The importance of analytical methods in the interpretation of data from natural systems – Accounting for all forms of phosphorus in the water and sediment of Upper Klamath Lake, OR

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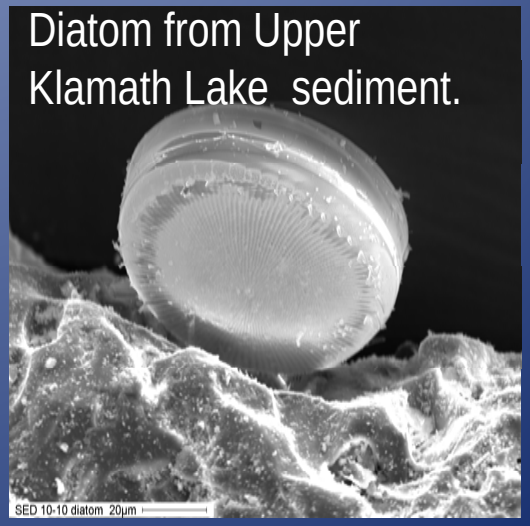
National Environmental Monitoring Conference
Bellevue, WA August 16, 2011



Diatom from Upper Klamath Lake sediment.

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News about anticipated shortages of phosphorus in the future has called attention to phosphorus in the environment.

Phosphorus Famine: The Treat to Our Food Supply

"This underappreciated resource - - a key component of fertilizers - - is still decades from running out. But we must act now to conserve it, or future agriculture could collapse. "

June 2009 Scientific American

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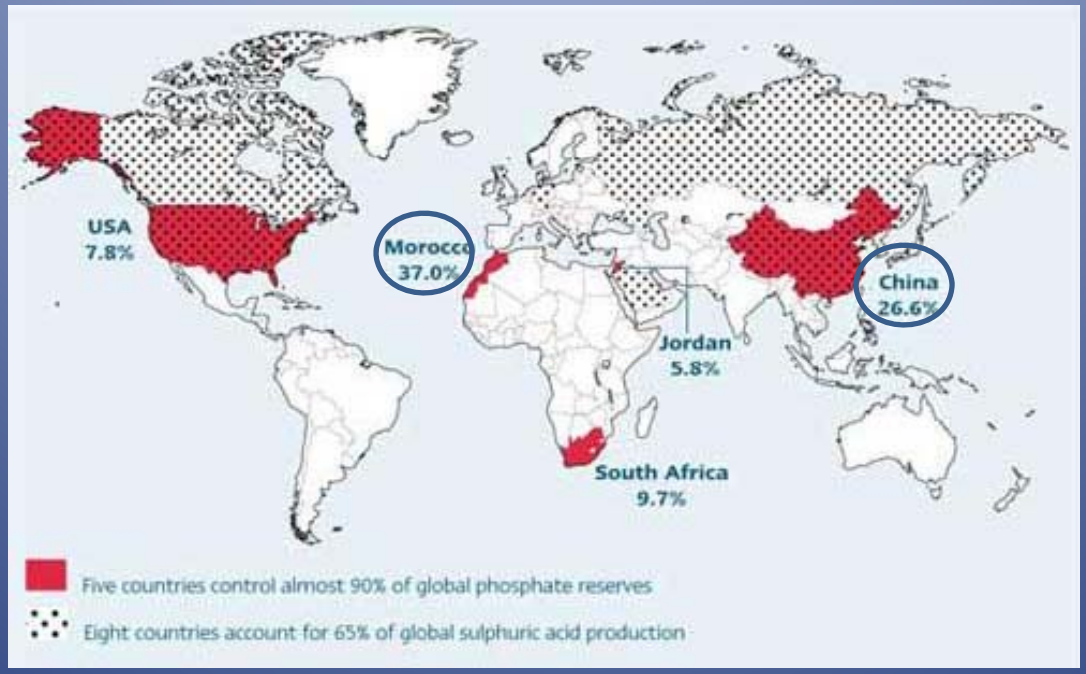
The United States holds less than 8% of the world's phosphate resources.

More than 60% of the world's resources are held by Morocco and China



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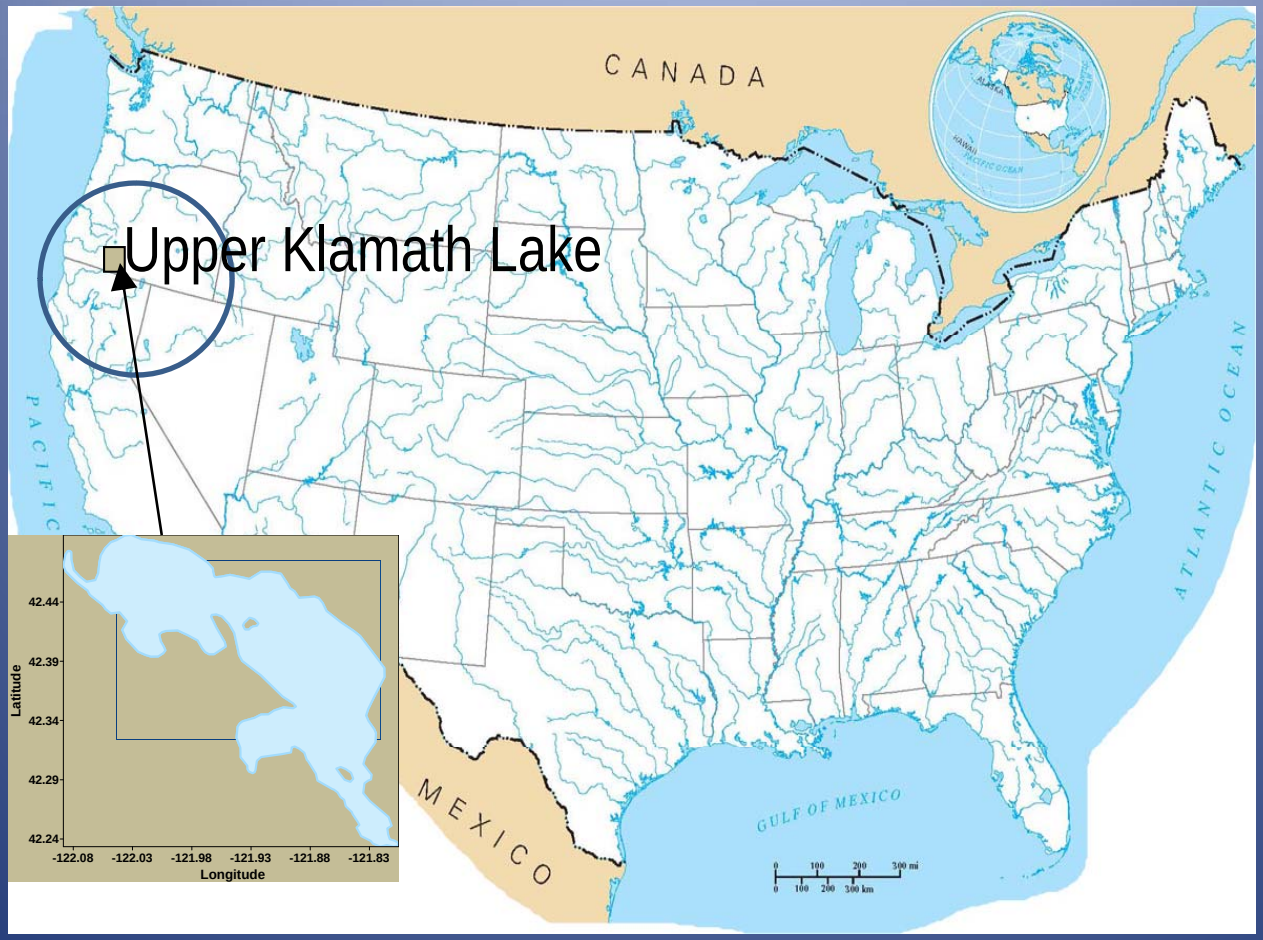
Major effort being made to understand the phosphorus cycle in Upper Klamath Lake, OR.



Hypothesis:

Decreasing phosphorus in UKL sediments will increase oxygen concentrations in water the column for endangered suckers.

Lost River sucker

Short nosed sucker

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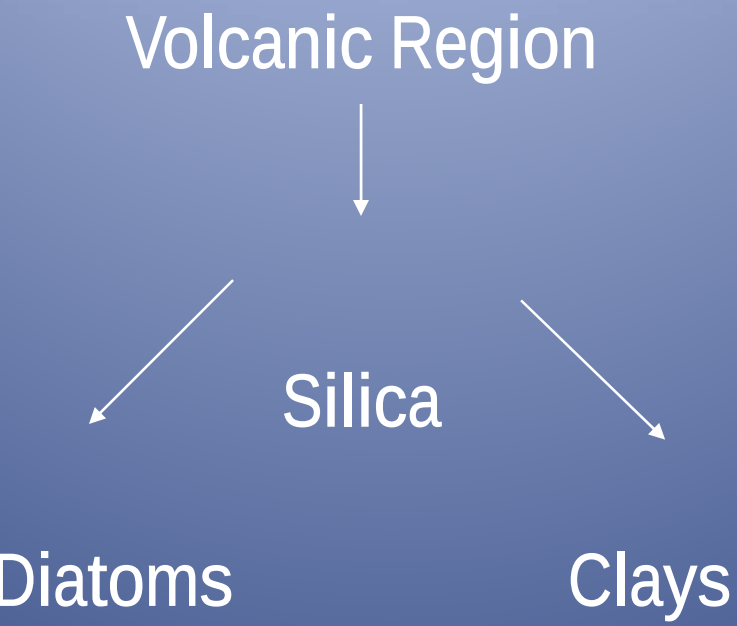
Upper Klamath Lake, OR



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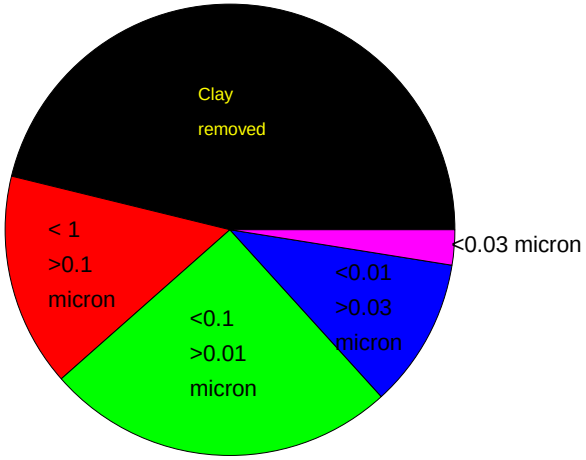
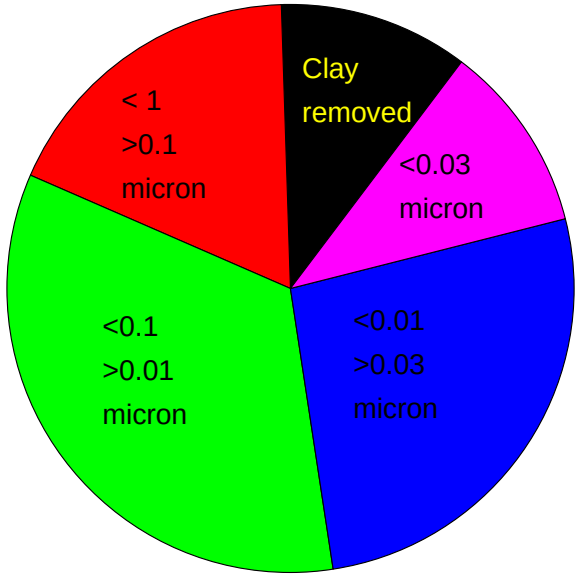
The clay size fraction is approximately 50 percent by weight of the surface sediment from the Mid North site, Upper Klamath Lake, OR. Approximately 90 percent of the total phosphorus concentration was found in the smectite fraction.

Percent by weight of particle size fraction in bottom sediment





Percent of total P in each particle size fraction.

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The future of phosphorus studies in Upper Klamath Lake, OR, will include clay mineralogy in the watershed.

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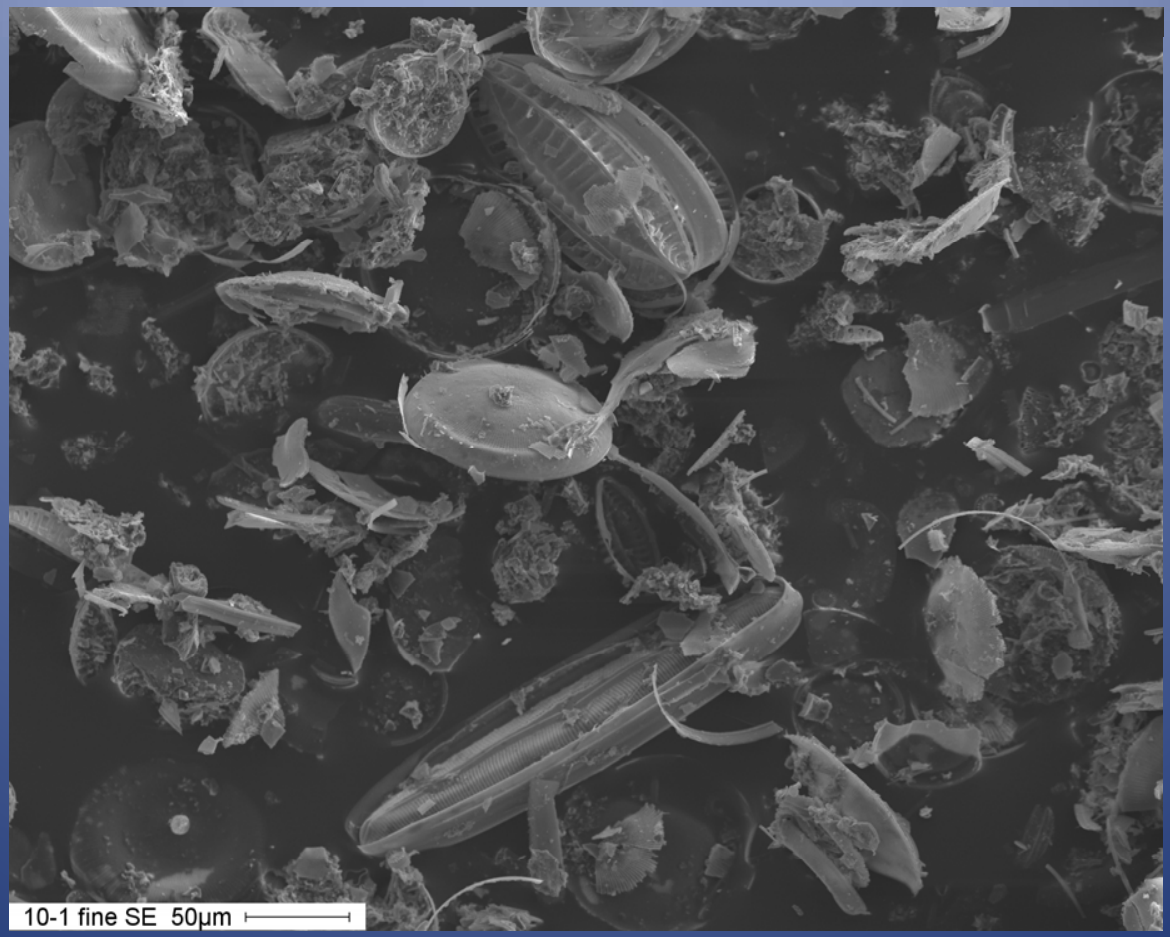
Upper Klamath Lake sediment: < 63 m particle size fraction contains abundant diatom frustules.



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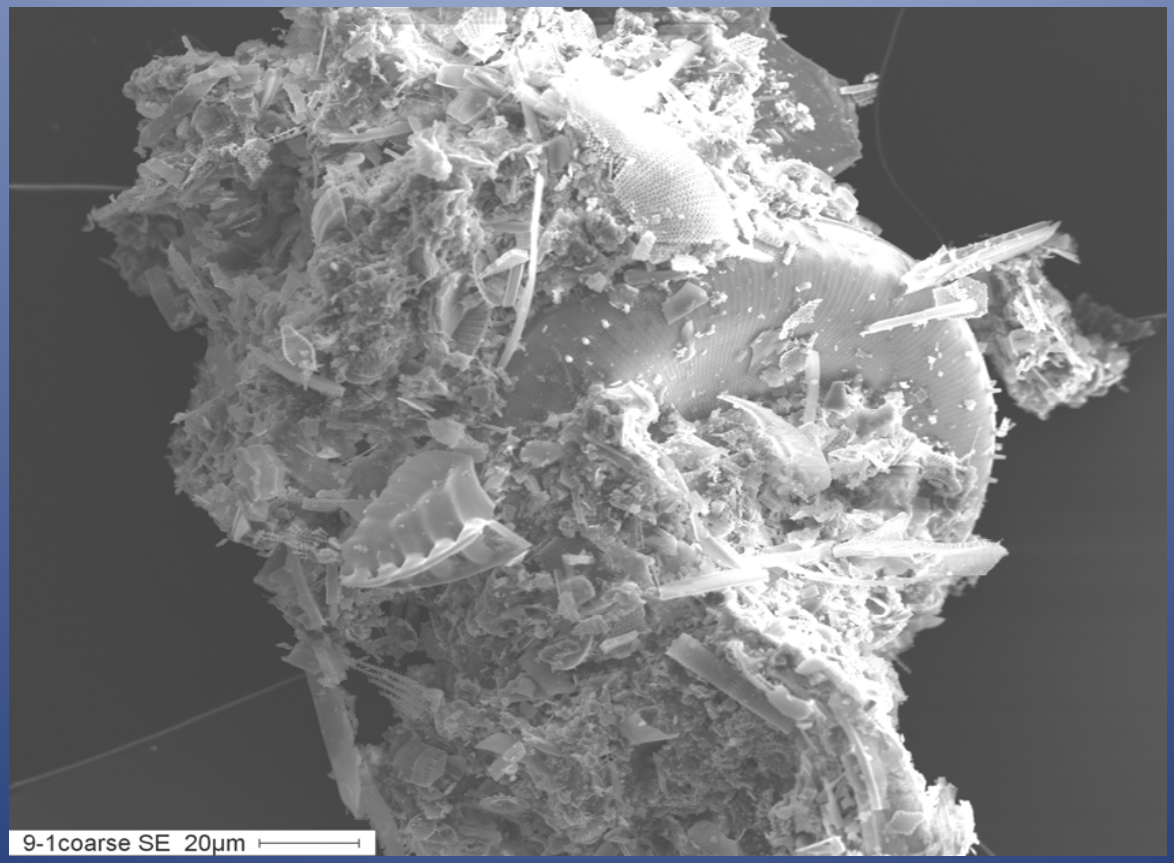
Upper Klamath Lake sediment : > 63 m particle size fraction contains aggregates of diatom frustules.



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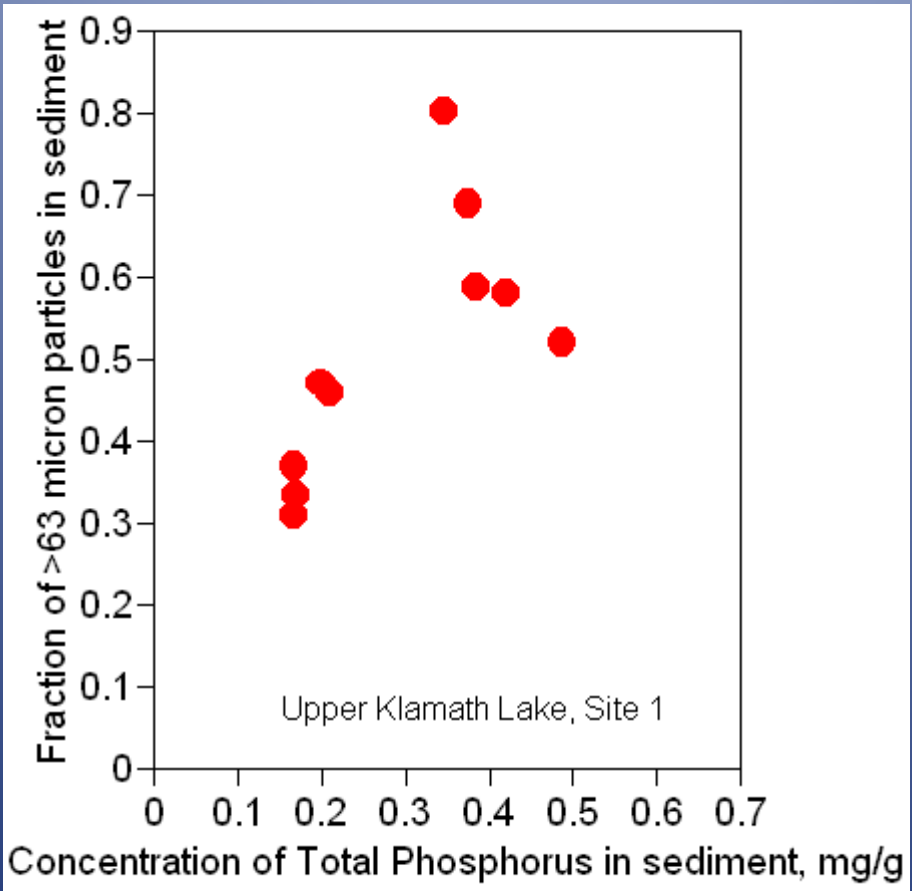
In sediment cores collected in October 2006 from Upper Klamath Lake, OR, total phosphorus concentrations were larger in the >63 micron particle size. This is reflected in the distribution of total phosphorus for whole sediment samples (combined fractions of <63 and >63 micron particles).



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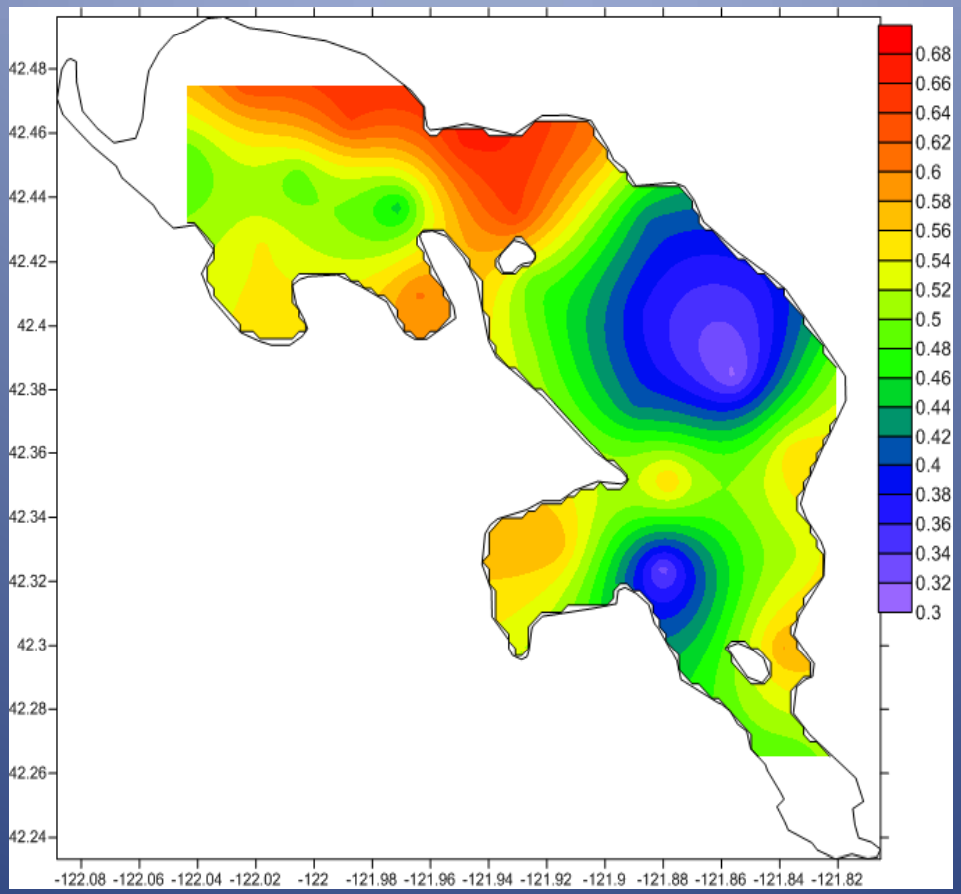
Concentrations of total phosphorus mg g^{-1} at 1 cm depth in UKL sediment. Cores collected in October 2006.



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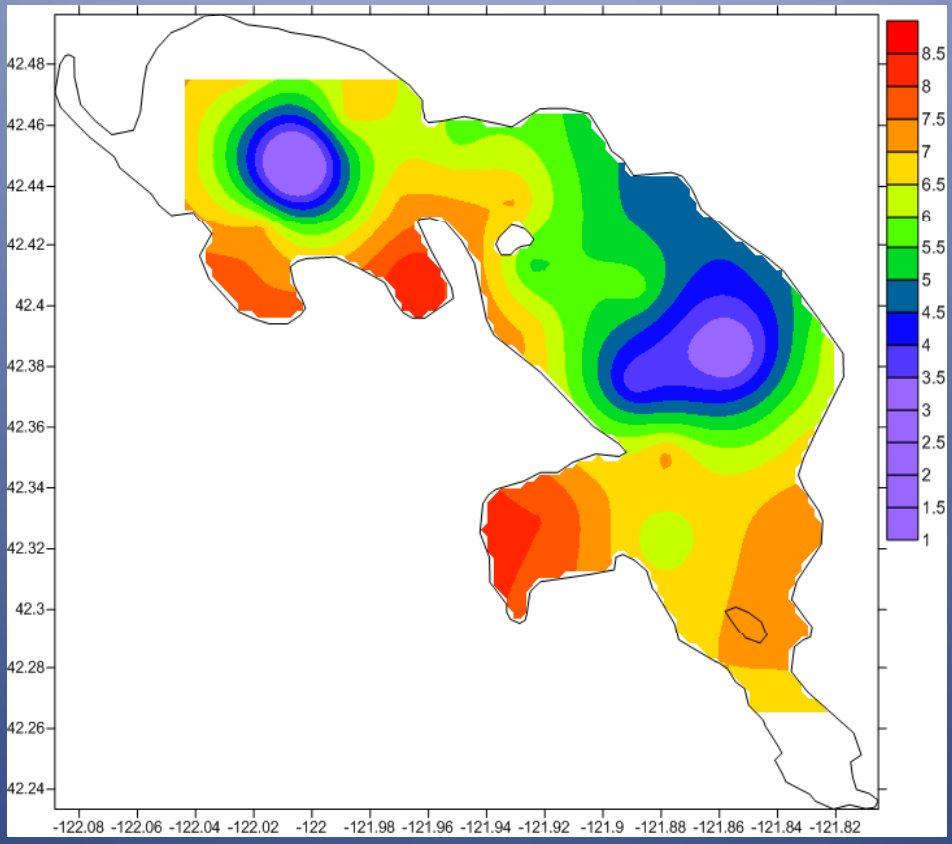
Concentrations of total carbon (%) at 1 cm depth in UKL sediment. Cores collected in October 2006



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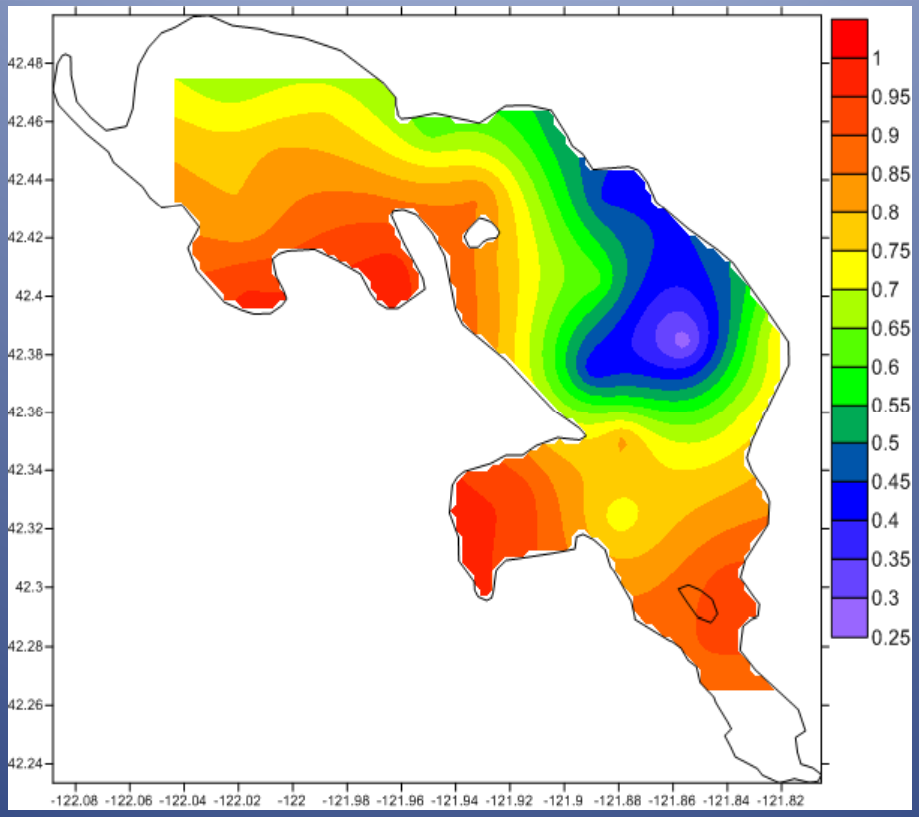
Concentrations of total nitrogen (%) at 1cm depth in UKL sediment. Cores collected in October 2006.



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Large blooms of *Aphanizomenon flos-aquae* in Upper Klamath Lake, OR, are attributed to an internal load of phosphorus from bottom sediments. There is variation in the concentrations of algae in the water column.

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Aphanizomenon flos aquae (AFA) algae in Upper Klamath Lake, OR.

Upper Klamath Lake algae bloom near Upper Klamath NWR
Photo by Brett Cole - "Oregon Wild"

http://www.true-blue-green-algae.net/History.html

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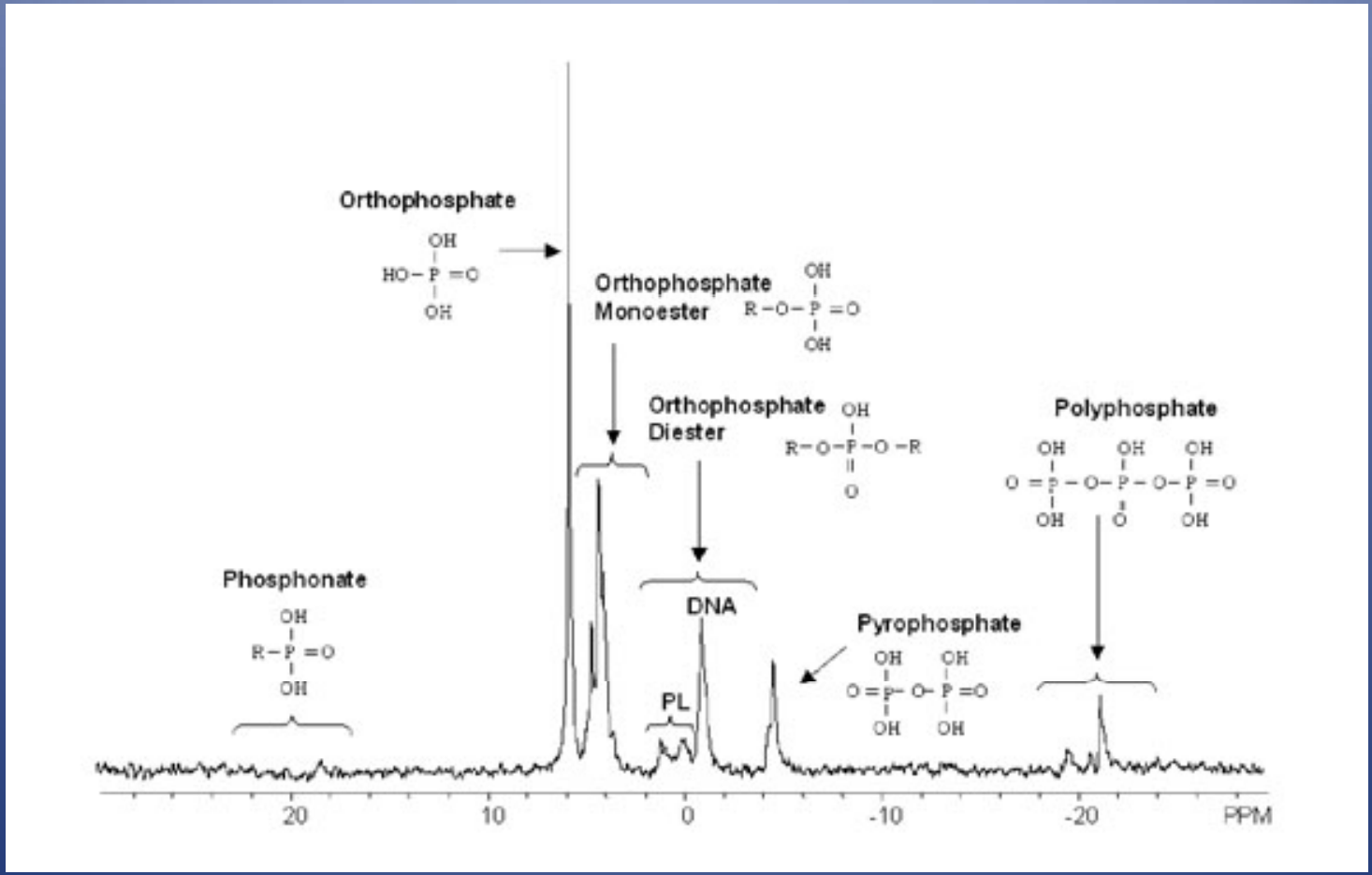
Classes of organic P compounds determined using ^{31}P NMR.



From Cade-Menun, Talanta, 2005

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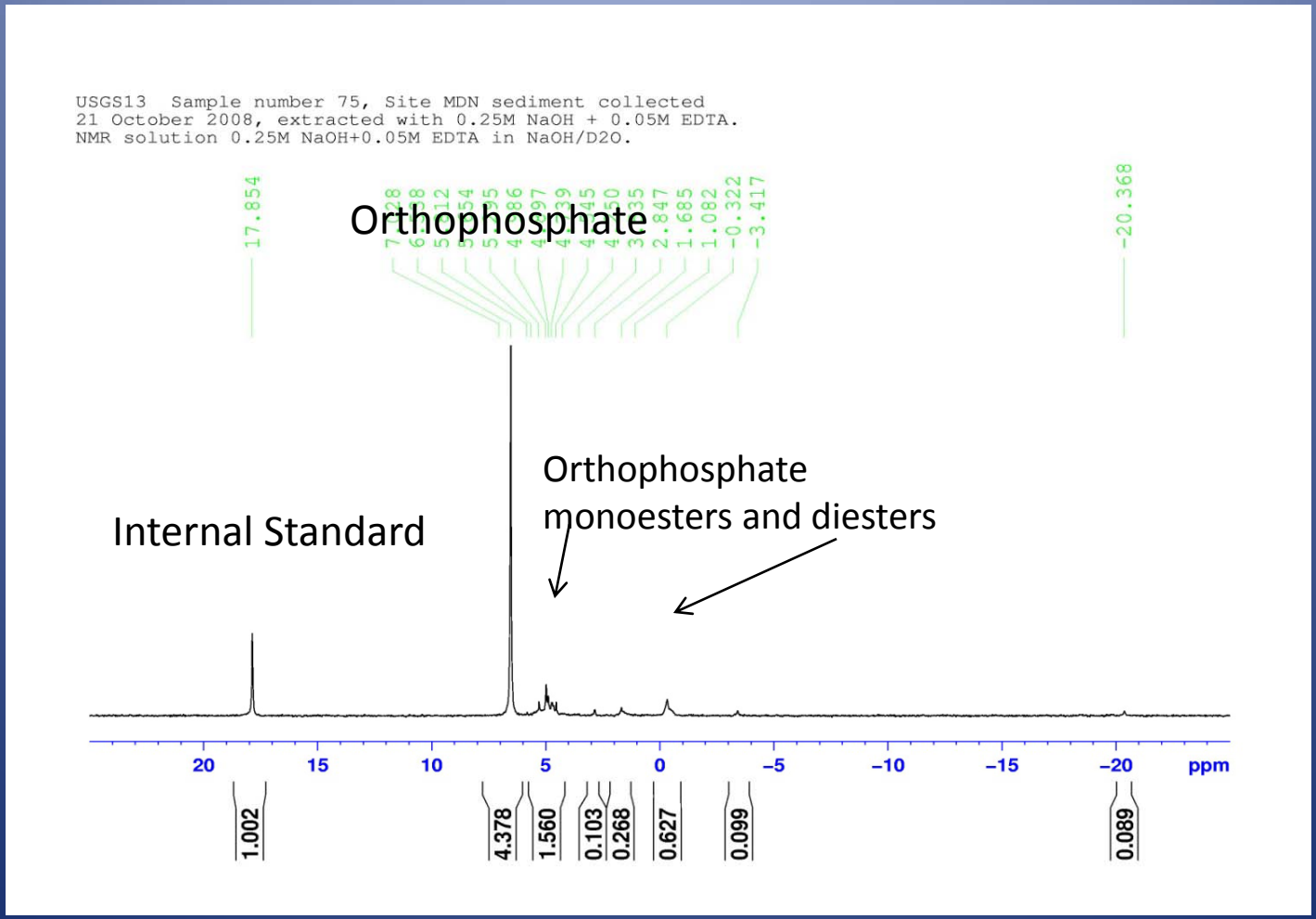
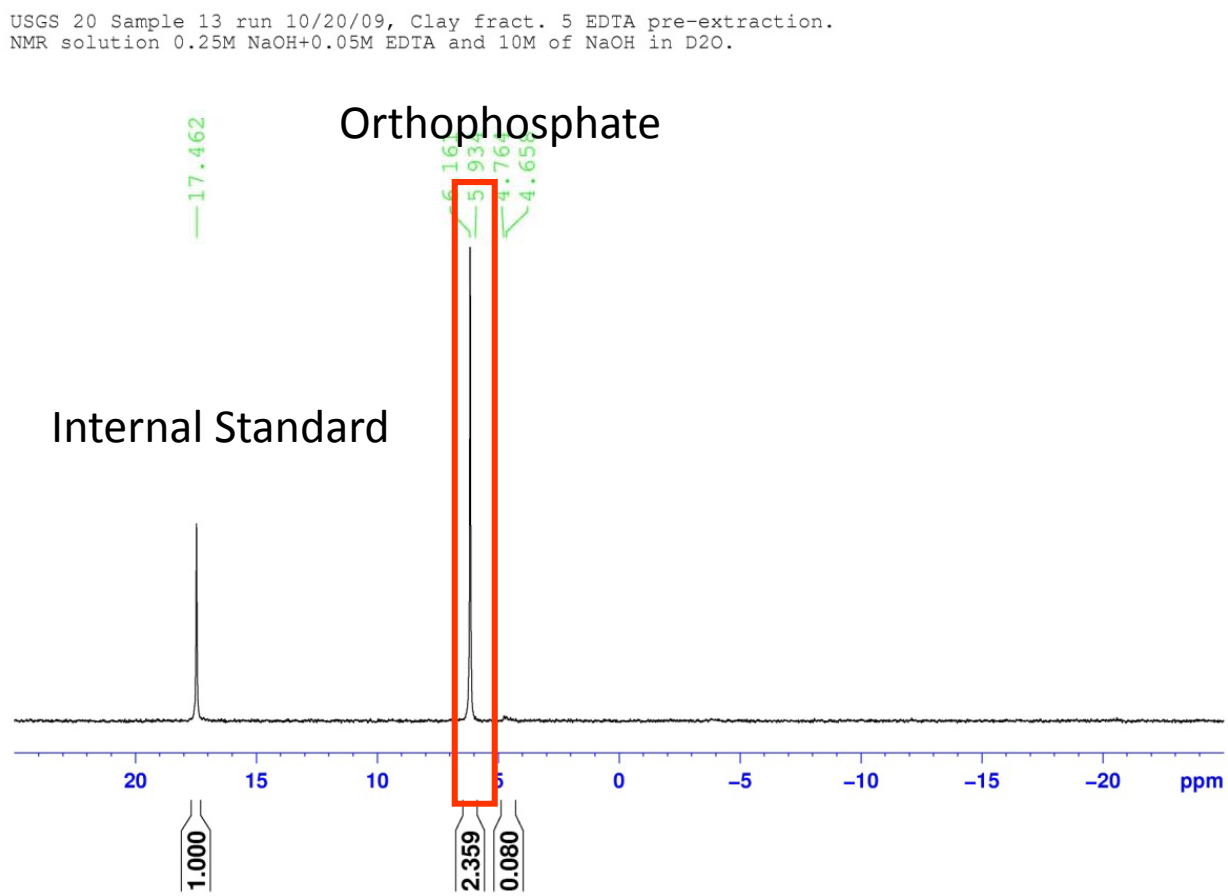
^{31}P NMR spectrum of NaOH/EDTA extract of sediment from Upper Klamath Lake, OR. Chemical shifts are evident for orthophosphate, phosphate sugars, DNA/RNA and pyrophosphate.



Extraction of ≥ 0.03 mm particles (smectite) from Site 22 sediment using EDTA solution released orthophosphate.



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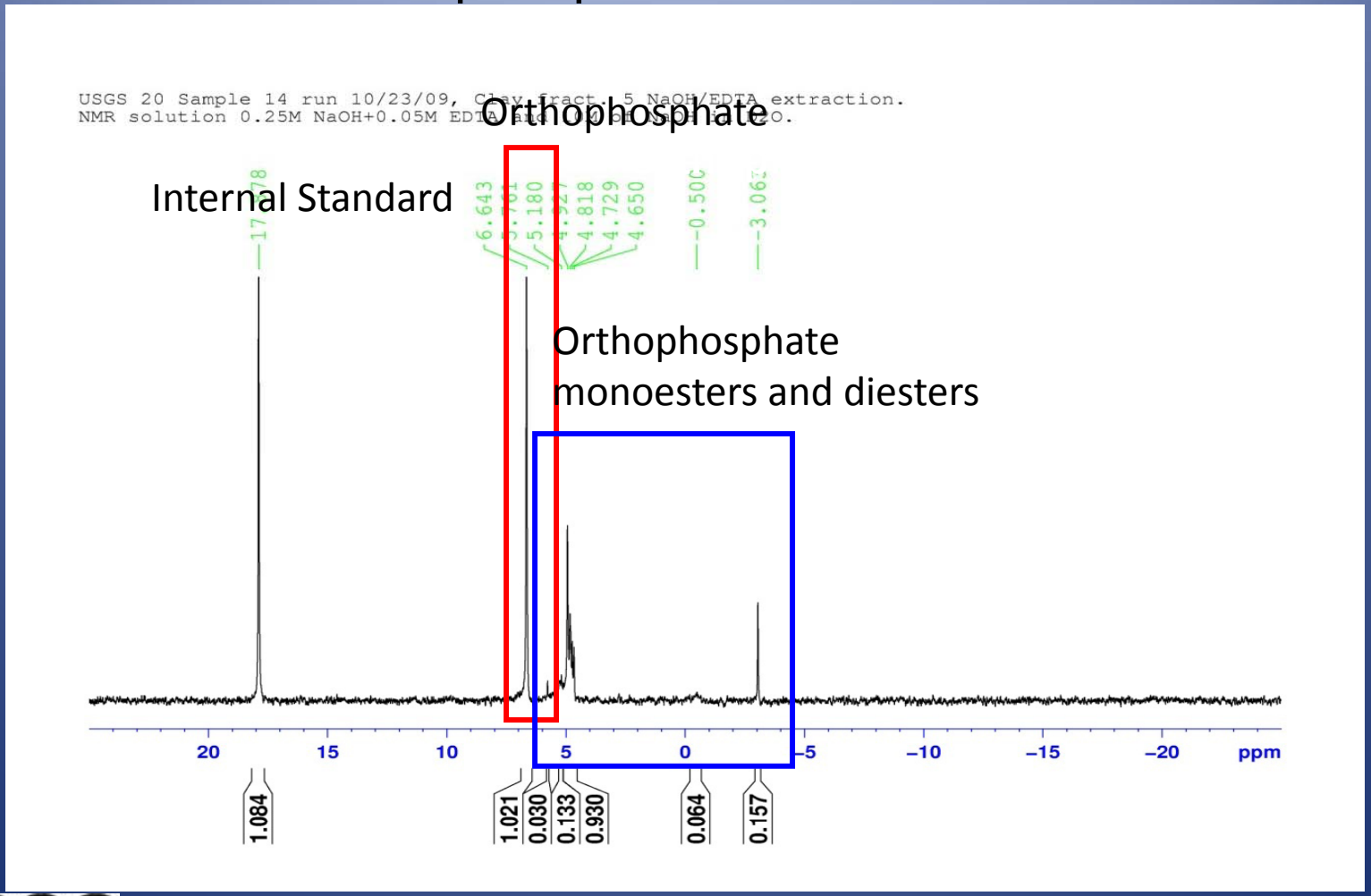
Extraction of ≥ 0.03 mm particles (smectite) from Site 22 sediment using NaOH/EDTA solution released orthophosphate and orthophosphate monoesters.



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The algae (AFA) in Upper Klamath Lake, OR, contain polyphosphates. Neither total phosphorus or dissolved reactive phosphate analyses would detect polyphosphates in water samples.

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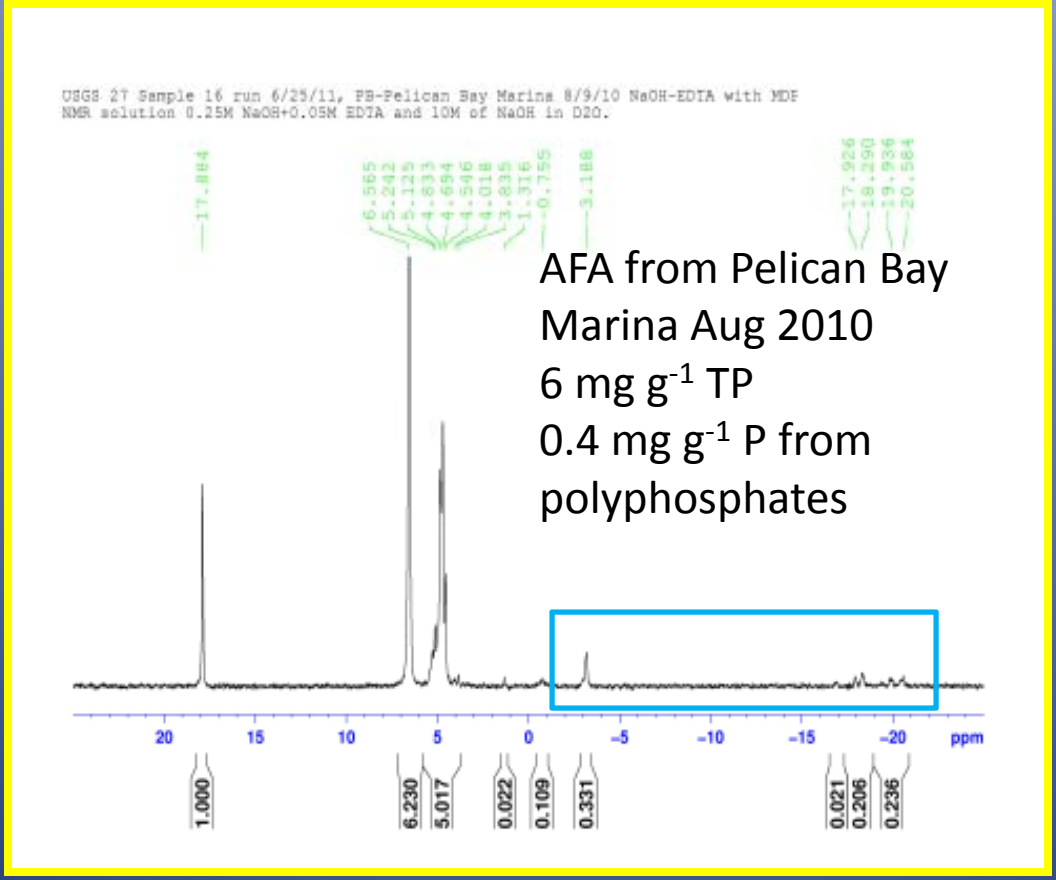

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Data for the calculations of biomass were collected by
KLAMATH TRIBES NATURAL RESOURCES DEPARTMENT

The data are listed in:
PROVISIONAL COMPILATION OF KLAMATH TRIBES UPPER KLAMATH LAKE WATER QUALITY DATA, 1990-2008

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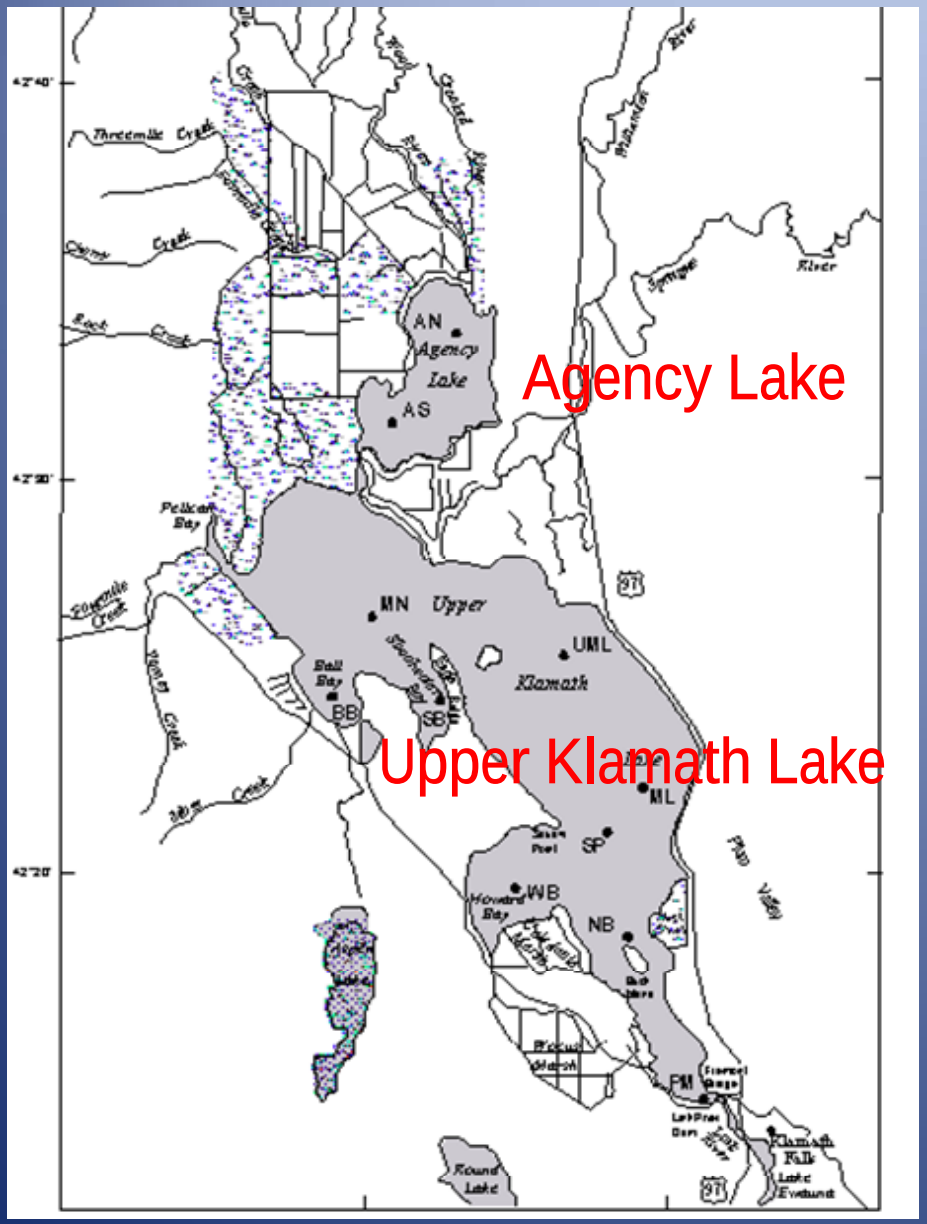

Agency Lake is sometimes considered part of Upper Klamath Lake. Two sites (AN and AS) from Agency Lake are included on the following slides.

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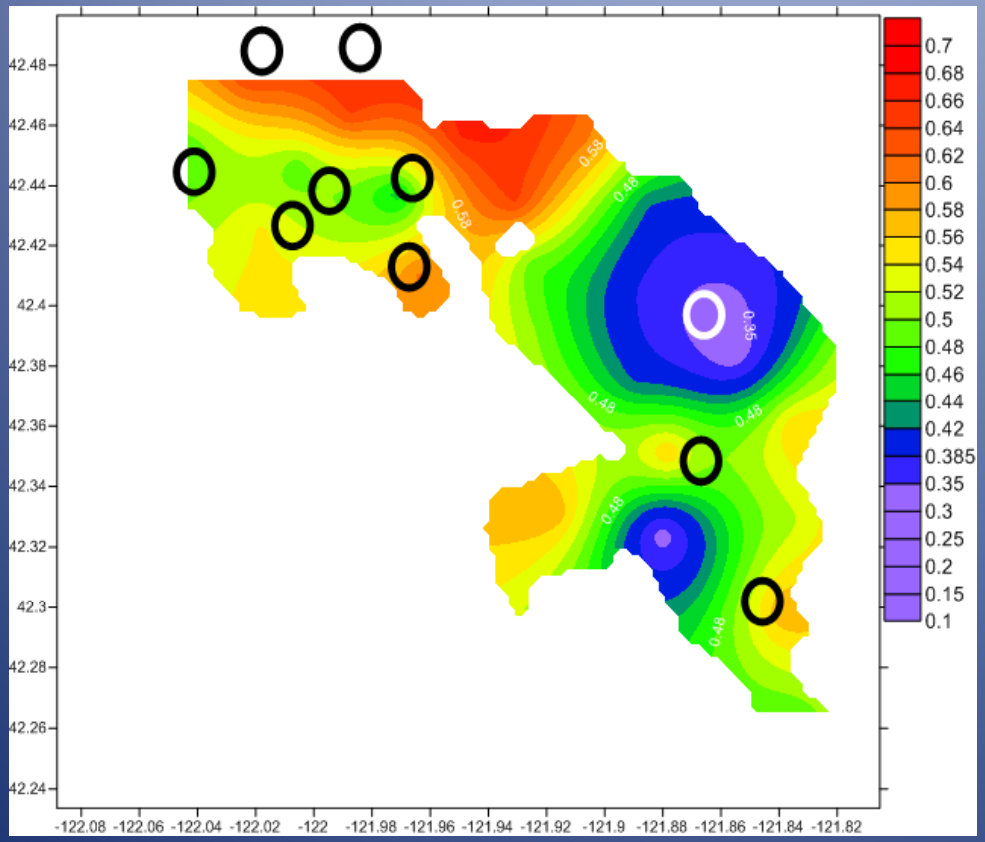
Outline of Upper Klamath Lake :



Contours show total phosphorus concentrations in surface sediment. Circles mark sampling sites where the ratios were greater than 25 for biomass values calculated using total phosphorus and Chla.

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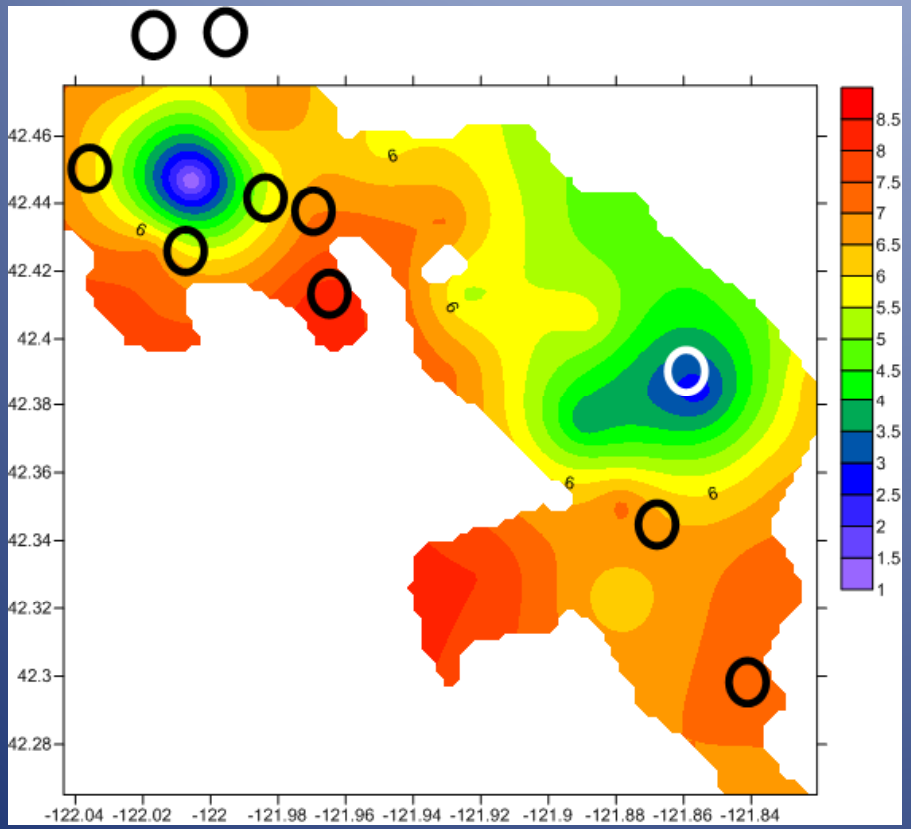
Outline of Upper Klamath Lake :



Contours show carbon concentrations in surface sediment. Circles mark sampling sites where the ratios were greater than 25 for biomass values calculated using total phosphorus and Chla.

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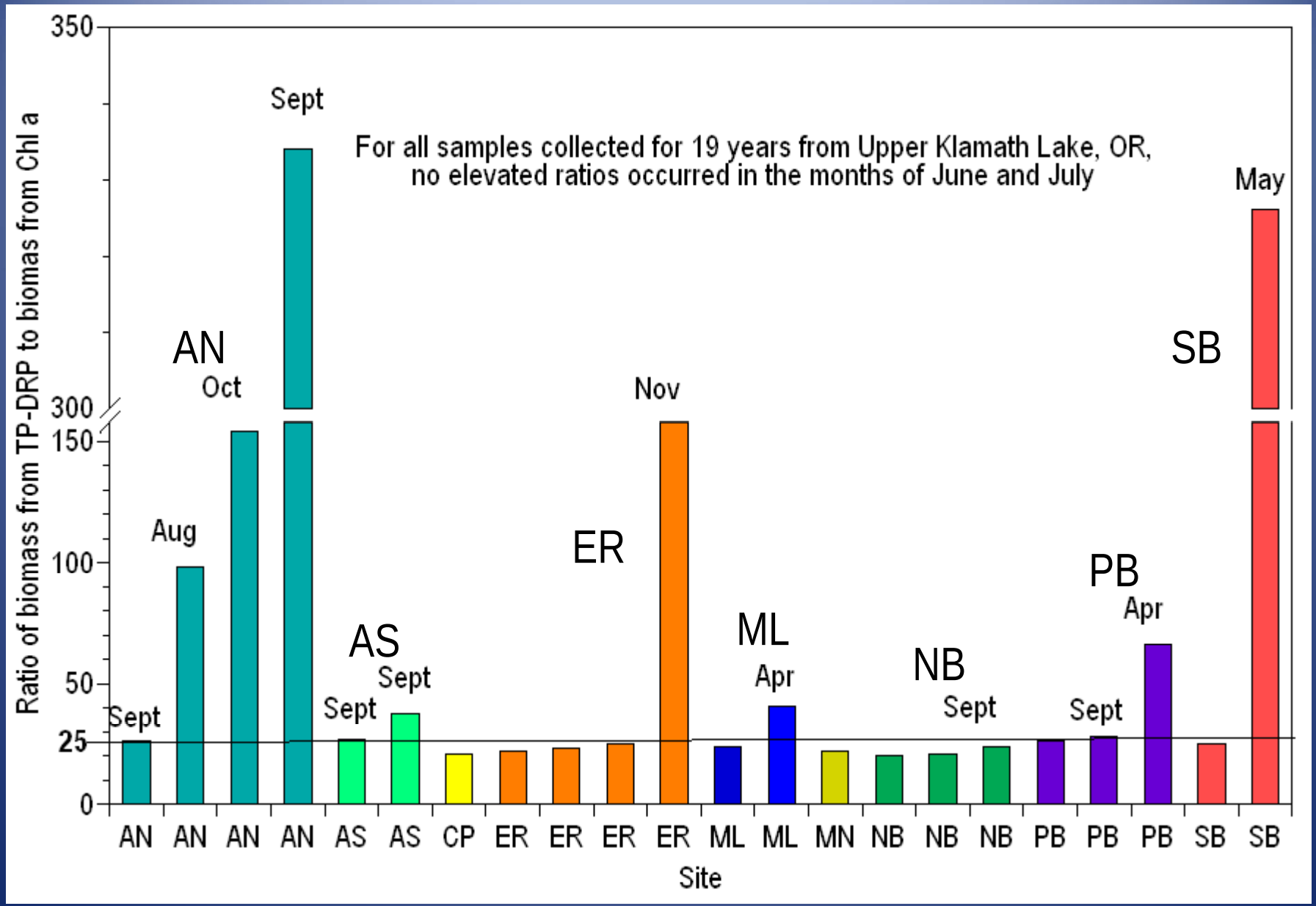

Calculated water column biomass: Total P/ Chlorophyll a

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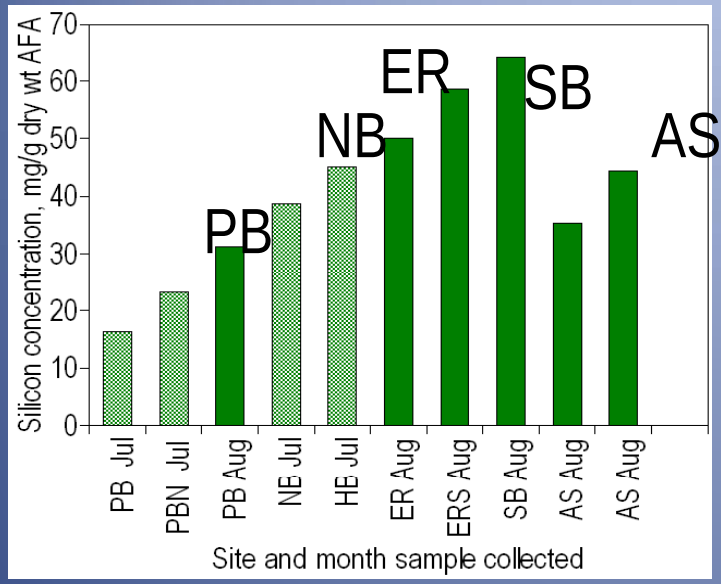
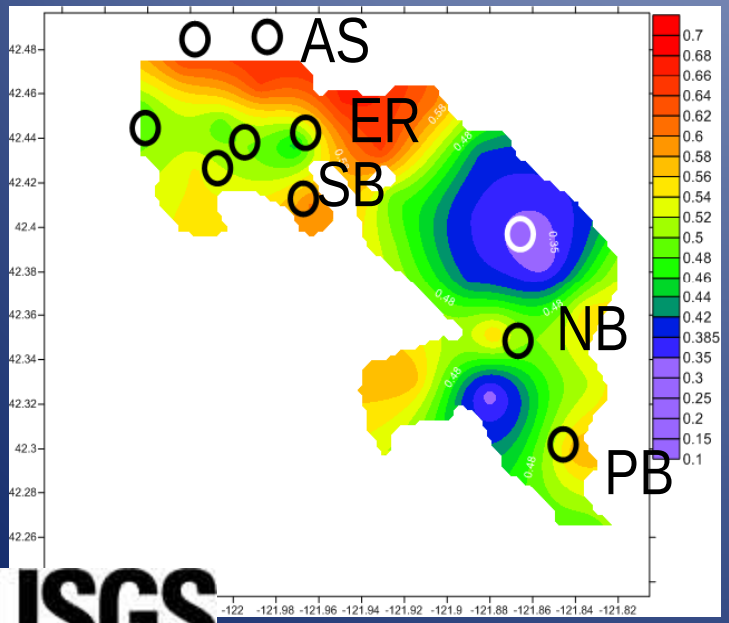


Silica concentrations in Aphanizomenon samples collected in 2010 from Upper Klamath Lake.



Circles on map indicate the locations where the ratio of calculated biomass from total phosphorus compared with calculated biomass from ChlA were > 25. Red color on the map indicates the areas of largest concentrations of phosphorus in surface sediment.

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Silica is a positive interference in the molybdate method for determination of phosphate.
Could silica be an interference in total phosphorus analyses in Upper Klamath Lake?

Is silica present in the dense algae from the UKL water column?

YES

Does silica dissolve during persulfate digestion of water samples ?

YES

If silica dissolves, is it in a form that is reactive with the molybdate reagent in the phosphate analysis?

YES

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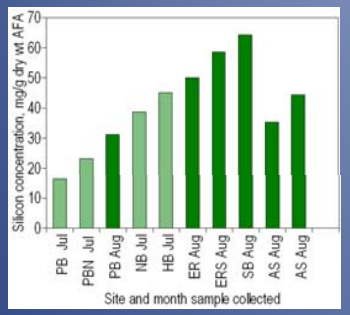

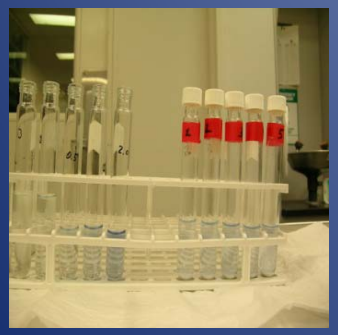

Can AFA in a whole water sample plus the natural concentration of Si in the water sample affect the concentration of total phosphorus in water samples determined using the persulfate digestion method? Uncertain.

<u>Observations:</u>

Response of silica in phosphate reaction

140 ppm Si ~ 0.3 ppm

Assume (a) 10 ppm Si in water

(b) Si in AFA ~ 60 ppm

(c) Amount of AFA (dry wt) in 1 liter of a water column sample ~ 0.5 g

The combination described above would add ~ 85 µg L^{-1} to total phosphorus concentration in water determined using persulfate digestion.

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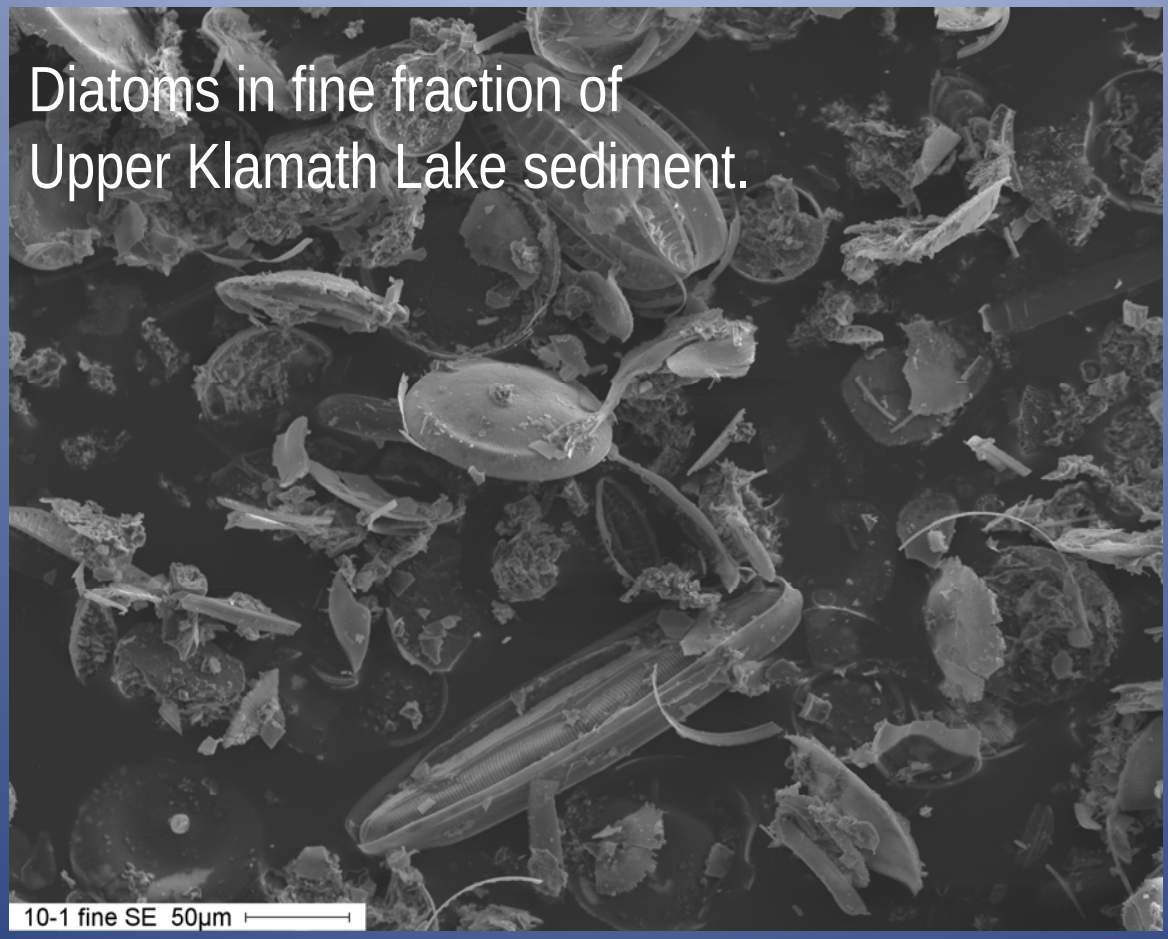
Diatoms in fine fraction of
Upper Klamath Lake sediment.



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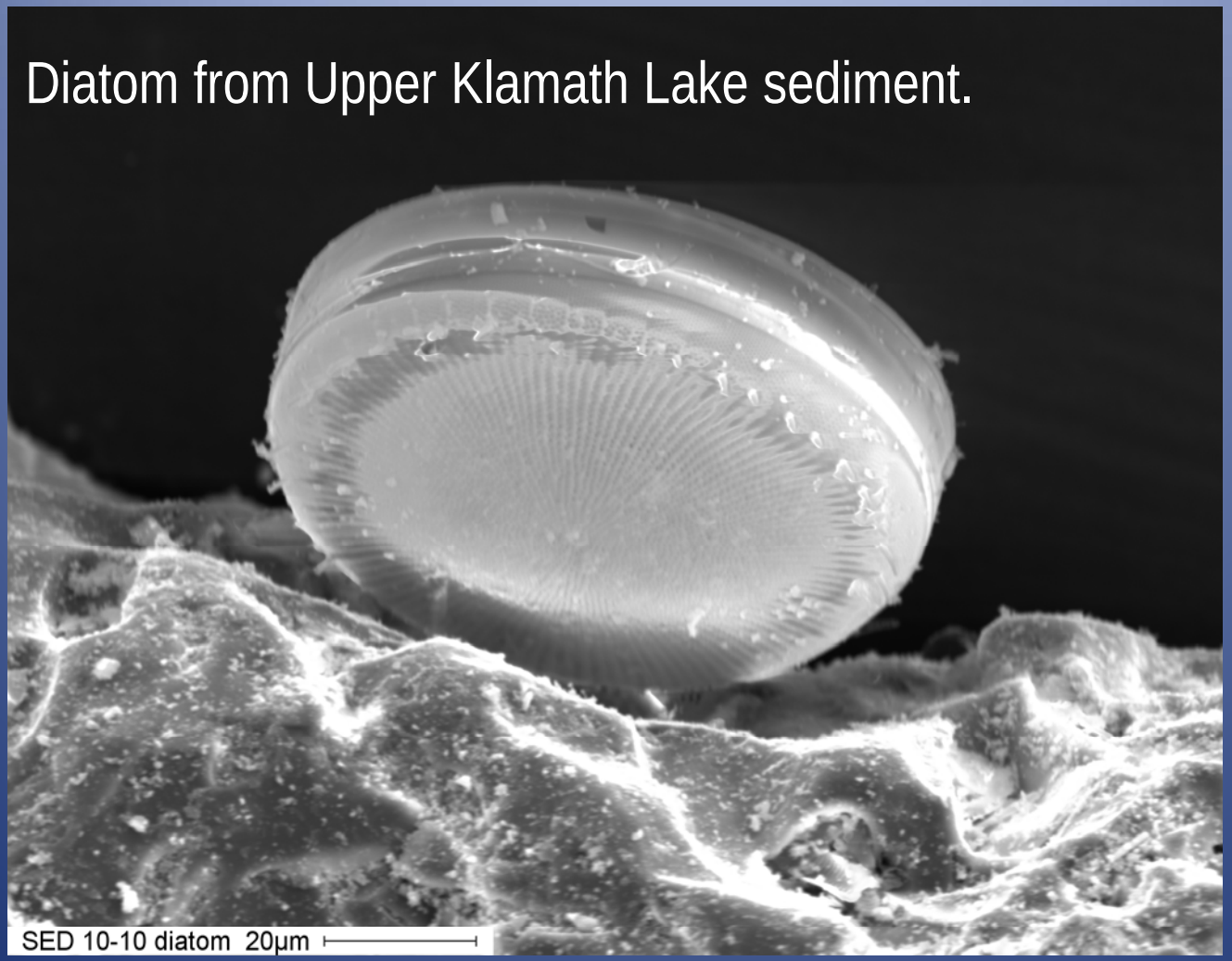
Diatom from Upper Klamath Lake sediment.



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