

Trace Metal Pollution in the Scheldt River and Sediment Enrichment of Metals

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Introduction: Trace metals can enter the aquatic environment through surface runoff from impermeable surfaces in urbanized areas, direct discharge of industrial wastewater, groundwater leakage, atmospheric deposition and erosion of contaminated soils (Luoma and Rainbow, 2005). Once entered the aquatic system, trace metals can be transported rapidly to the river mouth or bind and accumulate in large amounts to freshwater and marine sediments. In the aquatic environment sediments can act as an important sink for metals and metalloids, representing a large amount of metals in potentially bioavailable and toxic form. In an attempt to relate sediment geochemistry to the onset of metal toxicity in anoxic sediments, Di Toro et al. (1990) formulated the SEM-AVS toxicity model. This model predicts that when, on a molar basis, AVS concentrations in sediment exceed SEM concentrations (SEM-AVS<0), all metals will be bound to sulfides and the sediment pore water is considered as non toxic. In contrast, when the sediment contains an excess of SEM (SEM-AVS >0), metals will be released into the sediment pore water and become potentially toxic to the aquatic life, if they are not bound by other sediment fractions. Discharge of untreated domestic and industrial waste in many European rivers resulted in low oxygen concentrations and contamination with trace metals, often concentrated in sediments. Under these anoxic conditions, the formation of insoluble metal sulfides is known to reduce metal availability. So, the metal availability and concentration levels at the Scheldt river sediments were researched in this work.

Methods: The Scheldt estuary is a turbid, macrotidal and eutrophic system (Meire et al., 2005) which gets a considerable large input of trace metals (Baeyens et al., 2005). In this study area, three sampling sites were selected and in July 2012, water samples and sediment core samples were collected from a flat area in front of Lippenbroek; another flat area, Balloi and one more flat area through the Scheldt river. Three sediment core samples with 10 cm. depth were taken from each location and slices of each core as 0-5 cm. and 5-10 cm. were analyzed for routine and metal measurements. Routine water quality parameters (i.e. PO₄-P, NO₂-N, NO₃-N) and sediment quality parameters (i.e. loss on ignition (LOI), pH, total p & N) were analyzed at each sample. Hot block digestion was used for total sediment metal concentration analysis. Digested sediment samples were analyzed using ICP-AES for total metal analysis (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn). Further work was also carried for sediment AVS measurements. AVS was extracted from wet sediment using the purge-and-trap method and the

extracted amount of sulfides were measured with an ORION 96-16 ion-selective sulfur electrode (De Jonge, 2012). Analytical accuracy was verified by the use of blanks and certified reference materials both for sediment (CRM 320) and water analysis.

Results: The water quality of the Scheldt river was in the range of (0.16-0.26) mg PO₄⁻³ - P / l, (0.15-0.26) mg NO₂⁻ - N / l, (3.66-4.06) mg NO₃⁻ - N / l and 9.37 - 11.51 mg SiO₂ / l. The routine sediment analysis results of the samples were such that : pH 7.50-8.27, LOI (loss on ignition) 1.2 -3.4 %, P_{total} 1280 - 3429 mg/kg, N_{total} 812 - 3442 mg/kg. Heavy metal concentrations in the size order of Zn>Pb>Cr>Cu>As>Ni>Co>Cd. AVS measurements on sediment samples were in the range of 0.02 - 32.8 and the average value was 8.76 μmol/g dw. Sediment enrichment factors (SEF) were also calculated and it was observed that the metals, As extremely severe, Zn very severe, Cd and Pb severe, Cu moderately severe, Cr and Mn moderate, Co and Ni minor, where different pollution degree, but sediment samples were mainly polluted with trace metals (Table 1).

Table.1. Sediment quality of the Sheldt Sediment samples

Metals	Average Concentration (mg/kg dw)	SEF (average)	Flemish Sediment criteria(mg/kg dw)
As	22.4	71.40	19
Cd	4.1	19.12	1
Cr	62.3	3.52	62
Cu	46.5	8.76	20
Co	8.9	2.64	-
Pb	67.2	16.2	40
Ni	16.7	1.87	16
Zn	340.2	23.47	147

Discussion: The environmental contamination results can provide information to be referenced for managing the Scheldt river. It was observed that there is a severe level of trace metal contamination of the sediment samples of the Scheldt river. Further, ecotoxicological studies will be done on the collected sediment samples in order to evaluate the relationship between sediment geochemistry, AVS and both metal bioavailability and toxicity.

References: [1] Luoma and Rainbow (2005) Environmental Science & Technology **39** (7): 1921-1931. [2] Di Toro et al. (1990) Environmental Toxicology & Chemistry **9** (12): 1487-1502. [3] Meire et al. (2005) Hydrobiology **540**: 1-11. [4] Baeyens et al. (2005) Hydrobiology **540**: 141-154. [5] De Jonge (2012) Environmental Pollution **158**(5): 1381-139.