Alum doses and phosphorus responses in contrasting streams

THE UNIVERSITY OF WAIKATO
Te Whare Wānanga o Waikato

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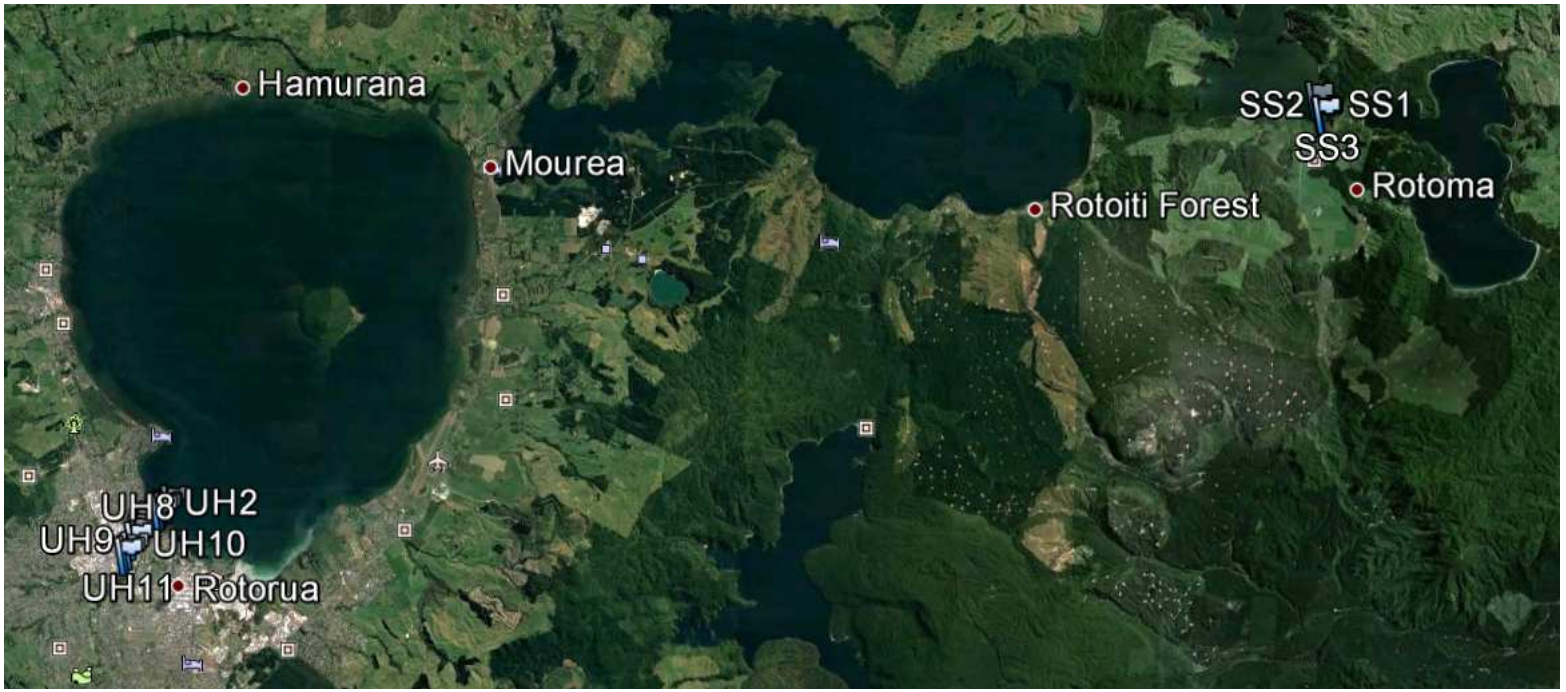
Study Sites


Hamurana
Mourea
Rotoiti Forest
SS2
SS1
SS3
Rotoma
UH8
UH2
UH9
UH10
UH11
Rotorua


Rotorua Core 2
Te Ruapeka Bay
UH1
Rotorua Core 1
UH2
UH3
UH4
Ohinemutu
UH5
UH6
UH7
UH8
Mangakakahi
UH9
UH10
UH11


Te Wairoa Bay
Rotoehu Core 1
SS2
SS4
SS3
SS5
SS10

What's happening with alum?

Aluminum sulfate $KAl(SO_4)_2 \bullet 12H_2O$ is soluble in water, and dissociates into aluminum ions and sulfate ions.

$KAl(SO_4)_2 12H_2O \rightarrow K^+ + Al(H_2O)_6^{3+} + 2SO_4^{2-} + 6H_2O$ (Dissolution)

The reaction of aluminum ion with water produces hydrogen ions, which makes the solution acidic.

$Al(H_2O)_6^{3+} + 3OH^- \rightarrow Al(OH)_3(H_2O)_3 + 3H_3O^+$ (Hydrolytic Reaction)

Reactions with P

$$Al^{3+}_{(aq)} + 3H_2O \longrightarrow Al(OH)_{3(s)} + 3H^+$$ (Gibbsite)

$$Al(OH)_3 + HPO^{2-}_{4(aq)} + H_2O \longrightarrow AlOH(HPO_4) \cdot H_2O_{(s)} + 2OH^-_{(aq)}$$
(Adsorption)

$$Al^{3+}_{(aq)} + PO^{3-}_{4(aq)} \longrightarrow AlPO_{4(s)}$$ (Varisite)

Methods

Water samples: three samples across cross-section of stream (pooled), 0.45 mm filtration, major anions, cations, alkalinity.

Sediments: Three samples (Ponar grab) across cross-section of stream, pooled and subsampled. Samples were dried in an oven at 60^{o}c for ~3 days and homogenised using a Ring Mill.

***Total Digestion*:** Aqua Regia
***Sequential Phosphorus Fractionation*:** The procedure followed was adopted from Psenner *et al.*[10]

NH_4Cl (labile fraction)
$NaHCO_3$, $Na_2S_2O_4$ (iron hydroxide bound)
NaOH (aluminium hydroxide bound)
HCl (mineral bound)

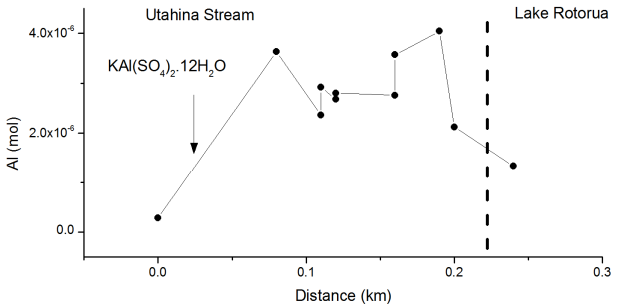
Summary: Water Quality

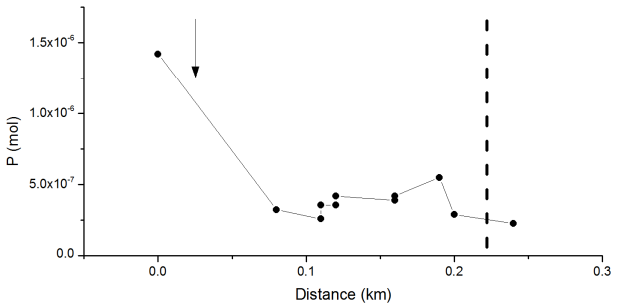
- UH (mildly alkaline ca. pH 8, low T) favours gibbsite. P removed by dosing, but adsorption likely to be weak/exchangeable due to high pH. This reinforced by coupling of dissolved Al and P in UH, implying release of P by dissolution of Al phases downstream. Vivianite ($AlPO_3$) not stable and this is consistent with stoichiometry.
- SS (mildly acidic ca. pH 6, high T, geothermal) favours vivianite. P removed by dosing, likely by AlPO4 formation. No coupling of Al and P in water indicating minimal re-release of P by dissolution of Al phases.

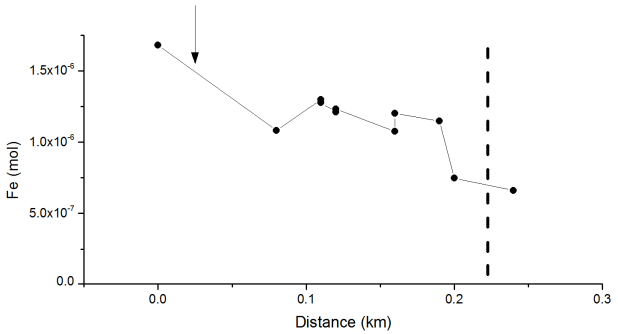
Summary: Sediments

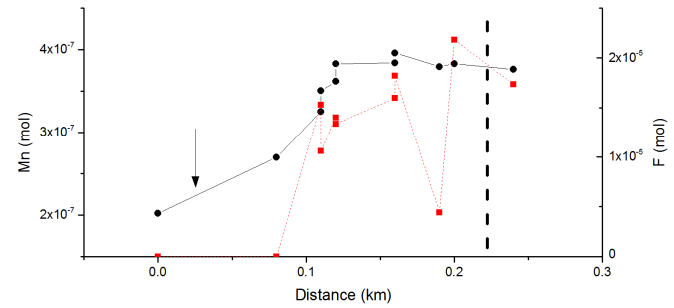
- UH sediments comparable weight %'s of Al and Fe and indeed both show high degree of correlation with P
- SS sediments had slightly higher Al than UH, but order of mag higher Fe, consistent with dominance of Fe oxyhydroxides in sediments. P nor As correlated with Al at SS, but correlated with Fe.
- These inferences from totals borne out by sequential extracts.

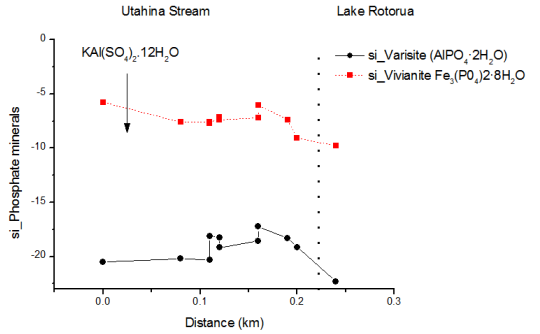
Utahina water chemistry and mineral saturation indices

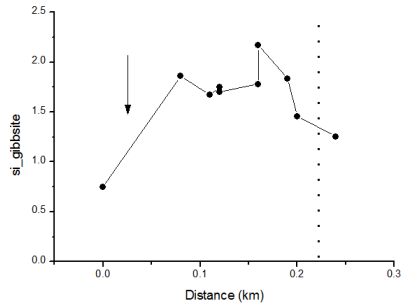


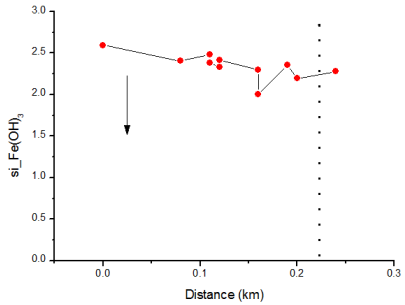


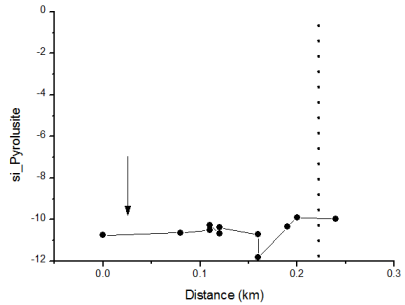




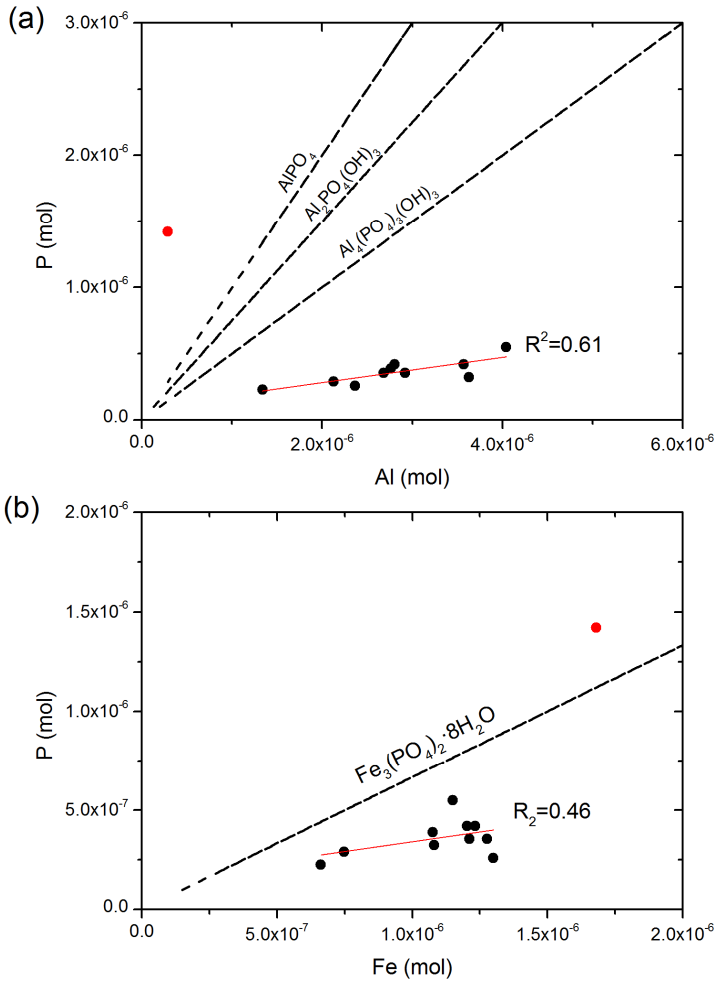




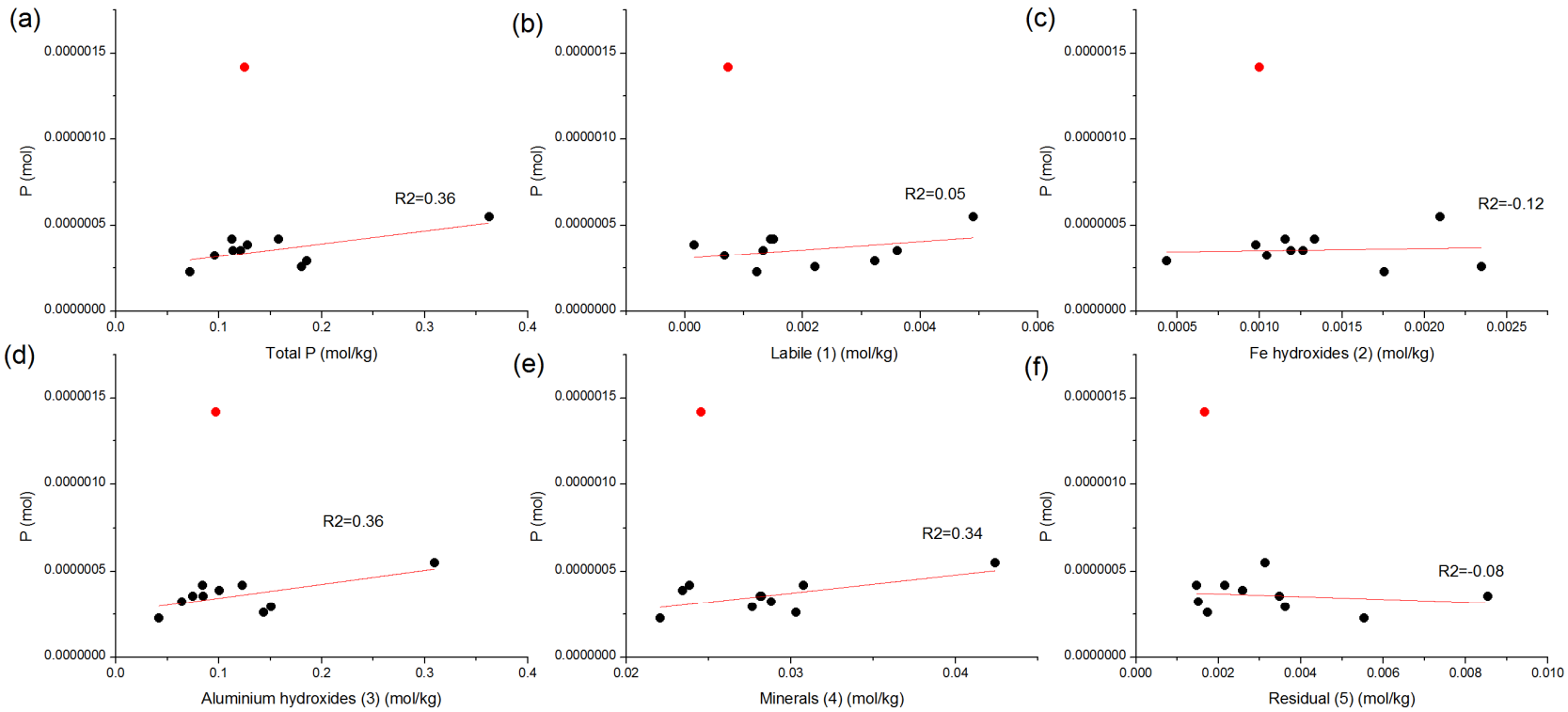




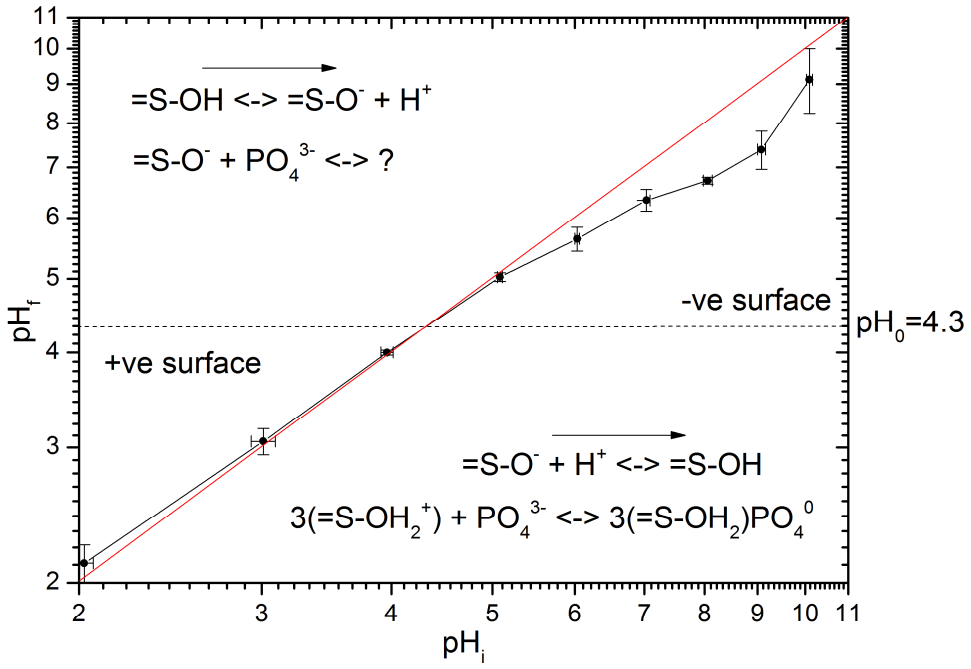
Correlations between P, Al and Fe (UH)



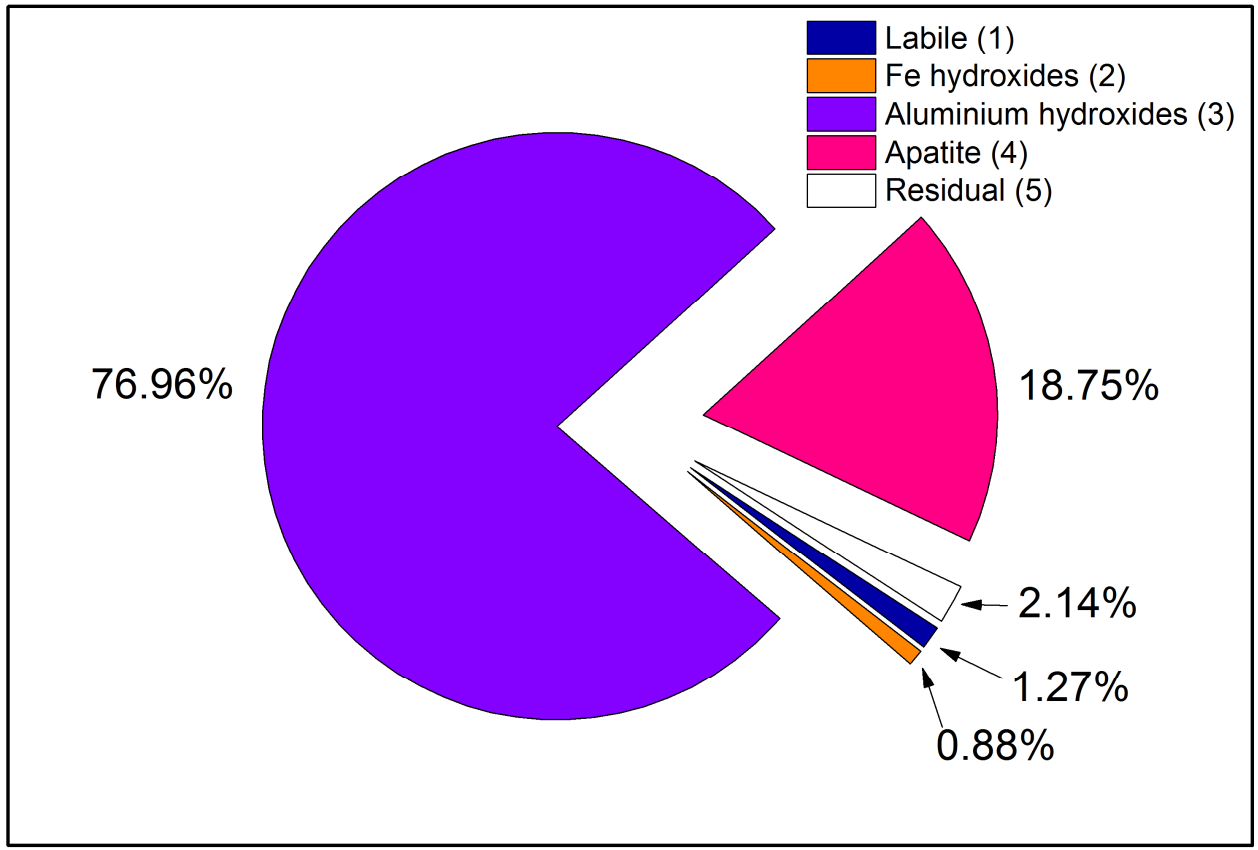
Correlations between P in water and sediment fractions (UH)



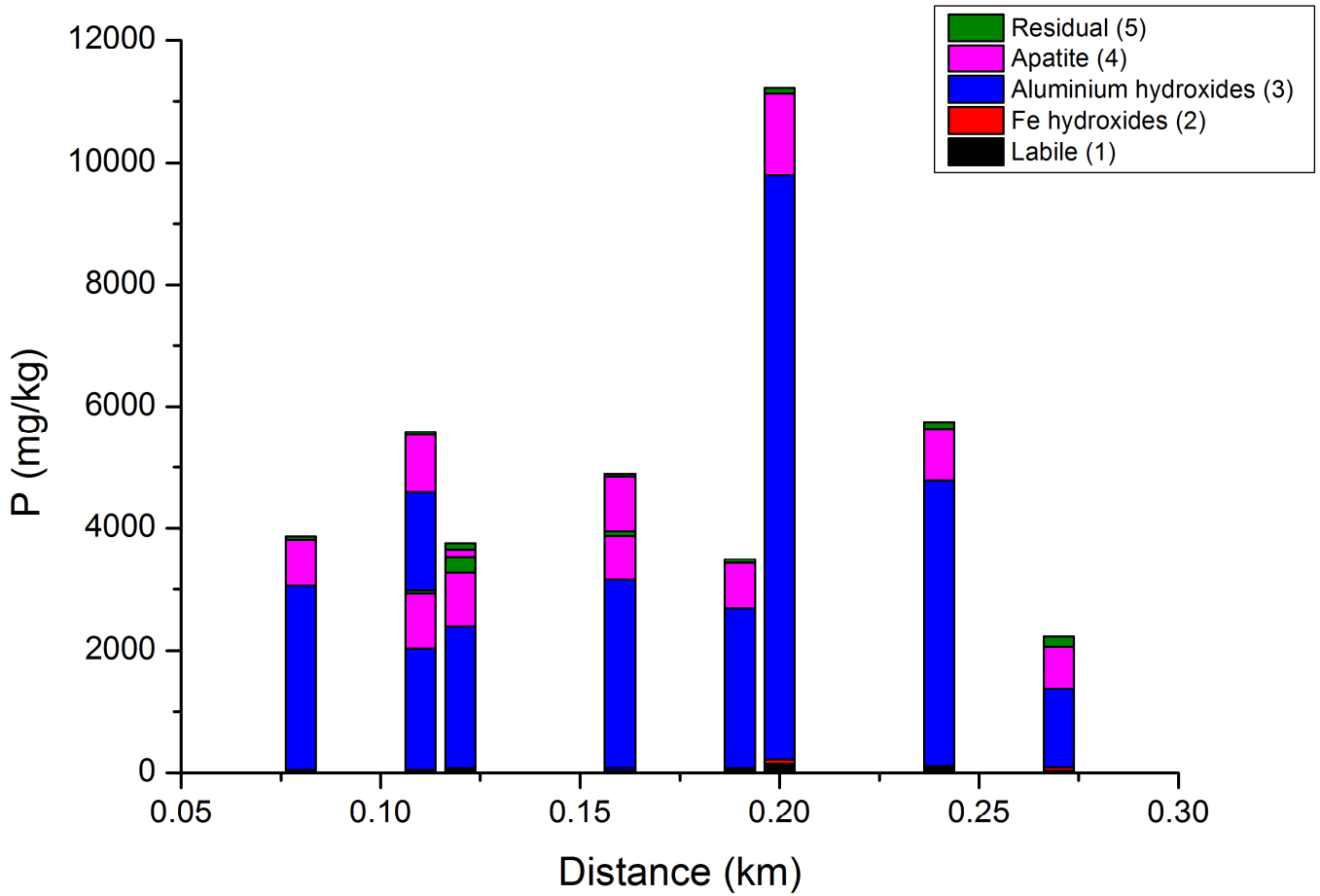
PZC experiment on $Al(OH)_3$



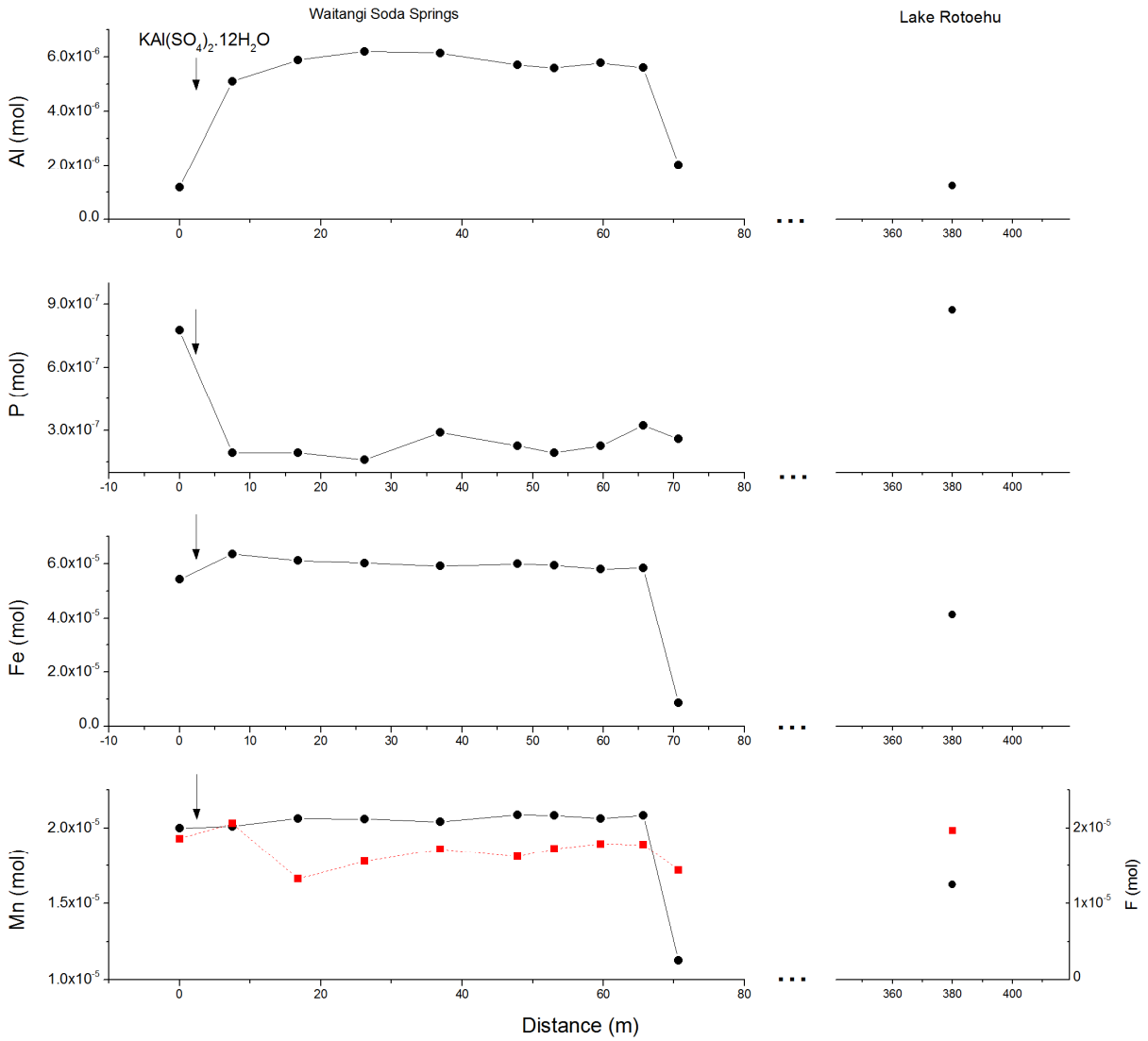
UH sediment P speciation



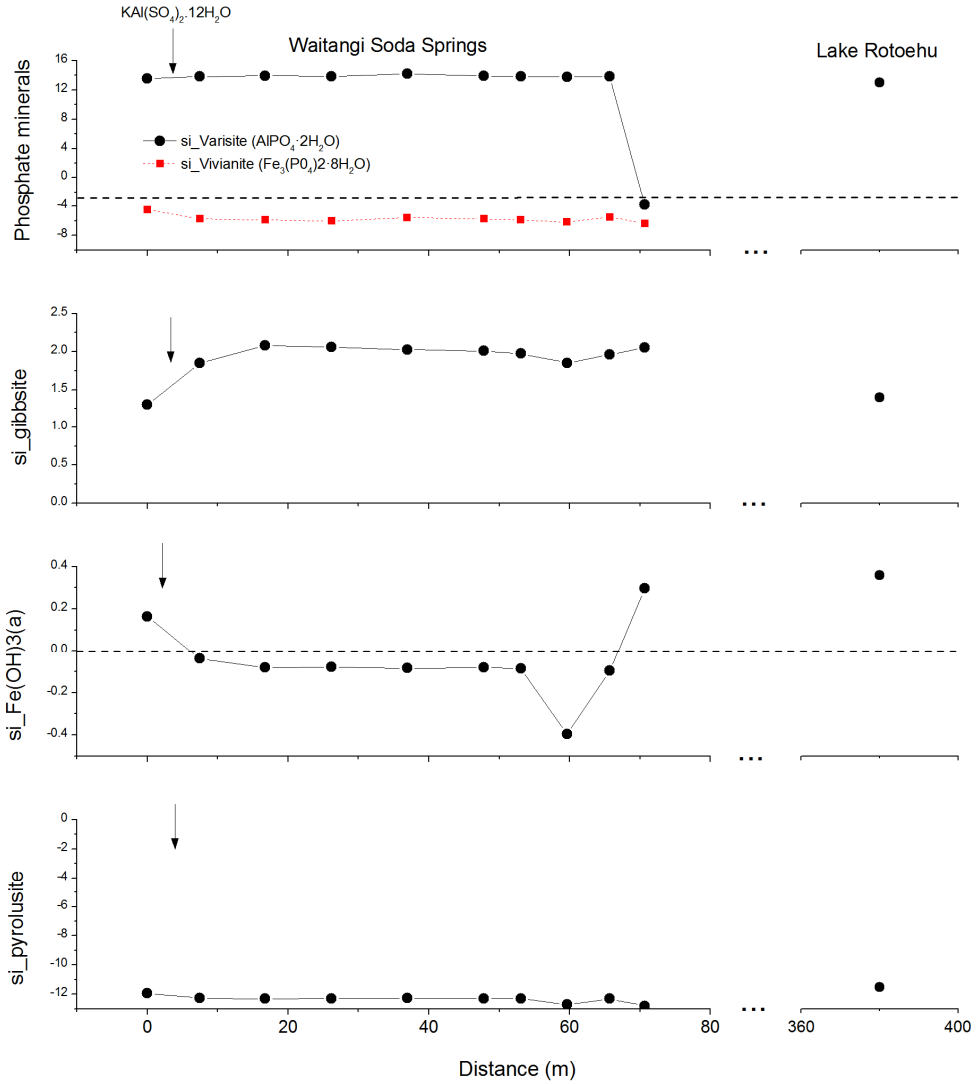
Longitudinal sediment P speciation (UH)



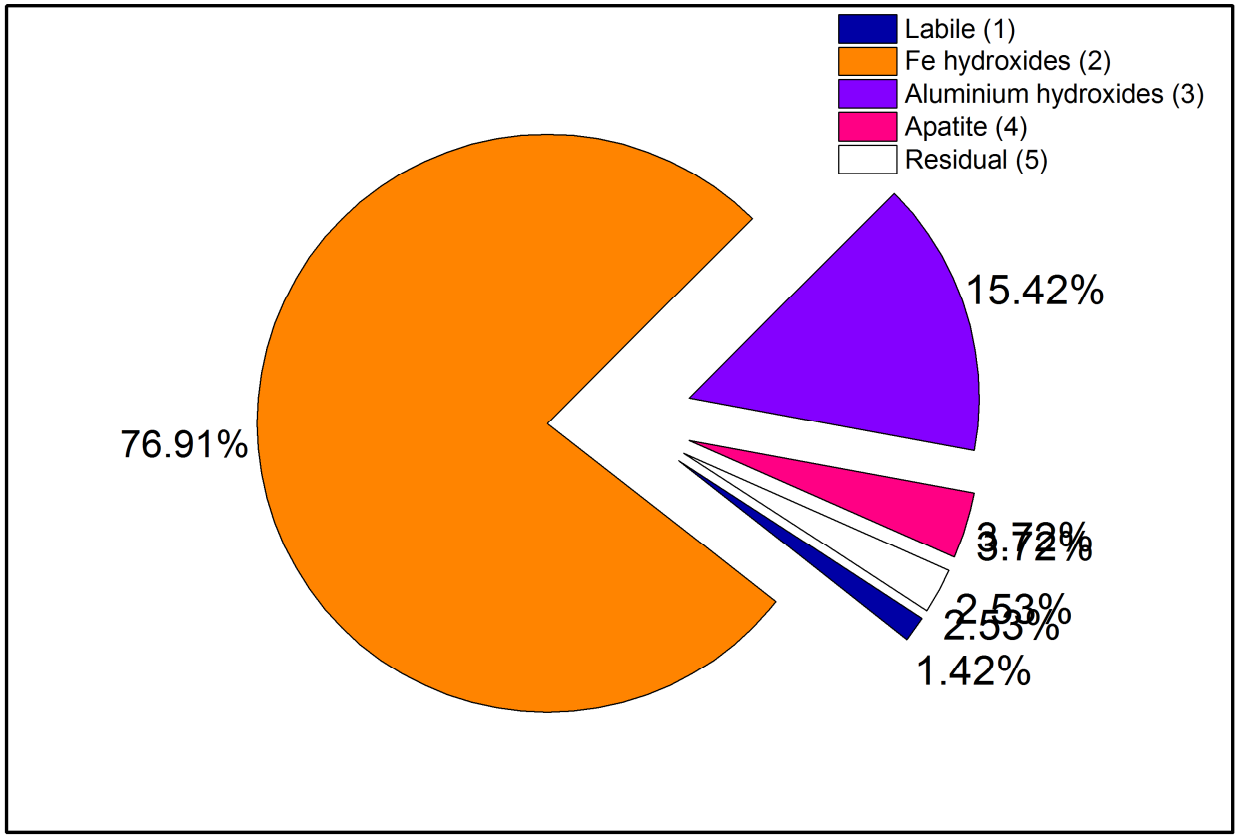
Waitangi SS stream chem



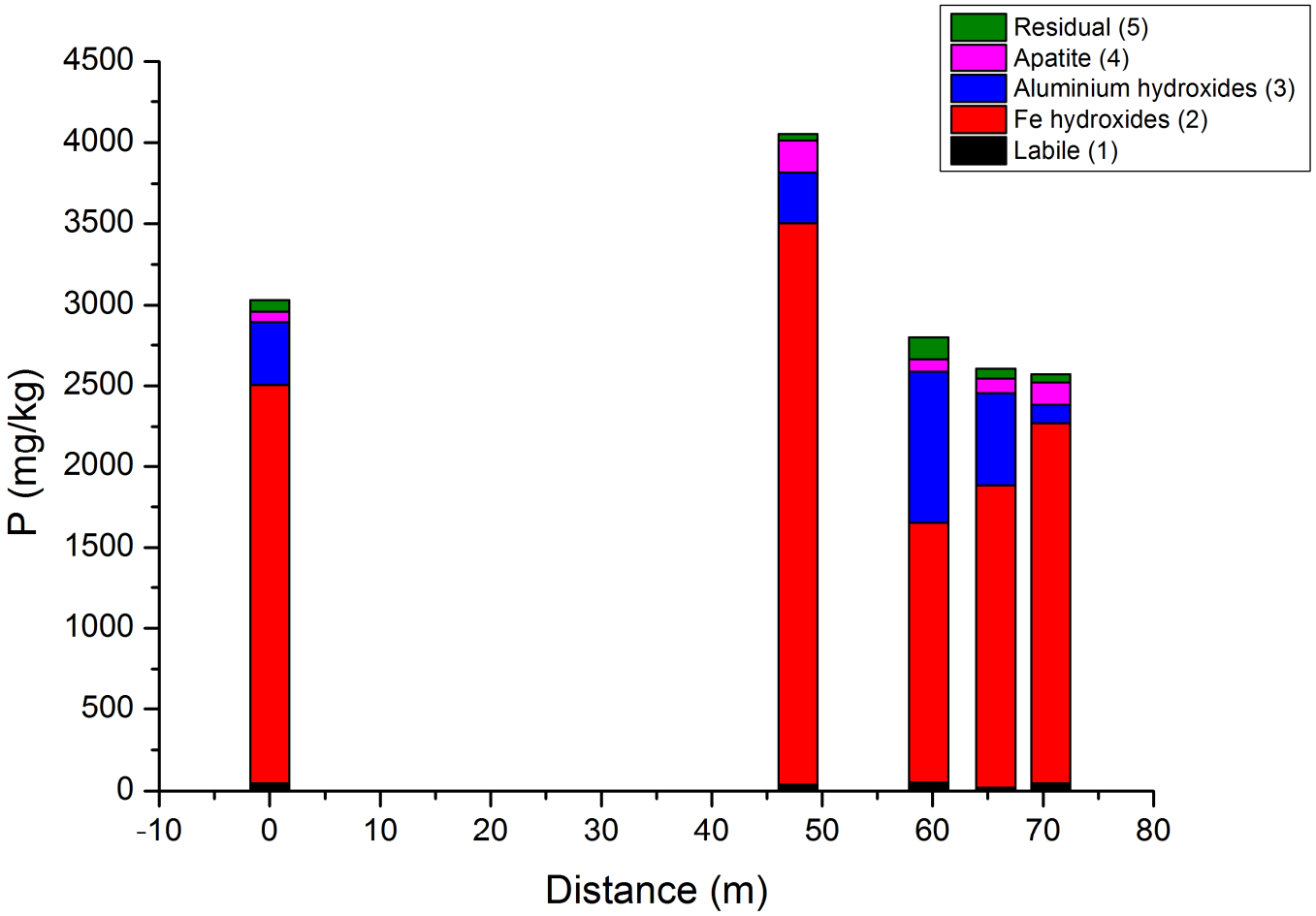
Waitangi SS mineral saturation indices



Waitangi SS sediment P speciation



Waitangi SS sediment P speciation



Take home messages

- UH and SS are geochemically very different
- Al doses and P responses are similarly distinct
- **UH:** Al hydroxides dominate, but are likely to weakly remove P. Re-release due to resuspension/dissolution/surface exchange.
- **SS:** $AlPO_4$ more chemically stable, but $FeOH_3$ dominate. Dosing may be effective, but multiple diffuse P inputs are a problem.