

ICP-MS

For multi-element analysis of particulate major elements and selected trace metals, samples were filtered through pre-weighed Millipore Isopore membrane filters (polycarbonate, pore size 0.4 μm).

The PC-filters were treated overnight with 1 ml HNO_3 and 2 ml HClO_4 in closed PTFE autoclaves (PDS-6; Heinrichs et al. (1986) *Zeitschrift fuer Pflanzenernaehrung und Bodenkunde* 149, 350-353.) at room temperature to oxidize organic matter. Afterwards the filter material was decomposed by evaporating the acids at 160°C. The TSS residue was digested in the same PTFE vessels at 180°C for 6 h after adding a mixture of 1 ml HClO_4 and 3 ml HF. After digestion the acids were evaporated at 180°C and were re-dissolved and fumed off three times with 2 ml semi-concentrated HCl and diluted with 2 vol. % HNO_3 to a final dilution factor of 2500 to 5000. All acids were cleaned by sub-boiling distillation, except for HF (suprapure quality).

Samples for analysis of dissolved metals in freshwater were taken with PE-syringes and 0.45 μm SFCA syringe filters, acidified to 1 vol. % HNO_3 and stored in pre-cleaned PE-bottles.

Particulate Ag, Ba, Bi, Cd, Co, Cr, Cs, Cu, Li, Mo, Ni, Pb, Rb, Sb, Sc, Sr, Th, Tl, U, V, Y, Zn, Zr and REE (freshwater and seawater TSS) and dissolved Cd, Co, Cr, Cu, Mo, Ni, Pb, Rb, Re, Sb, Th, Tl, U, V, Y, Zn, Zr and REE (only freshwater samples) were measured by ICP-MS (Thermo Finnigan MAT ELEMENT). Dissolved trace metals were determined directly from syringe-filtered samples.

Dissolved trace metals in seawater were determined directly from 25-fold diluted samples. The analytical procedure applied is similar to the method published by Rodushkin I. and Ruth T. (1997) Determination of trace metals in estuarine and sea-water reference materials by high resolution inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry* 12(10), 1181-1185.

Contamination effects were excluded by measurement of filter and procedural blanks. Precision and accuracy of all measurements were checked by parallel analysis of international and in-house reference materials. We used GSD-4 and an in-house shale standard TW-TUC for particulate samples. Analysis of dissolved metals was checked by the riverine water reference material SLRS-4 as well as CASS-3 and CASS-4 for seawater.

DOC

Samples were filtered through pre-weighed Whatman glass microfibre filters (glass fibre, pore size 0.7 μm , heated to 400°C for 4 h before use to remove carbon contamination). The filtrate

was stored in brown glass bottles and acidified with half-concentrated HCl (200 µl per 100 ml).

DOC measurements were done on GF-filtrates by combustion and IR-detection with a multi N/C 3000 analyser (Analytik Jena). The analysis was checked by measurements of K-hydrogenphthalate solutions with appropriate concentrations.

TSS (POLYCARBONATE FILTER)

Samples were filtered through pre-weighed Millipore Isopore membrane filters (polycarbonate, pore size 0.4 µm). The filtered amount ranged from 100 to 750 ml for freshwater samples and from 250 to 1000 ml for seawater samples depending on the TSS-load of the respective sample.

After filtration, filters were rinsed with ca. 50 ml of purified water, dried for two days at 60°C and weighted for determination of TSS.

TC, TIC, POC

Samples were filtered through pre-weighed Whatman glass microfibre filters (glass fibre, pore size 0.7 µm, heated to 400°C for 4 h before use to remove carbon contamination). The filtered amount ranged from 100 to 750 ml for freshwater samples and from 250 to 1000 ml for seawater samples depending on the TSS-load of the respective sample.

After filtration, filters were rinsed with ca. 50 ml of purified water, dried for two days at 60°C and weighted for determination of TSS.

Total carbon (TC) was determined from the GF-filter by high temperature combustion and coulometric detection of CO₂ with a Ströhlein Coulomat 702. Total inorganic carbon (TIC) was determined coulometrically from a parallel GF-filter with an UIC instrument. Particulate organic carbon (POC) was calculated as the difference of TIC and TC.

As TC in freshwater samples is relatively high, and measured values for TIC were below the detection limit, the TIC content was determined only in selected samples. Thus, TC is equivalent to POC in the investigated freshwater environment.

ICP-OES

For multi-element analysis of particulate major elements and selected trace metals, samples were filtered through pre-weighed Millipore Isopore membrane filters (polycarbonate, pore size 0.4 µm).

The PC-filters were treated overnight with 1 ml HNO₃ and 2 ml HClO₄ in closed PTFE autoclaves (PDS-6; Heinrichs et al. (1986) *Zeitschrift fuer Pflanzenernaehrung und Bodenkunde* 149, 350-353.) at room temperature to oxidize organic matter. Afterwards the filter material was decomposed by evaporating the acids at 160°C. The TSS residue was digested in the same PTFE vessels at 180°C for 6 h after adding a mixture of 1 ml HClO₄ and 3 ml HF. After digestion the acids were evaporated at 180°C and were re-dissolved and fumed off three times with 2 ml semi-concentrated HCl and diluted with 2 vol. % HNO₃ to a final dilution factor of 2500 to 5000. All acids were cleaned by sub-boiling distillation, except for HF (suprapure quality).

Samples for analysis of dissolved metals in freshwater were taken with PE-syringes and 0.45 µm SFCA syringe filters, acidified to 1 vol. % HNO₃ and stored in pre-cleaned PE-bottles.

Particulate Al, Ti, Fe, Ca, Mg, Na, K, P, Mn, and Zr (freshwater and seawater TSS) and dissolved Ca, K, Mg, Na, Al, B, Ba, Fe, Li, Mn, P, S, Si, and Sr (only in freshwater) were analysed by ICP-OES (Perkin Elmer Optima 3000XL). Dissolved trace metals were determined directly from syringe-filtered samples. Contamination effects were excluded by measurement of filter and procedural blanks. Precision and accuracy of all measurements were checked by parallel analysis of international and in-house reference materials. We used GSD-4 and an in-house shale standard TW-TUC for particulate samples. Analysis of dissolved metals was checked by the riverine water reference material SLRS-4 (Canada).