Divergent behaviour of dissolved cobalt and manganese in freshwater aquatic systems; influence on particle and colloid adsorption

A. Albrecht   EAWAG, Überlandstr. 133, CH-8600 Dübendorf, Switzerland
L. Sigg
H. Xue

V. Lazarev   SPSTU, St. Petersburg, Polytechnicheskaya, 29, 195251 Russia

The transition from high temperature geochemical to low temperature biogeochemical systems forces cobalt to abandon its siderophile behaviour reflected by the association with Ni. Its pathways in this new world have been described mostly by adsorption to Mn oxy-hydroxides (Means *et al.*, 1978) and complexation with dissolved organic substances (Killey *et al.*, 1984). The preference of Co in aquatic systems to adsorb either to Mn bearing phases or to remain in solution in the form of organic complexes is essential for modelling the behaviour of ^{60}Co, an important waste products in the nuclear industry. We have used radionuclides of Co and Mn, discharged by nuclear installations, to elucidate convergence and divergence of their behaviour. Constrained to sites downstream of Swiss nuclear installations, from where the radionuclides ^{60}Co and ^{54}Mn are discharged, we will present in-situ results for rivers and aquifers and laboratory results carried out with river water. Using a combination of particle and colloid separation with fractionation of the dissolved phases by resin chromatography, the chemical forms of Co and Mn are evaluated. The results strengthen the applicability of equilibrium based chemical speciation models for natural systems.

Co and Mn on suspended particles, on colloids and 'in solution'

The difficulty of working with stable metals can be illustrated by plotting the total Co concentration of suspended particles and sediments collected in the Aare and Rhine below the Swiss nuclear reactors as a function of total Ni and Mn. The correlation between Ni and Co is stronger ($R^2 = 0.88$) than the correlation between Mn and Co ($R^2 = 0.73$), indicating that the geochemical imprint overwhelms the possible correlation between Mn and Co in adsorption

processes in aquatic systems. Using radionuclides from waste water discharges of nuclear reactor allow an assessment of the biogeochemical behaviour of Co and Mn, which is independent of a geochemical overprint. Knowing the ^{60}Co/^{54}Mn ratio in waste waters and comparing them with the same ratio in particles collected after different coordinated discharges below the nuclear power plant Mühleberg indicate the stronger preference of Mn for the particulate phase (Fig. 1). In all samples the raw waste water had ratios significantly higher than what was found in suspended particles.

The colloidal fraction obtained by cross-flow filtration with a nominal cut-off of 5000 Dalton, is for both metals relatively unimportant, and represents only in a few cases more than 10 % of the total. To obtain further information on the fraction that passes both centrifuge and cross-flow filtration, ion exchange tests were carried out using both cationic and anionic BioRad resins (Dowex$^®$, 50W-X8, H$^+$
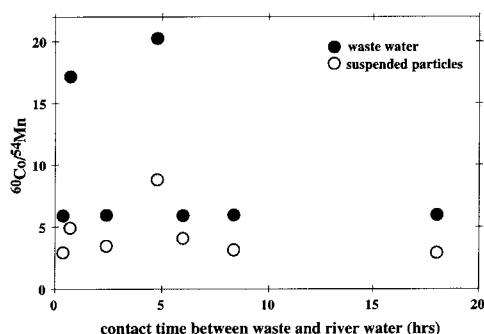

FIG. 1. Comparison of ^{60}Co/^{54}Mn measured in raw reactor waste water and on suspended particles (> 0.5, res. 1 µm, separated by continuous flow centrifugation or in-situ filtration) illustrates the relative preference of Mn compared to Co for adsorption to particle surfaces.

TABLE 1. Speciation of radionuclides in filtered reactor waste water on the basis of BioRad resins (values represent % of total activity)

	Anionic resin	Anionic eluate	Cationic resin	Cationic eluate
^{60}Co	10−60	20−90	75-100	0−15
^{54}Mn	0−15	80−90	100	0

form; AG$^{®}$, 1-X8, Cl^{-} form, both 100−200 mesh). For the dissolved fraction of the pure waste water, the cationic resin held back 100% in most cases. On the anionic resin only traces of ^{54}Mn were measured, whereas for ^{60}Co up to 60% were found (Table 1).

For waste water in contact with river water the same trend is observed. Of the dissolved fraction, ^{54}Mn was found entirely on the cationic resin, whereas the cationic fraction of ^{60}Co dropped significantly with a related increase in the anionic fraction (Table 2).

Discussion

These results shed further light on the mobility of cobalt in aqueous systems. Enhanced complexation leads to a reduced adsorption tendency. These findings confirm the observation of Killey et al. (1984) and Qian et al. (1998), who evaluated anionic complexation of ^{60}Co and stable Co in ground water and surface freshwater. The exact nature of the complexing ligands can not be derived from resin experiments because of their insufficient specificity. The tendency of radiocobalt to remain both on the cationic and anionic resins, with a total significantly larger 100% indicates that some weak anionic complexes might break down in the cation exchanger and would thus be retained by both. Ligands responsible for Co complexation must, to a strongly varying proportion, already exist in the reactor waste water, but their importance clearly increases in natural rivers. For Mn the loss of approximately 20% might relate to a species not captured by any of the 4 separation methods applied. The large variance in K_D, related to differences in the concentration of coarse particles, illustrates the difficulty of K_D interpretation.

The correlation of Mn and Co in biogeochemical systems, strongly suggested in the literature seems to be related mostly to the Mn redox cycle and breaks down under oxygenated conditions, which usually prevail in rivers, oligotrophic lakes and unpolluted aquifers. In these systems the tendency of Co to react with dissolved organic substances explains its divergence from Mn. The reduction in particle adsorption due to enhanced complexation can be seen by the presence of ^{60}Co in Swiss aquifers with important Aare or Rhine infiltration and by the transport across lakes and reservoirs with efficient particle scavenging. It can be modelled based on chemical equilibrium, taking into account the conditional stability constants (log K) of natural ligands ranging between 9.5 and 11.6 and ligand concentrations [L] between 1.4 and 7.6 nM as measured by Qian et al. (1998) for Swiss aquatic systems.

References

Killey, R.W.D., McHugh, J.O., Champ, D.R., Cooper, E.L. and Young, J.L. (1984) Environ. Sci. Technol., **18**, 134−57.

Means, J.L., Crerar, D.A., Borcsik, M.P. and Duguid, J.O. (1978) Nature, **274**, 44−7.

Qian, J., Xue, H., Sigg, L. and Albrecht, A. (1998) Env. Sci. Technol. in press.

TABLE 2. Speciation of radionuclides in 200 l Rhine water samples after 2 (A) and 4 (B) days contact time between waste and river water (values represent % of total activity)

(A)	Particles > 0.45 μm	Colloids > 5000 Dalton	Cationic resin	Anionic resin	K_D (l kg^{-1}, cut-off 0.45 μm)
^{60}Co	15	4	48	35	45000
^{54}Mn	28	4	38	0	97000
(B)					
^{60}Co	17	3	50	30	28000
^{54}Mn	36	5	35	0	78000