Chemical fractionation of Pb and Zn and determination of Pb isotopes in deposited blast-furnace sludge

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Blast-furnace sludge is a waste of pig iron production and was deposited in large surface landfills. Since it contains high amounts of Zn and Pb it is of environmental concern. The first aim of this study was to investigate the solubility and binding forms of Zn and Pb in this industrial waste.

We performed a five step sequential chemical fractionation on 32 samples: (A) 1 M NH_4NO_3; (B) 1 M NH_4OAc, buffered at pH 5.4; (C) 0.2 M NH_4-oxalate-buffer, pH 3.25; (D) 0.1 M ascorbic acid + 0.2 M NH_4-oxalate-buffer, pH 3.25; (E) aqua regia.

The second aim was to determine the Pb isotope ratios of representative bulk samples (n = 10) and related fractions (n = 3) with MC-ICP-MS.

Total contents of Zn ranged from 15, 720 to 86, 400 mg kg^{-1} (median 30, 360 mg kg^{-1}) and from 1, 420 to 19, 510 mg kg^{-1} (median 9, 835 mg kg^{-1}) for Pb. The proportion of the mobile fraction (A) ranged from 0.09 to 2.11% (median 0.26%) for Zn and from 0 to 0.3% (median 0.04%) for Pb. For the easily mobilized fraction (B) we obtained a range from 2 to 23% (median 7%) for Zn and from 5 to 68% (median 19%) for Pb. In contrast to Zn, which is largely associated (63 to 96%, median 85%) to fraction C, i.e. poorly crystalline iron oxides, Pb is much more distributed over the fractions D (4 to 26%, median 18%), i.e. crystalline iron oxides, and E (9 to 64%, median 39%). Sequential fractionation indicates that Zn and Pb are bonded differently in blast-furnace sludge, resulting in a contrasting mobility of these two elements.

The Pb isotope ratios of the bulk samples are clearly distinguishable and ranged from 18.088 to 18.634 ($^{206}Pb/^{204}Pb$), 15.595 to 15.670 ($Pb^{207}/^{204}Pb$) and 37.709 to 38.402 ($^{208}Pb/^{204}Pb$). In contrast, the isotope ratios of the different fractions show little variation, especially the ^{207}Pb-^{204}Pb ratios overlap within analytical uncertainty. No mass-dependent fractionation was observed between the different fractions, because variation is higher for $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ than for $^{208}Pb/^{204}Pb$.

Seasonal variation in the clay mineral and Sr-Nd isotopic compositions of the suspended sediments of the lower Changjiang River at Nanjing, China

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The clay minerals and Sr-Nd isotope signatures have been extensively used to characterise the provenance of detrital sediments and wheathering processes. The Changjiang (CR) River is one of the largest rivers in the world. The CR originates on the Tibetan Plateau and enters the East China Sea. A large part of the CR Basin has a subtropical monsoon climate. To examine seasonal changes in clay minerals and Sr-Nd isotopic compositions of the CR, suspended sediment (SS) samples were collected monthly for two hydrological cycles in Nanjing city.

The results indicate that the concentration of CR SS ranges from 11.3 to 152 mg/L and is highly correlated to the rate of water discharge with a higher concentration in flood season. Illite dominates the clay minerals of the CR SS, followed by chlorite, kaolinite and smectite. Illite and kaolinite show distinctly seasonal variations; SS has more illite and less kaolinite contents during flood season than the dry seasons. The illite chemistry index and crystallinity as well as kaolinite/illite ratio all indicate intense physical erosion in the upper CR basin during the flood season.

The Sr-Nd isotopic compositions (silicate fraction) also show distinctly seasonal variations. The results indicate that the $^{87}Sr/^{86}Sr$ ratios of CR SS ranges from 0.725352 to 0.738128, and the εNd (0) values ranges from −10.55 to −12.29. The relative decrease in $^{87}Sr/^{86}Sr$ ratios and increase in εNd (0) values during the flood season can be interpreted to reflect an increasing in the mechanical erosion rate in the upper basin and contribution of more radiogenic Nd and non-radiogenic Sr to the suspended load in flood season.

The Sr-Nd isotopic compositions correlate well with the clay mineral associations, indicating that the seasonal variations primarily reflect the controls of provenance rocks and erosion between different sub-catchments. Furthermore, these signatures can be now used to decipher past discharge and flow regimes of the rivers from sediment cores offshore.