with the treatment columns, the changes in TP in the control column can be expressed in terms of a release rate equal to -0.9, -0.9, and 0.7 mg/m^2/day for phases I, II, and III, respectively (table 2). Thus, TP concentration in the control declined during phase II while the SRP concentration increased. Interpretation of the TP concentration during phase I is complicated by a rapid increase of approximately 7 µg/L during day 1 of the experiment (fig. 6). The only logical explanation for this increase was a slight contamination of the control column. The change in TP through phase I, therefore, was calculated using 46.7 µg/L as the initial concentration, which resulted in a decrease of 0.9 mg/m^2/day.

The decrease in TP in column D (control) through phases I and II indicates that phosphorus was lost from solution. During phase III column D gained TP, suggesting that some of the lost TP returned to solution. All columns, including D, exhibited visible settling of a light colored flocculent precipitate.

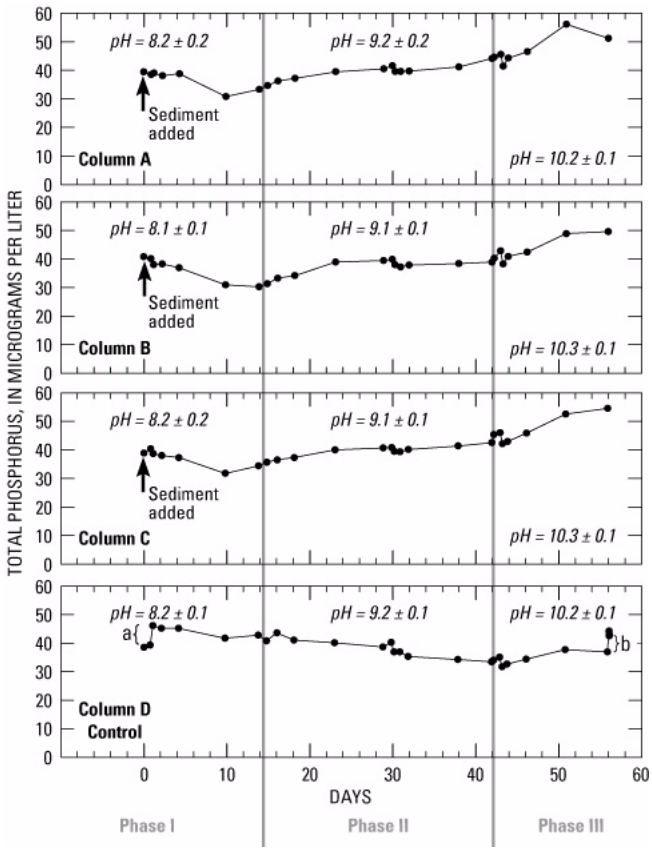


Figure 6. Total phosphorus (TP) concentrations divided into three phases for each column during the Stable Interface Study. During phase I, all columns were sparged with ambient air. During phase II, all columns were sparged with CO_2-reduced air (CRA). At the beginning of phase III, all columns were titrated to a pH of 10.2 or 10.3. Columns A, B, and C were treated identically, and column D had no sediment in the sediment cup. a = increase most likely due to contamination, b = intentional resuspension of flocculate.

It is believed that the phosphorus lost from solution was incorporated into this flocculent. It was not possible to determine the composition of the precipitate, but two possibilities are (1) phosphates incorporated into large molecular weight organic molecules such as fulvic and humic acids that precipitate and settle out, or (2) coprecipitation of phosphate with calcite. Because the solubility of calcite decreases over the range of pH from 8 to 10, the second possibility seems less likely. Given the oxic state of the water column, it seems unlikely that the precipitate would contain iron hydroxides. In either case it would seem that the titration to a pH above 10 reversed the trend and the flocculent, whether organic or inorganic, started to dissipate. At the end of the experiment, the flocculent in column D was resuspended and TP was measured. The final TP concentration was 43.1 µg/L, about 94% of the initial concentration of 46.1 µg/L, after allowing for early contamination of the column. Thus, the flocculent accounted for nearly all of the lost TP. If it is assumed that the same rate of precipitation and dissolution of solids occurred in the control column and treatment columns, and the TP release rates are corrected accordingly, then the average flux rates of TP in the treatment columns are -0.8, 1.9, and 1.3 mg/m^2/day during phases I, II, and III, respectively (table 2).

Resuspended Sediment Study

The suspended sediment did not show a potential to repartition rapidly into the aqueous phase in any of the treatment columns regardless of the conditions of pH, background aqueous concentration, or alkalinity tested (fig. 7). In order to facilitate a comparison with the Stable Interface Study, release rates of phosphorus from the sediments were calculated for Phases I and II of this experiment and are summarized in table 3. The Phase I release rates of SRP were zero or negative in every treatment column (fig. 7), reflecting the fact that the tendency of the sediments for the first 10–15 days after being suspended in the columns was to take on SRP, not release it (table 3). This was true of the column in which the pH had been raised to 9.1 (column A), the column that had been preconditioned to create low aqueous phase concentrations (column B), the column in which the pH was kept at the ambient value (column C), and the column in which the pH was raised to 10.2 while greatly increasing the alkalinity (column D). The affect of the higher pH in columns A and D as compared to column C during this phase seems to be to moderate somewhat the ability of the sediment to take on SRP from the water column. This is likely because at higher pH the substitution of hydroxide ions for phosphate ions on iron hydroxides introduces a geochemical gradient that opposes the process that is driving the uptake of SRP by the sediments, but the gradient is not strong enough to override the opposing process.

During Phase II of this experiment, the sediment in treatment columns A, B, and C released SRP to the water column (fig. 7). The release rates during this phase in column A at pH 10 and column C at pH 7.9 (table 3)were comparable at 0.9 and 0.5 µg/L/day,

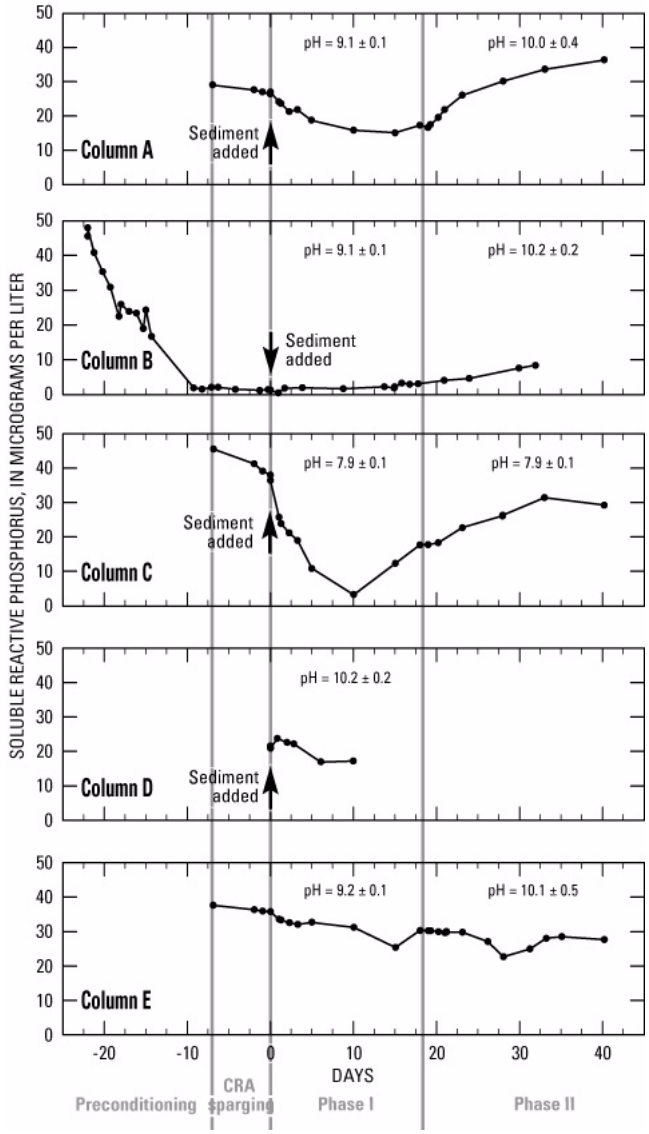


Figure 7. Soluble reactive phosphorus (SRP) concentrations in each column during the Resuspended Sediment Study. Column B was preconditioned, as described in the text, to remove SRP from the water column. Columns A, B, and E were sparged with CO_2-reduced air (CRA) for 6 days prior to adding sediment, which raised the pH in these columns to approximately 9.1. Column C was sparged with ambient air during this time. Phase I began with the addition of sediment to columns A, B, C, and D and lasted 18 days. Columns A, B, and E continued to be sparged with CRA during phase I, column C continued to be sparged with ambient air, and column D was titrated to a pH of 10.2. At the beginning of phase II, columns A, B, and E were titrated to a pH of 10 or greater, while column C continued to be sparged with ambient air.

respectively, indicating very little influence of pH during days 20 to 40 of the experiment. The lowest release rate of 0.4 µg/L/day was calculated for the column that had been pre-conditioned to have very low aqueous phase concentrations at the start of the experiment, so this evidence also suggests that phosphorus transfer between the sediments and the water is not controlled by a simple partitioning process that one would expect to respond dramatically to a change in the geochemical gradient.

The control column E to which no sediment was added showed a decline in SRP over time (fig. 7), indicating that SRP was slowly converted into other P forms. Therefore the Phase II release rates of SRP from the sediments calculated for the other treatment columns may be underestimated, but the rates calculated for column E (-0.3 and -0.1 µg/L/day for Phases I and II, respectively) do not indicate that the correction would be large (table 3).

Phosphorus Fractionation Study

Results of the phosphorus fractionation study are summarized in table 4. SRP was the largest dissolved fraction, except in column C where SRP had been stripped from the water by preconditioning. The results do not indicate that a large fraction of either DOP or DAHP was liberated from resuspended sediments throughout the course of the experiment, although the total dissolved unreactive phosphorus (DUP=DOP+ DAHP) was a nontrivial fraction of the TDP, and was the largest fraction of the TDP in column C, where SRP had been stripped from the water by preconditioning.

Notably in column B, to which no sediment was added, a significant fraction of TSP developed between the time that the column was filled with filtered water and the time that the fractionation was done, about 27 days. This seems to be evidence that over time colloidal material and particles larger than 0.45 µm are formed, incorporating phosphorus. This is consistent with the flocculation noted in the Stable Interface Study. The beginning of the experiment showed that SRP was 68% of TP, leaving DUP with 32%, assuming that TSP immediately after filtering was 0%. Therefore, 14% of the TP that originally was SRP, and 9% of the TP that originally was DUP, were converted into the TSP pool over a period of 27 days. The same type of conversion could be occurring in the other columns to which sediment was added, which would suggest that roughly 40% of the TSP in column A and 30% of the TSP in columns C and D was generated within the column.

Table 3. Column pH and release rates by phase for the Resuspended Sediment Study
[μg/L, micrograms per liter; mg/kg, milligrams per kilogrgam]

Column	Phase	Median pH	Soluble reactive phosphorus (SRP) release rate	
		pH units	μg/L/day[A]	mg/kg/day[B]
A	I	9.1 ± 0.1	-0.5	-0.2
	II	10.0 ± 0.4	0.9	0.3
B	I	9.1 ± 0.1	0.0	0.0
	II	10.2 ± 0.2	0.4	0.1
C	I	7.9 ± 0.1	-1.0	-0.3
	II	7.9 ± 0.1	0.5	0.1
D	I	10.2 ± 0.2	-0.4	-0.1
E	I	9.2 ± 0.1	-0.3	no sediment
	II	10.1 ± 0.5	-0.1	no sediment

[A]Release rates were derived from the difference between the beginning and the ending phosphorus concentration divided by the number of days.

[B] Release rate in milligrams of SRP per kilogram of suspended sediment (dry) per day.

Table 4. Resuspended Sediment Study column pH, SRP concentration, and percent of the total phosphorus as dissolved organic phosphorus (DOP), dissolved acid-hydrolyzable phosphorus (DAHP), soluble reactive phosphorus (SRP), and total suspended phosphorus (TSP)
[Column B was sampled prior to and after titration to pH 10.4; μg/L, micrograms per liter; %, percent]

Column	pH	SRP μg/L	% DOP	% DAHP	% SRP	% TSP
A	10.0	33.6	11	1	31	57
B	9.0	29.9	0	23	56	21
B	10.4	30.0	12	11	54	23
C	10.4	2.1	17	2	4	77
D	7.9	26.1	4	3	21	72

DISCUSSION

The maximum rate of phosphorus release from the sediments to the water column observed during the Stable Interface Study was approximately 1 and 2 mg/m^2/day of SRP and TP, respectively. The effect of raising the pH from 8.1 to first 9.1 and then to 10.2 on the release rate was not pronounced and did not indicate a strong dependence of the dominant processes on pH. The treatment columns were consistent in showing that initially upon being put into contact with the lake water the sediments removed SRP from the water column rather than releasing SRP to the water column. After about 5 days the water in the column was largely depleted of SRP and the trend reversed; the sediments slowly released SRP to the water column over the next 50 days until the experiments were terminated.

The results of the Resuspended Sediment Study showed that even when diffusion limitations on the processes responsible for the transfer of phosphorus across the sediment-water interface were eliminated, the phosphorus in the sediments did not rapidly repartition into the aqueous phase. This was true under all the conditions tested: ambient and photosynthetically elevated pH, very low SRP concentration in the aqueous phase, and elevated pH accompanied by a large increase in alkalinity. The treatment columns in the Resuspended Sediment Study were notable for their similarities: all showed that initially upon suspension in the water, the sediments took up phosphorus from solution. After a period of 10 to 15 days the columns still being monitored showed that the exchange of

phosphorus reversed and that SRP was slowly released to the water column through the remaining 10 to 20 days of the experiments. It also was shown in the Resuspended Sediment Study that the initial uptake of phosphorus by the sediments was reduced at a photosynthetically elevated pH of 9.1 or 10.2 compared to uptake at an ambient pH of 8, probably because of the substitution of hydroxide ions for phosphate ions on iron hydroxides. This substitution is the geochemical process that, it was hypothesized, would cause rapid desorption of phosphorus from the sediments at high pH, i.e., internal loading. The results of the column experiments have indicated that this geochemical process has a moderating influence on the exchange of phosphorus between the sediments and the water, but that it is not the most important process governing that exchange.

The rapid increase in chlorophyll *a* (fig. 2) in late May and early June for Shoalwater Bay in 2001 corresponds to an increase in pH of 2.5 units and TP concentrations that increase 10 µg/L/day. The data shown are from one site in 1 year, but the trend in TP is typical of the increase observed in most years at multiple sites in Upper Klamath Lake monitored by the Klamath Tribes. Because the release rates from bottom sediments measured in these experiments are only about 10 percent of the actual phosphorus release rate calculated during times of maximum internal loading in Upper Klamath Lake, it is difficult to conclude that pH is the primary factor controlling the timing and magnitude of P release during these internal loading periods.

It should be noted that sediment collected from a single site, Shoalwater Bay, may have responded differently than would sediments from other parts of the lake. Additionally, the timing of the sample collection may have been less than optimal. While it could be assumed that the sediment had already undergone phosphorus release due to high lake pH prior to sample collection, during preliminary laboratory studies using lake sediment collected on May 25, 2001, phosphorus release/uptake rates similar to those in tables 2 and 3 were observed. Additionally, data from these preliminary experiments indicated a sequence of SRP uptake and release similar to the data presented in figures 5, 6, and 7.

The classic theory for redox-driven phosphate release from iron hydroxides at the sediment/water interface was developed by Einsele (1938) and Mortimer (1941; 1942). Later, the theory for a strictly geochemical mechanism for the release of phosphate from iron hydroxides under oxic conditions that was greatly enhanced at high pH was developed (MacPherson et al., 1958; Anderson, 1975; Lijklema, 1976). Based on the literature, either geochemical or microbiological processes might control phosphorus release, but it is not clear what set of environmental conditions (redox, pH, temperature, etc.) is likely to result in control by one or the other type of process. However, because sediment bacteria mineralize organic detritus that falls to the bottom, these bacteria must be involved at some point in recycling the phosphorus that is incorporated annually into algal biomass. Whether these bacteria represent a transient phosphorus pool that can be ignored or a persistent reservoir of phosphorus in the sediments that must be considered is a matter of debate (Gachter and Meyer, 1993), but it has been demonstrated that benthic bacteria can operate as a short-term sink for bioavailable phosphorus (Montigny and Prairie, 1993; Tornblom and Rydin, 1998; Clavero et al., 1999; Khoshmanesh et al., 1999). How and under what conditions the phosphorus stored in sediment bacteria is returned to the water column is also a matter of debate, but it probably occurs under both aerobic and anaerobic conditions. Polyphosphate-metabolizing bacteria store polyphosphates under aerobic conditions when phosphate is available in excess of immediate requirements for growth. These bacteria use the stored polyphosphate as an energy source when conditions turn anaerobic (Davelaar, 1993; Gachter et al., 1988; Khoshmanesh et al., 2002), which releases phosphate to the surrounding medium. Alternatively, the release of phosphorus incorporated into bacterial cells under aerobic conditions has been attributed to cell lysis (Montigny and Prairie, 1993; Tornblom and Rydin, 1998; Clavero et al., 1999).

For comparison, a summary of the results of several laboratory studies that measured phosphorus release from a stable sediment-water interface is provided in table 5. The release rates found in the literature vary widely, and the results depend not only on the character of the sediments involved but also on the experimental conditions. Several studies of phosphorus release from sediments under oxic conditions found release rates similar to those presented here (Drake and Heaney, 1987; Boers and van Hese, 1988; Boers, 1991; Appan and Ting, 1996; Anderson and Ring, 1999; James et al., 2000). In cases where the same sediments were tested under oxic and anoxic conditions, the release rate under anoxic conditions generally was found to be greater (Boers

et al., 1994; Appan and Ting, 1996; Moore et al., 1998; Anderson and Ring, 1999; James et al., 2000). Anderson (1975) found a large phosphorus release rate of 20-80 mg/m^2/day under oxic conditions, but the system was dominated by calcium rather than iron chemistry. Some studies have demonstrated greatly enhanced release of phosphorus from sediments at high pH, which was not found in this study, but usually the pH was increased with a strong base in these studies (Jacoby et al., 1982; Drake and Heaney, 1987; Appan and Ting, 1996). Boers (1991) concluded that raising the pH with strong base enhanced phosphorus release rates relative to raising the pH by removing CO_2. A few studies have demonstrated the importance of temperature (Kelderman, 1984; Anderson and Ring, 1999), which is usually taken as an indication of a biologically mediated reaction, and one study (Boers and van Hese, 1988) concluded that temperature affected the outcome of the experiments more than pH. In the context of table 5, the results presented here are not atypical.

The results of this study indicate that the current understanding of internal loading in Upper Klamath Lake should be revised to include a more important role for microbiology. Our observations in the columns would not have detected any change in the way the phosphorus was partitioned within the sediments, yet it appears likely that some transfer to and from bacterial biomass within the sediments occurred. The switch between sediment uptake of phosphorus to sediment release of phosphorus at several weeks into the experiments may indicate either (a) biological uptake under initially favorable conditions followed by cell lysis when conditions became unfavorable, or (b) the superposition of opposing biological and geochemical reactions operating at different time scales. Tornblom and Rydin (1998) suggested the former interpretation to explain their results of measuring phosphorus release from sediment cores collected from Lake Erken, Sweden. Their results had many similarities to those presented here—sediment cores were observed to take up SRP for the first 12 days of the experiment, then a reversal occurred and the cores released SRP between days 12 and 20. These investigators also tracked bacterial biomass through the course of the experiment and were able to show that biomass decreased coincident with the switch between SRP uptake and release. This paper also was one of several recent works that have demonstrated that NaOH extraction, a standard step in sequential extractions for sediment phosphorus, likely extracts bacterial polyphosphates that go undetected because they do not react to the colorimetric techniques used to analyze the NaOH extract (Hupfer et al., 1995; Goedkoop and Pettersson, 2000; Khoshmanesh et al., 2002). Goedkoop and Pettersson (2000) found the nonreactive fraction of NaOH extractable P (NaOH-nrP) to be 13–20% of total P in Lake Erken sediments; Tornblom and Rydin (1998) found the NaOH-nrP fraction to be greater than the reactive fraction (NaOH-rP) in Lake Erken sediments, and NaOH-nrP amounted to 23–40% of the total P in their cores.

The results of previous work with Upper Klamath Lake sediments are inconsistent with the idea that the phosphorus source in the sediments could be bacterial or organic in nature. Wildung et al. (1974; 1977) showed that the spring 1969 increase in biological activity in the lake coincided with a reduction in the inorganic P sediment fraction, in particular the fraction extractable in NaOH and associated with iron hydroxides. There are at least two reasons why the conclusions of Wildung et al. (1974; 1977), that the source of phosphorus in the sediments is primarily inorganic, could be flawed. First, these conclusions were strongly supported by data from only one site, Howard Bay, and the phosphorus in these sediments was shown to be more labile in laboratory experiments than phosphorus in sediments from other sites (Wildung and Schmidt, 1973). Thus, the sediments from Howard Bay may not be representative of sediments over the rest of the lake. Second, it is possible that these investigators did not detect changes in a significant fraction of bacterial phosphorus in the sediments because it was extracted by NaOH but was not reactive to colorimetric techniques. Yet another possibility is that the primary source of phosphorus really is the inorganic fraction, and that bacteria play an important role not only in the mineralization of organic matter, but also in the solubilization of inorganic phosphate. Bacteria that can solubilize phosphate salts under aerobic conditions have been isolated from Upper Klamath Lake sediments (Harrison, 1970; Harrison et al., 1972).

Table 5. Experimentally determined areal release rates of phosphorus exchange between sediments and water

[Non-italicized text indicates exchange rates of orthophosphate as P. Italicized text indicates exchange rates of total phosphorus as P. The pH was elevated by the addition of strong base unless indicated by an *. The term amb is used for ambient. °C, degrees Celsius. The term DO is used for dissolved oxygen]

Reference	Rate ($mg/m^2/day$)	pH	Oxidation conditions	Notes
Anderson (1975)	20 –80	10	oxic lakewater	dominated by calcium chemistry, not iron chemistry
Andersen and Ring (1999)	1.27, 2.48	amb	oxic lakewater	the two rates are at 12°C and 19°C, respectively; these rates are for littoral sediments, generally lower rates were observed for profundal sediments
	7.19, 9.78	amb	anoxic lakewater	
Appan and Ting (1996)	0.2, 0.6 *0.3, 5.3*	6.5	oxic lakewater	the two rates are results for sediments from two different reservoirs
	1.2, 2.3 *1.0, 7.6*	9		
	1.7, 3.6 *2.1, 10.3*	6.5	anoxic lakewater	
	3.3, 4.9 *3.0, 14.8*	9		
Boers and van Hese (1988)	*0.2 – 4*	8.3	oxic	pH effects were found to be minor; temperature effects were more important
	0.2 – 5	9.5		
Boers, et al. (1994)	19	amb	oxic "synthetic" lakewater	maximum values as extracted from figure 2
	28	amb	anoxic "synthetic" lakewater	
Boers (1991)	1.8	8.3*	oxic "synthetic" lakewater	
	3.8	9.3*		
	15.6	9.5		
Drake and Heaney (1987)	2 (estimate)	7.6	oxic lakewater	
	75	10.6		
Fisher and Wood (this study)	1.0, *1.9*	9.2*	oxic lakewater	Stable sediment interface—no strong dependence on pH, sediments adsorb phosphorus for first 4 days.
	0.7, *1.3*	10.3		
Jacoby, et al. (1982)	5.6	10	oxic lakewater	first 30 days at amb pH the sediment appears to adsorb phosphorus
James, et al. (2000)	4.9	amb	oxic lakewater	average of values determined from sediment in a sediment accumulation zone; values much less for sediment elsewhere
	8.3	amb	anoxic lakewater	
Kelderman (1984)	0.4, 2.6, 7, 11	amb	oxic	rates obtained at 5, 10, 15, and 20°C, respectively
Kleeberg and Kohl (1999)	*~28*	amb	~40% DO saturated lakewater	
	50.82	amb	~90% DO saturated lakewater	
Moore, et al. (1998)	5.79	amb	oxic lakewater	maximum values observed over several sites and sampling dates
	12.3	amb	anoxic lakewater	
Mozeto, et al. (2001)	219 – 493	amb	anoxic	calculated from porewater gradients
Ruban and Demare (1998)	18	6.4 – 6.7	anoxic lake water	
Sondergaard, et al. (1992)	4 – 12 60 – 70	amb	oxic lakewater	lower range for a stable sediment interface; higher range for resuspended sediments

The sediments used in this study were rich in phosphorus (1,027 mg/kg of dry sediment), yet the phosphorus exhibited relatively little mobility, at least when compared to the expectations for internal loading that have developed based on monitoring in the lake over the last decade. Neither high pH (9.2 to 10.2) nor resuspension of the sediment in a high pH environment had a marked effect on the ability of the sediments to release phosphorus to the water column. Either these experiments did not duplicate the environmental conditions in Upper Klamath Lake that mobilize the phosphorus in the sediments, or the manner in which the experiments monitored changes was flawed, or both.

These experiments relied on SRP concentration to indicate the transfer of biologically available

phosphorus from the sediments to the water column. This reliance on SRP may be misguided, for two reasons. First, in the water column, SRP is likely to be highly transient in the presence of consumers—planktonic bacteria or algae—and, in any event, SRP may overestimate free orthophosphate by 1–2 orders of magnitude (Eisenreich and Armstrong, 1980). Second, both bacteria and algae can utilize DOP, although the degree of preference for phosphate or DOP, as well as the competitive advantage of bacteria or algae in utilizing DOP is a matter of debate (Currie and Klaff, 1984; Cotner and Wetzel, 1992). The results of the fractionation study did not indicate that a conversion of sediment-bound phosphorus to the dissolved phase as either DOP or DAHP took place; if anything, part of the dissolved phosphorus appeared to be incorporated into particles larger than 0.45 µm over time. In this case, therefore, it does not appear that the monitoring of SRP alone caused us to miss a large release of organic phosphorus from the sediments to the water in the column. It seems likely, then, that our experiments did not duplicate some important environmental conditions that mobilize the sediment phosphorus in the lake.

Observations of internal loading in the lake are not based on SRP, but rather on TP; in fact, SRP concentrations often remain low while the most rapid internal loading occurs, as happened in 2001 (fig. 2). The observed increase in TP is assumed to reflect an increase in algal biomass. This assumption is supported by the fact that TP and chlorophyll *a* are correlated (Kann, 1998), but certainly *A. flos-aquae* is not the only compartment containing the TP—there must be phosphorus incorporated into zooplankton, rotifers, and bacteria (Vadstein et al., 1993) as well as dissolved organic matter. It is not just the cycling of phosphorus between the sediments and the water column that supports the algal bloom, but the cycling among all of the water column compartments. For example, Kann (1998) discussed the occurrence of *Daphnia pulicaria* in Upper Klamath Lake, and possible links between the dominance of *Daphnia* and *A. flos-aquae*. This points to additional speculation as to why these experiments were unable to demonstrate phosphorus transfer from the sediments to the water column of the magnitude observed in the lake—perhaps the consumers must be in place to drive (or at least accelerate) the transfer. For example, the production of alkaline phosphatase would have been inhibited in these experiments because the water was filtered to remove most bacteria and algal growth was prevented. This alkaline phosphatase would allow consumers to use an organic P source from the sediments if they were brought into contact with it either at the sediment-water interface or during a re-suspension event. The source of phosphorus would not have to be organic; however, sediment bacteria can solubilize inorganic phosphates when an adequate energy source is available (Harrison, et al., 1972). Harrison (1970) concluded that this solubilization mechanism also was stimulated by the geochemical disequilibrium caused by biological uptake of phosphates in the water column.

SUMMARY

Upper Klamath Lake sediments collected from the lake bottom and then placed in contact with lake water at a stable sediment/water interface exhibited an initial capacity to take up SRP from the water column rather than release phosphorus to the water column. After about 4 days, and after the sediments had taken up most of the SRP in the water, the transfer of phosphorus reversed and the sediments began to release phosphorus back into the water column. This trend continued for about 50 days until the experiments were terminated, during which the pH was increased twice, first from 8.1 to 9.2 and then from 9.2 to 10.3. In both cases the effect of raising pH on the phosphorus release rate was insignificant. The release rates of SRP were 1.4, 1.0, and 0.7 $mg/m^2/day$ for the first 2 weeks at pH 8.1, the next 4 weeks at pH 9.2, and the next 2 weeks at pH 10.3, respectively.

Sediments suspended in the water column also exhibited an initial capacity to take up SRP from the water rather than release it. Immediately after suspension in the water column and for at least the next 10 days, the sediments pulled SRP from the water column at all the pH values tested. The effect of increasing the pH was to slow the uptake, as can be seen by comparing columns A and C in the Resuspended Sediment Study. At pH 8 in column C, the rate of phosphorus uptake was 1.0 µg/L/day, and at pH 9 in column A it was 0.5 µg/L/day (table 3). The transfer of SRP reversed between 10 and 15 days into the experiments, and the sediment continued to release SRP slowly for the next 30 days until the experiments were terminated. The effect of increasing the pH during this time was to accelerate the release rate of phosphorus to the water column, as can be seen by comparing columns A and C again. The rate of phosphorus release was 0.5 µg/L/day at pH 8 in column

C, and 0.9 μg/L/day at pH 10 in column A (table 3). These experiments demonstrated that even when the diffusive limitations on phosphorus transfer that might have been present at the stable sediment-water interface were removed, the phosphorus in the sediments did not rapidly repartition into the aqueous phase. While some effect due to increased pH was apparent, these experiments were not able to demonstrate that either pH-driven desorption from iron hydroxides or wind-driven sediment resuspension are critical in explaining the internal loading that occurs annually in Upper Klamath Lake.

The results of the column experiments suggest that sediment bacteria may play an important role in the cycling of phosphorus between lake sediments and the water column. This study was designed to measure phosphorus release as a geochemical phenomenon, in particular the release of phosphorus adsorbed to iron hydroxides and released under conditions of elevated pH or increased surface area contact with the water (resuspension), and therefore cannot confirm a large role for sediment bacteria. For this reason, further work on defining the mechanism of internal loading to Upper Klamath Lake should consider evaluating the following processes:

1. An important fraction of the phosphorus stored in the sediment may be incorporated into benthic bacteria, and this fraction may grow in response to environmental conditions, such as warming water and sediment temperatures.
2. The release of phosphorus to the water column may be microbially driven and triggered by conditions that lead to massive lysis of bacterial cells and a rapid release of the phosphorus stored in benthic bacteria to the water column.
3. Consumers may need to be present to initiate or accelerate the transfer of phosphorus from the sediments to the water column. For example, *A. flos-aquae* may be producing alkaline phosphatase in Upper Klamath Lake, which might promote P release from the sediments.
4. Planktonic bacteria may play an important role in the phosphorus cycle, and that internal loading may be manifested first as an increase in this phosphorus compartment, which then works its way through the food chain, but is rarely manifested as a significant increase in SRP.

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APPENDIX

APPENDIX A: SUMMARY OF DATA QUALITY

Preliminary Column Tests

A preliminary test was conducted on both the acrylic sediment cup and the acrylic laboratory column to determine if the acrylic material sorbs phosphorus. For this test, a column was filled with 23.2 L of deionized water spiked with KH_2PO_4 to make a 40 µg/L SRP solution. The column was sampled for SRP over a period of 18 days. During this time the average SRP concentration was 41.9 µg/L based on 10 samples, indicating no loss of phosphorus to the column.

As an additional preliminary study, phosphorus uptake by bacteria colonizing the interior walls of the column was investigated. A column involved in a preliminary stable interface experiment was drained and sampled for TP at the end of the test to determine if phosphorus was lost over the course of the test. A section of the interior wall of the column 50.8 cm tall, 15.2 cm from the bottom of the column, and half of the interior circumference was sampled for TP by scraping with a plastic spatula. The spatula was then rinsed with deionized water into a collection bottle. Additional deionized water was analyzed as a TP blank. From these analyses it was concluded that as much as 5.3 µg of TP could have been sorbed to the interior wall. This would have amounted to a 0.23 µg/L decrease in the water column TP concentration when the column was full. This decrease is below the method detection limit and considered negligible.

Method Detection Limit

A method detection limit (MDL) was calculated for the ascorbic acid method used for both SRP and TP analysis as outlined in 1030, C2 in Standard Methods for The Examination of Water and Wastewater, 20th edition (Clesceri et al., 1998). The MDL is expected to fall within a range that is between one-fourth and one-fifth of the standard reference sample (SRS) concentration in order to be statistically relevant.

Three SRP reference samples were prepared (2.0 µg/L, 1.7 µg/L, and 0.9 µg/L) and analyzed from 9/4/01 to 1/7/02. The 2.0 µg/L and 0.9 µg/L SRSs both resulted in MDLs of 0.26 µg/L. The MDL for the 2.0 µg/L SRS was less than the expected range, while the MDL for the 0.9 µg/L SRS was greater than the expected range. The 1.7 µg/L SRS resulted in an MDL of 0.49 µg/L, which is also greater than one-fifth of the reference concentration. With two MDL determinations resulting in overestimates of the MDL and one resulting in an underestimate of the MDL, the average of all three (0.3 µg/L) rounded to the nearest tenth was taken as the SRP MDL for the study. All SRP concentrations in this study were above this MDL.

A 4.0 µg/L TP reference sample was prepared and analyzed from 9/6/01 to 11/29/01 to determine an MDL for TP. The resulting MDL (0.72 µg/L) was a small underestimate of the expected MDL based on the SRS concentration; however, the total phosphorus concentrations determined throughout this work were more than 20 times this level.

Quality Assurance/Quality Control

Internal Standard Reference Samples

An internal QA/QC program provided a measure of precision and accuracy for the phosphorus analysis from this work. SRP analysis was conducted on a 0.5 µg/L internal SRS from 6/5/01 through 7/3/01, and on a 42 µg/L SRS between 6/1/01 and 7/26/01. TP determinations were conducted on a 30 µg/L/day internal SRS from 8/9/01 through 9/27/01, and on a 42 µg/L SRS from 6/29/01 through 8/27/01. Figure A.1 shows accuracy and precision for SRP and TP, divided into two concentration ranges, as calculated by subtracting the SRS concentration from each analytical result. SRP concentrations show a nearly normal Gaussian distribution with no apparent bias in the low range (≤ 30 µg/L), while the higher range (> 30 µg/L) shows a positive bias that is less than 0.2 µg/L. This suggests that SRP concentrations above 30 µg/L could be slightly overestimated. TP shows no apparent bias in either the low or high range (fig. A.1).

External Reference Samples

The USGS Oregon District laboratory supplies monthly synthetic standard reference samples, river samples, and spiked samples to Clean Water Services of Washington County, Oregon, and the USGS National Water Quality Laboratory, as part of a quality-control program. Additionally, the Oregon District Laboratory conducts a yearly sample split among laboratories performing analytical work for the

Designated Management Agencies (DMA) of the Tualatin River Basin. Eight low range (≤ 30 µg/L) and 11 high range (> 30 µg/L) standard reference samples were analyzed for SRP in the Oregon District lab as part of the QA/QC program for this work. Fifteen of these samples were also analyzed for TP (high range). The percent differences from each reference sample's most probable concentration is given in table A.1. A Tualatin River sample and a spiked duplicate of this sample was obtained during the yearly DMA split. This set of samples was analyzed to determine the phosphorus recovery as part of the QA/QC program for this work. The percent recovery obtained by the Oregon District laboratory was 103.1% for SRP and 97.2% for TP.

As an additional measure of accuracy and precision, the USGS Branch of Quality Assurance (BQA) supplied an SRS at a concentration of 86 µg/L. Between 7/12/01 and 8/29/01, 15 SRP analyses were conducted on a 1:10 dilution of this reference sample resulting in a mean measured concentration of 8.4 µg/L, with a standard deviation of 0.13 µg/L. Between 7/12/01 and 7/23/01, the diluted reference sample was analyzed for TP. This resulted in a mean measured concentration of 8.5 µg/L, with a standard deviation of 0.37 µg/L. The percent differences from the BQA sample concentration are given in table A.1.

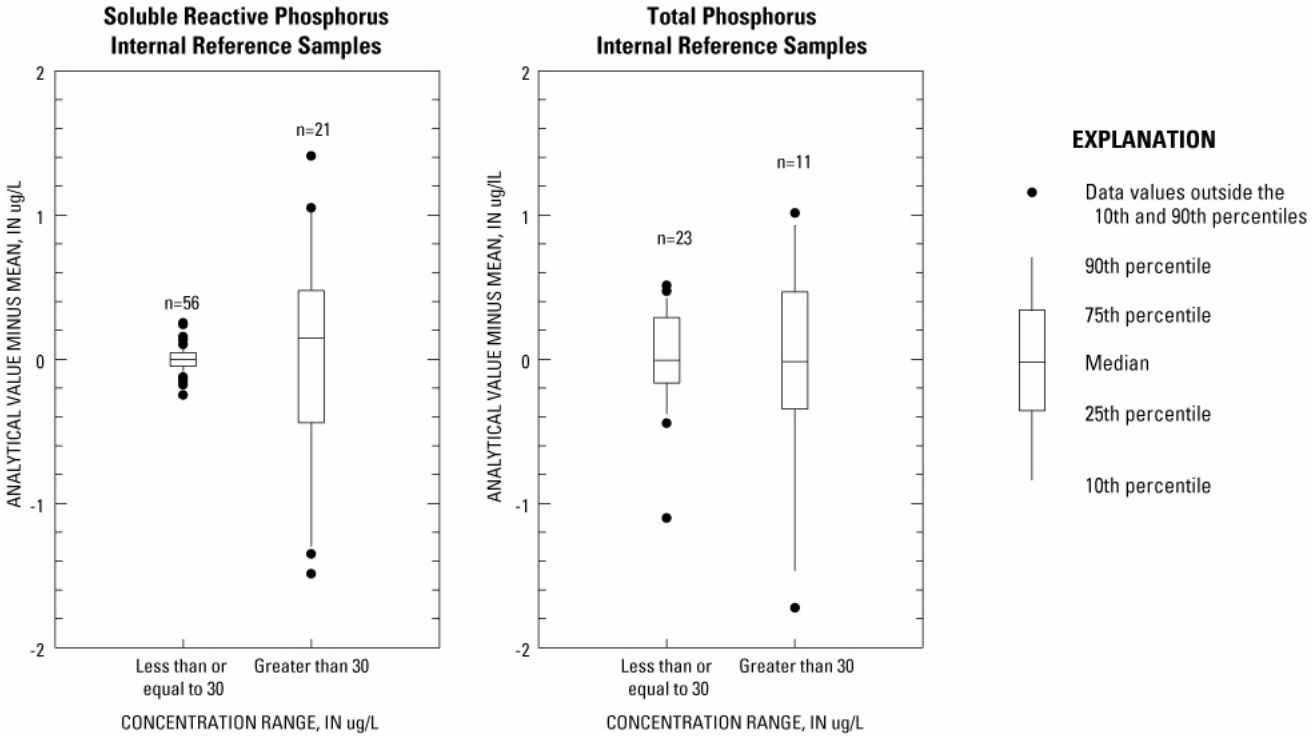

Figure A.1. Accuracy of analytical results for internal soluble reactive phosphorus and total phosphorus standard reference samples when compared to the reference sample mean.

Table A.1. External reference sample date, source, type, most probable concentration, and observed concentration and percent difference from the MPC grouped by concentration range for soluble reactive phosphorus and total phosphorus

Soluble reactive phosphorus external reference samples						
Range	Date	Sample source[A]	Sample type[B]	MPC[C] mg/L	Observed value[D] mg/L	Percent difference[D]
30 µg/L	5/7/01	OR Dist.	Synth.	0.029	0.029, 0.030	0.00, 3.45
	6/4/01	OR Dist.	Synth.	0.021	0.022, 0.022	4.76, 4.76
	7/2/01	OR Dist.	Synth.	0.025	0.026	4.00
	7/24/02	DMA	Stream	0.011	0.011, 0.011	0.00, 0.00
	8/6/01	OR Dist.	Synth.	0.017	0.016	-5.88
	10/1/01	OR Dist.	Synth.	0.022	0.024	9.09
	11/5/01	OR Dist.	Synth.	0.025	0.024, 0.024	-4.00, -4.00
	12/3/01	OR Dist.	Synth.	0.027	0.029, 0.028	7.41, 3.70
> 60 µg/L	5/7/01	OR Dist.	Synth.	0.039	0.040, 0.040	2.56, 2.56
	6/4/01	OR Dist.	Synth.	0.037	0.040, 0.041	8.11, 10.81
	7/2/01	OR Dist.	Synth.	0.035	0.038	8.57
	7/2/01	OR Dist.	Stream	0.046	0.053, 0.053	15.22, 15.22
	7/2/01	OR Dist.	Spike	0.062	0.070, 0.069	12.90, 11.29
	7/12/01	BQA	Synth.	0.086	0.084 ± 0.001, n = 15	-2.65 ± 1.69, n = 15
	7/24/01	DMA	Stream	0.095	0.099, 0.098	4.21, 3.16
	8/6/01	OR Dist.	Synth.	0.033	0.033	0.00
	10/1/01	OR Dist.	Synth.	0.039	0.042	7.69
	11/5/01	OR Dist.	Synth.	0.033	0.032, 0.032	-3.03, -3.03
	11/5/01	OR Dist.	Stream	0.066	0.067, 0.066	1.52, 0.00
	12/3/01	OR Dist.	Synth.	0.035	0.037, 0.037	5.71, 5.71

Total phosphorus external reference samples						
Range	Date	Sample source[A]	Sample type[B]	MPC[C] mg/L	Observed value[D] mg/L	Percent difference[D]
> 60 µg/L	7/2/01	OR Dist.	Synth.	0.061	0.059	-3.28
	7/2/01	OR Dist.	Synth.	0.109	0.091	-16.51
	7/2/01	OR Dist.	Stream	0.109	0.125, 0.126	14.68, 15.60
	7/2/01	OR Dist.	Spike	0.162	0.177, 0.177	9.26, 9.26
	7/24/01	DMA	Stream	0.077	0.090 ± 0.001, n = 3	16.88 ± 1.30, n = 3
	7/24/01	DMA	Stream	0.175	0.185 ± 0.006, n = 3	5.52 ± 3.49, n = 3
	8/6/01	OR Dist.	Synth.	0.071	0.066	-7.04
	8/6/01	OR Dist.	Synth.	0.106	0.106	0.00
	10/1/01	OR Dist.	Synth.	0.077	0.077, 0.077	0.00, 0.00
	10/1/01	OR Dist.	Synth.	0.122	0.122, 0.122	0.00, 0.00
	11/5/01	OR Dist.	Synth.	0.070	0.068	-2.86
	11/5/01	OR Dist.	Synth.	0.097	0.092	-5.15
	11/5/01	OR Dist.	Spike	0.185	0.174 ± 0.002, n = 3	-5.77 ± 0.83, n = 3
	12/3/01	OR Dist.	Synth.	0.064	0.066, 0.065	3.13, 1.56
	12/3/01	OR Dist.	Synth.	0.094	0.095, 0.095	1.06, 1.06

[A] **OR Dist**.—Oregon District USGS supplied reference samples obtained as part of a monthly QC program with Clean Water Services of Washington County, Oregon; **DMA**—USGS supplied reference samples as part of the Tualatin Basin Designated Management Agencies Interlaboratory Quality Control Sample Split (July 24, 2001); **BQA**—USGS Branch of Quality Assurance reference sample split and analyzed by various labs.

[B] **Synth.**—Synthetic reference sample; **Stream**—samples of stream water obtained from the Tualatin Basin by USGS for use in the monthly QC program with Clean Water Services of Washington County, Oregon; **Spike**—spiked stream water samples supplied by USGS.

[C] Most probable concentration. The MPC for Oregon District synthetic samples is the target concentration at which the reference was prepared. The MPC for Oregon District stream samples is the value reported by the USGS National Water Quality Laboratory. The MPC for the Oregon District spike references is the value reported by the USGS National Water Quality Laboratory plus the spike concentration. The MPC for DMA and BQA reference samples is the consensus of all labs participating in the sample split.

[D] Reference samples with a single analysis are shown as a single value. Reference samples analyzed in duplicate are shown as two values separated by a comma. Reference samples with three or more analysis values are reported as the mean ± a standard deviation followed by the number of samples analyzed.