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Diffusive gradients in thin films (DGT) and ultrafiltration were used to measure trace metal concentrations in the Baltic Sea. The results provide the first comparison of these two fundamentally different speciation methods for trace metals. Cd, Cu, Mn, Ni, and Zn were measured at two sites with different total trace metal concentrations. DGT units prepared with APA-gel as diffusive layer and Chelex 100 resin as binding agent were used throughout the study. The ultrafiltration was performed with Millipore Prep/Scale modules with cutoffs of 1 and 10 kDa. Concentration levels of Mn, Zn, and Cd measured by DGT agreed with the concentrations measured in 1 kDa ultrafiltered samples. For Cu and Ni the ultrafiltered concentrations exceeded the DGT-labile concentrations. The ability of DGT to preconcentrate metals was found to be an analytical advantage compared with ultrafiltration. DGT appears to be a good alternative to 1 kDa ultrafiltration for measurement of truly dissolved Mn, Cd, and Zn in the Baltic Sea.

Introduction

Distribution, mobility, and toxicity of metals in natural waters are strongly related to their aqueous speciation (1). The biological response of an organism depends not simply on total concentrations but on the activities of the metal ions and their complexes, and on the concentration of labile metal species in solution (2, 3). To understand the behavior of an aqueous element and the transformation between chemical forms there is a need for reliable methods that enable measurements of specific fractions of metals.

Ultrafiltration has frequently been used to study speciation of metals in natural waters (e.g., 4, 5). In a recent study, Ingri et al. (6) used cross-flow ultrafiltration technique to determine the size distribution of trace metals and organic carbon in the Baltic Sea. Various evaluations of ultrafiltration techniques have been performed (7, 8). Two cross-flow ultrafiltration

systems were optimized by Larsson et al. (9) for Baltic Sea surface waters. Some disadvantages are, however, associated with ultrafiltration. The procedure is complicated and demands a rigorous handling protocol for satisfactory results. The laboratory-based filtration process implies sampling and storage of water, which may trigger aggregation and oxidation of metals and result in a change in metal speciation (10, 11). Laxen and Chandler (12) found a change in metal speciation in water stored for more than 2 h between sampling and filtration. Since ultrafiltration is based on grab samples, extensive sampling is necessary if correct average concentrations or temporal variations are to be measured (13), particularly in dynamic waters such as coastal or estuarine waters where metal concentrations may fluctuate extensively. If sampling frequency is low, the measurements may represent a temporary increase or decrease in concentration level instead of the average metal concentration. Ultrafiltration is also an expensive and time-consuming procedure.

A possible alternative or complement to ultrafiltration is the emerging technique of diffusive gradients in thin films (DGT) introduced by Davison and Zhang (14). DGT has been used for trace metal speciation in natural waters (e.g., 15, 16) and provides an in situ measurement of labile metal species, which prevents problems with speciation changes associated with sampling and storage. DGT accumulates metals in proportion to time and produces a mean concentration over the chosen deployment period. The pre-concentration ability is an important quality in waters with extremely low dissolved metal concentrations. DGT is also a cheap, time-saving, and easy-to-use method. In several studies, DGT has been compared to other speciation methods in different types of natural waters. It has been used together with membrane filtration in estuarine waters (13) and compared to competitive ligand exchange followed by voltammetric measurements for measurement of the speciation of Cu in coastal marine waters (CLE-ACSV) (17), Cu and Zn in streamwater (CLE-DPASV or CLE-DPCSV) (18), and speciation of Cu, Zn, Ni, Cd, Pb, and Mn in eutrophic lake water (CLE-DPCSV) (16). DGT has also been used in conjunction with dialysis to study speciation of trace metals in lake water (19).

The aim of this study was to compare in situ DGT measurements of trace metals with concentrations measured in 1 kDa ultrafiltered water. Both techniques were simultaneously used in the Baltic Sea at two sampling points with different salinity and total trace metal concentrations (Table 1). The first point, Ekhagen (59°23N, 18°04E), is a low-salinity coastal bay in the vicinity of Stockholm, and the second point is Landsort (58°35N, 18°14E), 40 km off the Swedish coast in the open Baltic Sea. Sampling was performed in Ekhagen 6 times in 2003, and in Landsort 10 times in 2004. This study provides the first comparison of these two fundamentally different techniques for speciation of trace metals.

Materials and Methods

Diffusive Gradients in Thin Films (DGT). Standard piston-type DGT units (20) were used throughout this study. The units were prepared as described previously (21) with an APA-gel (15% acrylamide, 0.3% patented agarose-derived cross-linker) as a diffusive layer, a Chelex 100 resin (Na-form, 200–400 mesh) as a binding agent, and a 0.22 μm cellulose nitrate membrane filter as a protective outer layer.

Calculations were performed as explained elsewhere (20). With Fick's first law of diffusion and known diffusion coefficient of metal ions within the diffusive gel, the concentration of metal in the bulk waters can be determined

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TABLE 1. Mean Values of Salinity (‰) and Total Metal Concentrations^a at Ekhagen and Landsort during Sampling Periods, *n* = 6 for Ekhagen, *n* = 13 for Landsort

	salinity	Ca	Mg	K	Na	S	Fe	Cd	Cu	Mn	Ni	Zn
Ekhagen	3.3	1.28	4.53	0.857	39.0	2.48	589	0.223	33.2	224	32.9	52.1
Landsort	6.3	2.30	9.18	1.81	80.3	5.02	29.5	0.186	8.66	30.6	11.8	5.84

^a Concentrations in mM for Ca, Mg, K, Na and S, and in nM for Fe, Cd, Cu, Mn, Ni and Zn.

from the measured mass of metal accumulated in the resin according to eq 1.

$$C = \frac{M \Delta g}{DA t} \quad (1)$$

C is the concentration of metal in solution, *M* is the mass of metal accumulated in the resin, Δg is the thickness of hydrogel and membrane filter, *D* is the diffusion coefficient of the metal ion within the gel, *A* is the exposure area, and *t* is the deployment time. Diffusion coefficients provided by DGT Research Ltd. (22) were used for the average water temperatures calculated from in situ temperature measurements every second hour during the deployment periods. The hydrogel thicknesses were 0.75 ± 0.02 mm at Ekhagen and 0.77 ± 0.02 mm at Landsort. Membrane filter thickness was 0.13 mm for all DGT units and exposed diffusion area was 3.14 cm². The elution factor was assumed to be 0.8 for all metals in this study (20). Considering the turbulent marine environment, the diffusive boundary layer (DBL) was assumed to be negligible.

The DGT units were assembled under clean conditions and stored in clean plastic bags at 4 °C. All equipment was washed in 0.1 M HNO₃ and rinsed in MilliQ water prior to use. Powder-free disposable gloves were worn during all handling.

In Ekhagen the mean amount and the standard deviations of the blanks (*n* = 5) for each element were (in ng per disc) 3.87 ± 1.46 for Zn, 1.17 ± 0.77 for Cu, 0.35 ± 0.22 for Mn, and 0.12 ± 0.06 for Ni. The percentage masses of metal in the blanks compared to the amount accumulated in the field devices were 2% for Zn, 3% for Cu, and less than 1% for Mn and Ni. Measured masses in blanks from Landsort (*n* = 10) were (in ng per disc) 4.65 ± 2.44 for Zn, 1.51 ± 0.71 for Cu, 0.73 ± 0.37 for Mn, 0.42 ± 0.30 for Ni, and 0.028 ± 0.028 for Cd. The percentage masses of metal in the blanks compared to the amount accumulated in the field devices were 10% for Zn, 9% for Cu, 2% for Cd, and 1% for Mn and Ni. The masses of trace metals in these control blanks were used to correct the masses extracted from the devices deployed in the field.

Ultrafiltration. The ultrafiltration system used in this study was a MilliPore Prep/Scale system. Two Prep/Scale Spiral Wound TFF-6 modules were used with manufacturer-specified cutoffs of 1 and 10 kDa. For both modules the filter membrane area was 0.54 m² and the filter material was regenerated cellulose. A Watson Marlow peristaltic base-plate pump was connected to the system.

The sampled water in Ekhagen was pre-filtered through a 0.22 μm membrane filter before ultrafiltration, starting with the 10 kDa filter. During the filtration, the permeate (<10 kDa) was collected in an acid-cleaned plastic container. Colloidal material (>10 kDa) was retained in the retentate. The collected permeate (<10 kDa) was filtered again, this time through the 1 kDa filter. Material between 1 and 10 kDa was retained in the retentate and the permeate was collected in a new container. Samples were collected for analysis from 0.22 μm, 10 kDa, and 1 kDa permeate and from 10 kDa and 1 kDa retentate. At Landsort permeate from the 0.22 μm membrane filter was directly filtered through the 1 kDa Prep/Scale module. Samples were collected for analysis from 0.22 μm and 1 kDa permeate and from 1 kDa retentate.

TABLE 2. Mean Recoveries for Ultrafiltration^a

	Mn	Ni	Cu	Zn	Cd
Ekhagen (10 kDa)	88	90	88	89	
Ekhagen (1 kDa)	91	74	81	66	
Landsort (1 kDa)	96	73	94	73	78

^a Ekhagen (*n* = 6), Landsort (*n* = 13).

Concentration factors (CF) in Ekhagen were between 16 and 24 for the 10 kDa filter, and between 11 and 14 for the 1 kDa filter. Cross-flow ratios (CFR) (retentate flow/permeate flow) were >20 for the 10 kDa filter and >80 for the 1 kDa filter. At Landsort, concentration factors were between 16 and 22 and cross-flow ratios were >60 for the 1 kDa filter. CF and CFR were calculated as described previously (23). Mean recoveries for each metal are presented in Table 2. The recoveries for Cd in Ekhagen are left out of Table 2, because almost all values for Cd in Ekhagen were below the detection limit.

Before every new sampling occasion and after every filtration the filters were rinsed with MilliQ water and solutions of NaOH and HCl, according to a procedure described by Ingri et al. (23).

Field Work. Ekhagen. The sampling was done from a 40-m-long wooden pier in the Ekhagen Bay. Three replicate DGT devices were deployed for approximately 2 weeks in 6 deployment periods between April 2 and June 2, 2003. The units were suspended with plastic rope from a buoy to 4 m depth. A StowAway TidbiT temperature logger was connected to the DGT device to record temperatures every second hour during the deployment. The recovered DGT units were thoroughly rinsed with MQ water on the deployment site and then placed in clean, airtight plastic bags. On every deployment occasion 1–3 DGT units were chosen as control blanks. These devices were not deployed in the water column.

On 6 occasions between March 18 and June 2, 2003, usually at the start and end of the DGT deployments, water was collected at the sampling site for membrane filtration and ultrafiltration in laboratory. An all plastic Flojet diaphragm pump (ITT industries, flow rate ~5 L/min) was used to collect approximately 25 L of water from 4 m depth in an acid-cleaned polyethylene (PE) container. The water was immediately transported to the laboratory where the filtering process began within 2 h. Unfiltered water samples for direct analysis were also collected at the sampling point.

Landsort. All sampling was conducted from the ship M/S Fyrbyggaren. DGT units were deployed in duplicate, 10 times, for 2 to 4 weeks, over the period March 10 to September 9, 2004. At 5 m depth, the DGT units were attached to a rope suspended from a buoy and stretched out with a plastic-covered weight. The buoy was connected to another rope anchored at the bottom. As in Ekhagen, temperature loggers were attached to the DGT devices. The recovered DGT units were, as in Ekhagen, rinsed with MilliQ water and placed in plastic bags. On every sampling occasion two DGT units were assembled but not immersed in the water column. These units were used as blanks.

On 13 occasions between March 10 and September 9, 2004 water was collected at Landsort for filtration and

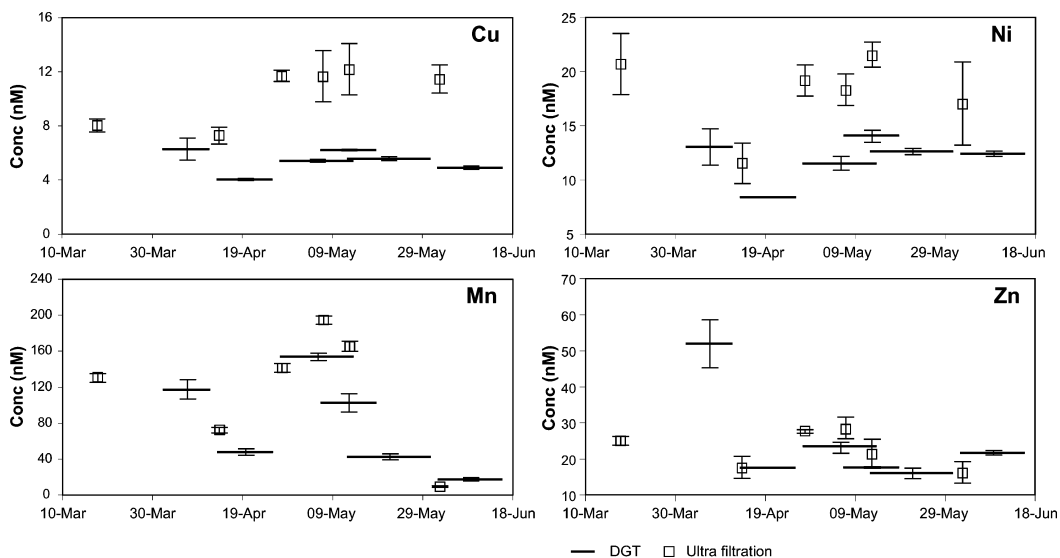


FIGURE 1. Concentrations of Mn, Zn, Cu, and Ni in Ekshagen measured by DGT and ultrafiltration.

unprocessed samples. Water was sampled from 5 m depth in an acid-cleaned polyethylene (PE) container using a Masterflex peristaltic pump. The tubing used to collect water was attached to a flagpole which was mounted to the bow of the ship. The water was therefore sampled approximately 10 m in front of the ship during slow steaming to avoid contamination derived from the hull. Filtration with 0.22 μm membrane filter was performed on board the ship immediately after sampling. The 1 kDa ultrafiltration was conducted in the laboratory within 24 h after sampling.

Analysis. All analytical work was performed in Class 100 clean room conditions. After sampling and transport to the laboratory, the DGT devices were disassembled and the resin gels were eluted in 5 mL of 5 M HNO_3 (suprapur). Concentrations of elements in DGT eluents, unfiltered samples, 0.22 μm membrane filtrate, and permeate and retentate from the ultrafiltration were determined by ICP-SFMS using an Element (ThermoFinnigan, Bremen, Germany). See Rodushkin and Ruth (24) for operating conditions and measurement parameters. Prior to analysis, water samples were diluted 4-fold with 0.16 M HNO_3 (suprapur) in MilliQ water. Matrix-induced signal variations and signal instabilities were corrected for using internal standards (25 ppb In and Tl) added to samples, blanks, and standards. Quality control was accomplished by regular analyses of in-house control samples.

Results and Discussion

Measurement Definition. Before the results are presented it is important to emphasize the basic differences between the measurement techniques. DGT measures a flux which is used to calculate an average concentration over the deployment period, and the discrimination of metal species in the gel is based on size and lability. A gel pore size of approximately 5 nm permits free metal ions, inorganic metal complexes, and small organic metal complexes to diffuse, while particles and large colloids are excluded (20, 25). Since the complexes must dissociate in the hydrogel to be measured, only complexes with sufficient dissociation rate will be retained in the resin (20). Kinetically inert species are excluded.

The ultrafiltration is performed in the laboratory and based on a grab sampling approach. The discrimination of metal

species by ultrafiltration is based on size. A pore size of 1 kDa equals approximately 2 nm. It should be noted that the pores of a filter with manufacturer-specified cutoff of 1 kDa range between ~ 0.7 and ~ 1.3 kDa (7) and also that the cutoff, in daltons, is a nominal value and that the real cutoff depends on the structure and chemical composition of the metal species present (9). Studies with CFF ultrafilters have shown that a manufacturer-defined cutoff of 1 kDa corresponds to a real cutoff of 2.1–2.5 kDa (7, 9). Since a major part of seawater colloids are just above 1 kDa in size (26) it can be expected that the 1 kDa CFF permeate, besides free metal ions, will contain different forms of complexes and colloids. The ultrafiltration will, unlike DGT, not discriminate inert and immobile complexes.

The metal concentrations in 1 kDa ultrafiltered permeate are compared with DGT-labile concentrations in the two sampling points in Figures 1 and 2. DGT results are presented as lines reflecting the deployment period and the ultrafiltered results are shown as points at the time of sampling. The error bars represent the instrumental deviation for ultrafiltered results and the standard deviation of replicate devices, simultaneously deployed, for DGT.

Mn, Zn, Cd. Concentrations of Mn, Zn, and Cd measured by DGT were similar to the concentrations measured in 1 kDa ultrafiltered samples, especially for Mn (Figures 1 and 2). The generally good agreement between the two techniques is likely due to the weak tendency of these metals to form organic complexes. Mn seems to exist predominantly in particulate fractions or in truly dissolved species in Ekshagen (6). Munksgaard and Parry (15) found that almost 100% of the dissolved Cd is labile in estuarine waters. The agreement between the two techniques is not as evident for Zn as for Mn and Cd. Studies have shown that Zn can be strongly bound in small nonlabile complexes (16). The measured concentrations of Zn in ultrafiltered water from Landsort were close to the detection limit for some samples, which must be taken into consideration.

Cu, Ni. For Cu and Ni the ultrafiltered concentrations clearly exceeded the DGT-labile concentrations (Figures 1 and 2). This indicates the existence of low molecular weight Cu and Ni species, small enough to pass through the 1 kDa ultrafilter but not labile enough to be retained in the DGT units. A substantial complexation by organic substances has

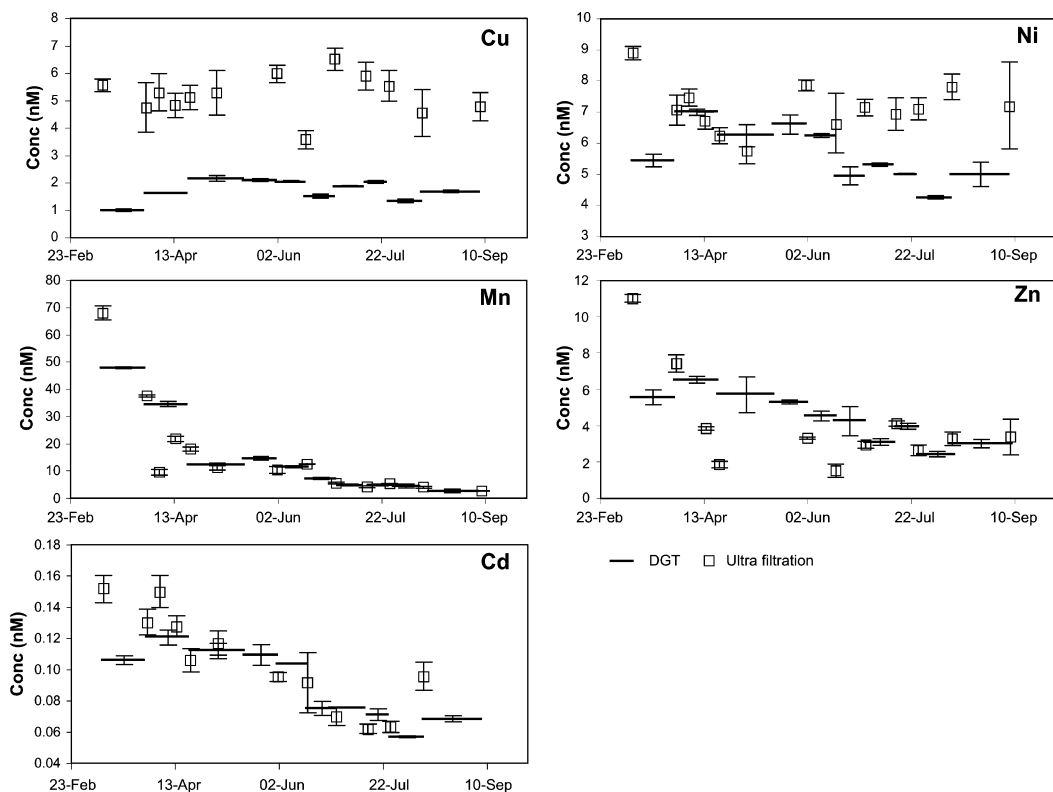


FIGURE 2. Concentrations of Mn, Zn, Cu, Ni, and Cd in Landsort measured by DGT and ultrafiltration.

been found for Cu and Ni in seawater (17, 27–29). Ingri et al. (6) found that 35% of the Ni $<0.22 \mu\text{m}$ and 54% of the Cu $<0.22 \mu\text{m}$ in Ekshagen was in colloidal forms. The organic complexes have diffusion coefficients substantially lower than free metal ions (30). Since diffusion coefficients for free ions are used in this study, the DGT-labile concentrations are probably underestimated, contributing to the difference in concentrations measured by the two methods.

Complexation by simple organic ligands such as nitrilotriacetic acid (NTA) or diglycolic acid (DGA) lowers the diffusion coefficient of trace metals in the gel by approximately 25%, whereas fulvic acid (FA) species will contribute to the mass of metal measured by DGT with approximately 20% of the sensitivity of uncomplexed metal (31, 32). If we use these reduced diffusion coefficients for Cu and Ni and assume that 100% of the concentration measured with DGT is complexed with simple organic ligands we do not reach the concentration measured in the ultrafiltered fraction. Assuming 100% complexation with FA gives concentrations in the DGT over the observed concentrations in the ultrafiltered fraction. For Cu, a combination of 20% free metal ions and 80% FA-species gives the same concentrations in the DGT and ultrafiltered fractions in Landsort. The combination for Ni is 70% free metal ions and 30% FA-species. In Ekshagen the figures are 40% and 60% for Cu and 60% and 40% for Ni, respectively.

General Assessment. Both methods have strengths and weaknesses. DGT measures a time-integrated average concentration, while the ultrafiltered concentrations are based on a single grab sample. The ultrafiltered concentrations can therefore be nonrepresentative for a period of time. On the other hand, if the results are supposed to be

compared to unfiltered grab samples or membrane filtrates, the ultrafiltration might render a more direct comparison. A comparison with DGT demands a composite sample comprising several grab samples collected during the DGT deployment period. This was addressed in a study by Dunn et al. (13). The importance of speciation change during transport and storage has been shown in earlier work (12, 19), and a change in metal speciation, during the time between sampling and filtration, cannot be ruled out for water collected for ultrafiltration in this study. The time and money saving factor using DGT is important, especially when sampling is conducted over prolonged time periods. In waters with very low metal concentrations, where analysis of ultrafiltration permeate results in values below detection limits, DGT is useful because of the pre-concentration capability.

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