Provenance and fates of the REEs and heavy metals in the suspended particulate matter off Luzon shelf in the South China Sea

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The study establishes the provenance of the suspended particulate matter (SPM), collected in the upwelling area at a water depth of 1,200 m off Luzon shelf using sediment traps during eleven sampling periods. The shale-normalized REE patterns of the SPM correlate with those of the volcanoclastic sediments of the Amburayan and Abra Rivers in NW Luzon, establishing their mutual provenance. These river systems drain Cu mine areas.

Knowing their mutual sourcing, we tried to correlate the REEs and heavy metals with their host matrices to ascertain their fates. The REEs, known to be chiefly geogenic, do not correlate with the heavy metals, such as Zn (R^2 = 0.002), Pb (R^2 = 0.020), and Cd (R^2 = 0.085), which are mine-derived. Cu, on the other hand, correlates fairly with the REEs, but not with the other heavy metals.

Cd is hosted by the Mn oxides, whereas, Zn and Pb have strong affinity with the clay minerals, especially smectite. These heavy metals take on soluble form when released from their sources and favor matrices that bond them as adsorbed or exchangeable cations. In contrast, the REEs are associated with the lithogenics and the organic matter. The same association is exhibited by Cu with the lithogenics, which is largely controlled by the presence of chlorites.

Though mutually sourced, the above geochemical scenarios for the REEs and the heavy metals establish that they share only the same provenance but not geochemical behavior once they are released from their source rocks. When released anthropogenically by mine activities or, geogenically, by weathering, the heavy metals become significantly more available for uptake, whereas, the REEs are more strongly bound by their particulate hosts.

The reactivity of raw and incinerated mammalian bone in the presence of aqueous metals

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The production of meat generates a range of by-products including meat and bone meal, the use of which, in applications such as animal feeds, has become severely restricted, due to possible contamination by pathogens (e.g. BSE). The material has to be incinerated and then disposed of in landfills, unless other applications are found.

Raw bonemeal has been previously used in the remediation of metal contaminated soils [1]. Thermal treatment of this material to remove the organic matrix has been suggested in order to increase its reactivity and eliminate pathogens. The purpose of the work presented here was to investigate metal removal capacity of both incinerated and raw bonemeal with a view of a potential application of this waste by-product in wastewater/acid mine water remediation.

Raw and incinerated bonemeal at temperatures ranging from 725-850ºC (as supplied by industry – PDM Group) were reacted with 1000 mg/L solutions of Pb, Zn and Cu. Synthetic HAP was used as a control. Metals in solution were measured using ICP-AES while the solid residues were characterised using analytical SEM, FT-IR and XRD.

Synthetic HAP outperformed both raw and incinerated bonemeal in the removal of all metals except for Pb. HAP removed 95% Pb, 86% Cu and 80% Zn. Both raw and incinerated bonemeal removed 99% of Pb. However, Zn and Cu were only eliminated from solution by 60% by the raw bonemeal and by 18% for Cu and below 10% for Zn by the incinerated bonemeal. Metal phosphates formed as a result of Pb, Cu and Zn reaction with HAP, as indicated by SEM analysis. In samples of raw and incinerated bonemeal only phosphates of Pb were found.

Incineration of bonemeal at high temperatures (700-850ºC) reduces its removal capacity for Zn and Cu, indicating a different removal mechanism to that of Pb, which appears to be always by precipitation of Pb phosphates. Incinerated bone has a strong pH buffering capacity and thus may prove effective in remediation of acid mine waters – leaching columns tests are now carried out to investigate this further.

References

[1] Hodson, M.E., Valsami-Jones, E. and Cotter-Howells, J.D., (2000), *Environ. Sci. Technol.* **34**, 3501-3507.