

# Predicting the degree of Cu, Pb and Zn adsorption to suspended particulate material in a lowland river system

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Minerals, diatoms and other components of suspended particulate material (SPM) in the water column of rivers, lakes and estuaries, have the ability to bind dissolved trace metals, thereby reducing their toxicity and influencing their fate. There are two principal agencies of dissolved metal removal by SPM; adsorption onto mineral or organic surfaces, and biological uptake, particularly by diatoms and algae. The degree of removal is an important consideration when assessing the environmental impacts of urban contaminants such as Pb, Cu and Zn. Removal processes need to be understood and quantified before reliable predictions can be made concerning the extent to which toxicity will be reduced and/or metals will accumulate in the sediments of a natural aquatic system.

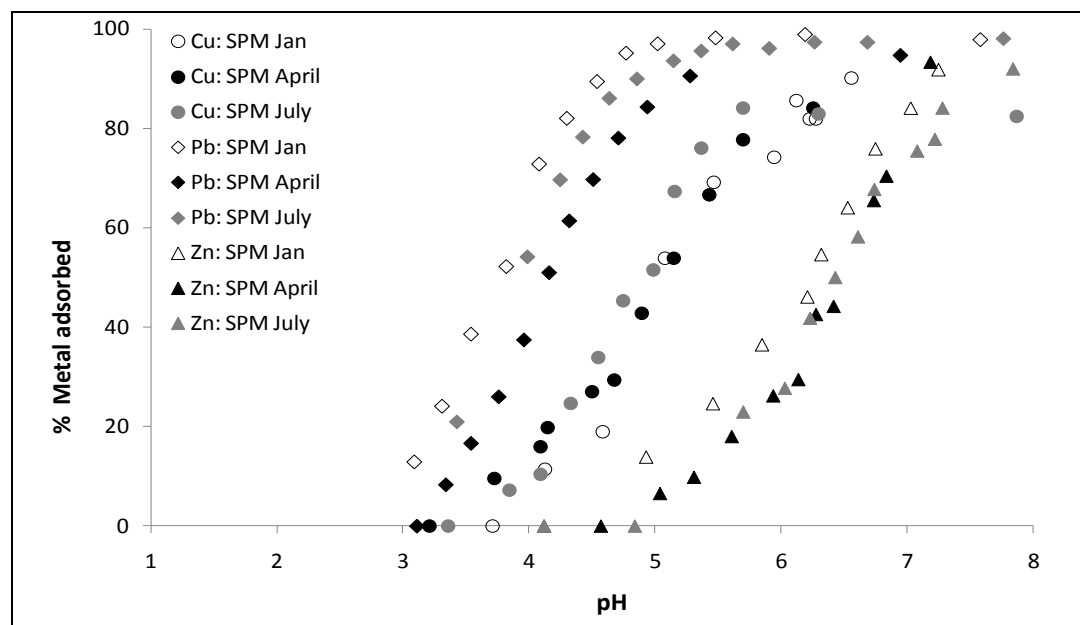
We have investigated the interaction of SPM and dissolved Cu, Pb and Zn in the lower Waikato River, a large lowland river in the North Island of New Zealand. Water quality monitoring data from the lower river was used, together with experimentally determined adsorption of Cu, Pb and Zn onto SPM collected from the river, sequential extraction of metals from SPM, and adsorption modelling, to identify important metal-SPM binding processes.

Water and SPM samples were collected monthly from Tuakau Bridge, over a 2-year period, and analysed for trace metals Fe, Mn, Cu, Pb and Zn using ICP-MS or GF AAS. SPM was collected onto pre-weighed 0.45  $\mu\text{m}$  Millipore cellulose membranes, and diatom and mineral components were identified using SEM. Larger samples of SPM were also collected at selected sites using ultrafiltration, some of which was freeze-dried for TOC analysis (CHN Analyser), measurement of surface area, use in adsorption experiments, sequential extraction and further mineralogical investigation (XRD and XRF).

Over the two years, significant seasonal variability in acid-soluble metal concentrations, and in SPM concentration and composition, in the river was observed, but little variability in other water quality parameters likely to affect metal concentrations. Low acid-soluble Cu, Pb and Zn concentrations in autumn corresponded to low SPM concentrations, under low river flow conditions. The SPM also changed in autumn from predominantly inorganic to organic material, with the lowest concentrations of Fe oxide (down to 3.8 wt%) and the highest concentrations of total organic carbon (up to 9.5 wt% TOC) and with abundant diatoms, particularly *Melosira granulata*, *Asterionella formosa* and *Fragilaria capucina*. Mass flux calculations confirmed that metals had been physically removed from the water column at this time.

Pb is predominantly adsorbed to SPM in the lower river (mean 71% adsorbed,  $n = 35$ ), whereas Cu and Zn are partly in the dissolved phase (mean 26% adsorbed for Cu, mean 47% adsorbed for Zn). The experimental adsorption of Cu, Pb and Zn onto freeze-dried SPM, collected from the river and resuspended in a 0.1NaNO<sub>3</sub>, showed that only Pb adsorption onto the SPM was significantly influenced by its composition change (Fig 1.1). Pb adsorption occurred more readily onto the Fe-rich SPM present in winter, while Cu and Zn adsorption onto the SPM was similar for the different seasonal SPM samples. Adsorption modelling used the geochemical speciation

model PHREEQC, assuming Fe oxide in the SPM to be the only adsorbing surface, with the characteristics of hydrous ferric oxide as specified in Dzombak & Morel (1990) and surface complexation constants for Pb, Cu and Zn as in Swedlund & Webster (2001). This reliably reproduced the Pb adsorption observed. However the degree of Zn and Cu adsorption was underestimated by up to 20%, indicating that additional adsorption surfaces, or other removal mechanisms, are important for these metals.



**Figure 1.1** Experimental adsorption of Cu (10 $\mu$ g/L), Pb ( $\mu$ g/L) and Zn (50  $\mu$ g/L) onto 100mg/L SPM collected from the river in summer (Jan), autumn (April) and winter (July), after the SPM had been freeze-dried and resuspended in 0.1m NaNO<sub>3</sub>.

Sequential extraction of freeze-dried SPM confirmed that Zn was consistently > 80% associated with Fe and Mn oxide phases, and Zn and Mn concentrations showed a positive correlation in the SPM. However, up to 46% of the Cu in SPM was associated with the organic phase, which is mainly comprised (volumetrically) of diatoms. The ability of live and dead diatoms to take up dissolved Cu from the water column was assessed by repeating the adsorption experiments described above, but using fresh hydrated (rather than freeze-dried) seasonal SPM, under light and dark conditions, and over 24 and 5 day periods. Hydrated SPM was a more effective adsorbent for Cu than freeze-dried SPM, but there was little evidence of Cu uptake during diatom growth.

We conclude that Pb binding to SPM is predominantly via Fe-oxide surfaces and can be reliably predicted using surface complexation adsorption modelling. Zn and Cu are also bound to Fe-oxide in the SPM, but removal from the water column is augmented by adsorption onto Mn oxide in the case of Zn and onto the organic surfaces provided by diatoms in the case of Cu.

## References

- Dzombak, D.A., Morel, F.M.M. (1990) *Surface Complexation Modelling: Hydrous Ferric Oxide*. John Wiley & Sons, New York.
- Swedlund P.J. and Webster J.G., (2001) Cu and Zn ternary surface complex formation with SO<sub>4</sub> on ferrihydrite and schwertmannite. *Applied Geochemistry* **16**, 503-511.