Bull Environ Contam Toxicol (2007) 79:147–152
DOI 10.1007/s00128-007-9095-9

Dissolved Organochlorine and PAH Pollution Profiles in Lithuanian and Swedish Surface Waters

**Per-Anders Bergqvist · Ilona Jegorova ·
Violeta Kaunelienė · Audronė Žaliauskienė**

Received: 3 July 2006 / Accepted: 15 March 2007 / Published online: 31 May 2007

Abstract In recent decades, knowledge and concern regarding persistent organic pollutants and the environmental hazards they may pose have increased considerably, leading to international agreements such as the United Nations environment program Stockholm convention on persistent organic pollutants (POPs), to minimize further release of POPs into the environment (UNECE Protocol, 1979; UNEP Stockholm convention, 2001; UNECE Convention, 1998). National POP monitoring programs should be designed to identify, characterize and address the release of the POPs listed in the Stockholm convention. However, analyses of grab samples only provide crude snapshots of total concentrations at single points in space and time, which may be highly unrepresentative of average concentrations, and fail to account for differences in the POPs' bioavailability and various other relevant factors. To obtain a better understanding of the fate and availability of pollutants in the environment it is necessary to obtain data regarding their site-specific and regional exposure levels. Exposure levels expressed in terms of total chemical concentrations do not reflect the actual exposure of organisms, and thus may not accurately reflect the true risks posed. Therefore, environmental monitoring programs would be improved by using reliable, integrative sampling methods that would not only allow time-weighted average concentrations of pollutants in the environment to be determined, but also facilitate assessments of the risks these chemicals pose to the environment.

Uncertainties in risk characterization are likely to be substantial for POPs such as polycyclic aromatic hydrocarbons (PAHs) because discharges may be episodic, and the pollutants in the small samples yielded by traditional water sampling techniques may be present in trace or even undetectable amounts (Crunkilton et al., 1997). During the last decade many research groups have been developing passive sampling equipment and methods such as semipermeable membrane devices (SPMDs), polar organic chemical integrative samplers (POCIS), solid-phase micro-extraction (SPME) and diffusive gradients in thin films (DGT) analyses, which could reduce the uncertainties (Södergren and Sabaliūnas, 1996; Strandberg et al., 1997; Bergqvist et al., 2006; Zhang and Davisson, 2000; Petty et al., 2000, and 2004; Alvarez et al., 2004). Lithuania is in the process of implementing a water framework directive (WFD) for the management of the rivers Neris and Nemunas. Substances considered in future monitoring programs should include long-lasting (persistent) contaminants that are discharged into the aquatic environment, e.g., polychlorinated biphenyls (PCBs), PAHs, hexachlorobenzene (HCBz), dichlorodiphenyltrichloroethanes (DDTs), polychlorinated dibenzo-p-dioxin (PCDD), polychlorinated dibenzofurans (PCDFs), heavy metals and organometallic compounds. Several of these compounds have not previously been monitored in Lithuanian waters (Twinning project, 2001). The objective

P.-A. Bergqvist (✉)
Environmental Chemistry, Umeå University, Umeå, Sweden
e-mail: Per-Anders.Bergqvist@chem.umu.se

I. Jegorova
Ministry of Economics, Gedimino ave. 38/2, Vilnius, Lithuania

I. Jegorova · V. Kaunelienė
Faculty of Chemical Technology, Kaunas University of Technology, Kaunas, Lithuania

A. Žaliauskienė
ExposMeter AB, Tavelsjö, Sweden

A. Žaliauskienė
Siauliai University, Siauliai, Lithuania

of the study reported here was to compare pollution by PCBs and PAHs, including POPs listed in the Stockholm convention, in these two Lithuanian rivers immediately before their confluence and at three sites in a stream close to the city of Umeå, Sweden. Data for the comparison, representing the integrated concentrations of specific contaminants at the sampling sites, were obtained during three-week periods in 2001. The analysis of time-integrated dissolved water concentrations of different compounds allowed site-specific risk assessments of the water courses, and interesting differences in both the concentrations and profiles of the pollutants were found that provide useful indications of their respective degrees and sources of pollution.

Materials and Methods

To investigate the bioavailable time-weighted average (TWA) concentrations of POPs in the surface water at five different sites (Table 1), the water was passively sampled in October 2001 using SPMDs.

To provide field controls, including estimates of the exposure of the SPMDs during their deployment in the field, two single SPMDs were exposed to air during deployment and retrieval in the same manner as the sampling SPMDs (Söderström and Bergqvist, 2003). A further SPMD was kept in an airtight tin can in a freezer and analyzed at the same time as the samples to provide a laboratory membrane blank. Standard analytical procedure for using SPMDs can be found elsewhere (Strandberg, 1998; Petty et al., 2000). Briefly, the SPMDs were manually brushed in water, shaken in *n*-hexane, cleaned up with hydrochloride acid (1 M), dried with Kleenex tissues (Söderström and Bergqvist, 2003), then dialyzed in 95:5 (v/v) cyclopentane:dichloromethane (two batches; 100 ml followed by 180 ml, both for 24 hours).

A 40 μl solution of toluene containing a series of labeled ^{13}C and deuterated compounds was added to each sample to provide internal standards and the remaining lipids were then separated from the POPs using high-resolution gel permeation chromatography. To the final sample a 40 μl solution of the recovery standard ^{2}H-dibenzofuran (RS) in toluene was added. The compounds were analyzed using a high-resolution gas chromatography/low-resolution mass spectrometery (HRGC/LRMS) system operating in selected ion monitoring (SIM) mode. Single membranes were analyzed from each location. The use of a multitude of labeled internal standards and recovery standards provides a sound foundation for the analysis. Earlier studies (Bennett et al., 1996) have also shown that replicate membranes from the same site usually give highly reproducible results, with deviations of less than 10%. PCBs were quantified using one isomer per congener group, except hexachlorobiphenyls, for which two isomers were used. For PAHs and pesticides each compound was quantified using a specific compound in the standard mixture. Water concentrations were quantified using laboratory-obtained calibration sampling rate data for the PAHs, PCBs and pesticide compounds. For the PCBs a single sampling rate was used for all congeners in the calculations. In all cases corrections were applied regarding the sampling time and water temperature when calculating sampling rates.

Results and Discussion

The concentrations of PCBs found in the surface waters at each of the investigated locations are presented in Fig. 1. Twenty-five of 27 targeted PCB congeners were detected in the rivers Neris and Nemunas. The concentrations of most of the PCB congeners in the river Nemunas (ranging from 0.06 to 0.3 ng/L for each congener) exceeded those at the background site. In the river Neris the concentration of PCB #28 (0.43 ng/L) was elevated compared with the concentration of other PCB congeners, such as PCBs #31 (0.24 ng/L), #44 (0.134 ng/L), #52 (0.14 ng/L), and #110 (0.164 ng/L). The concentrations of PCBs from fresh sources generally decrease with increases in molecular weight from PCB #28 to PCB #180, but the proportions of more lightly chlorinated congeners decrease in the PCB profiles from old sources due to aging processes (evapo-

Table 1 Description of the investigated sites

	Site	Occupational characteristics	Exposure time
1	Tvärån 1	Swedish stream (upstream of Tvärån 2 and Tvärån 3), background site	01.10.16–01.11.08
2	Tvärån 2	Swedish stream (downstream of small industrial facilities including scrap metal and lorry maintenance workshops, etc.)	01.10.16–01.11.08
3	Tvärån 3	Swedish stream (downstream of urban area, before confluence with the river Umeälven)	01.10.16–01.11.08
4	Neris	Lithuanian river (before confluence with river Nemunas)	00.11.06–01.01.17
5	Nemunas	Lithuanian river (before confluence with river Neris)	00.11.06–00.11.27

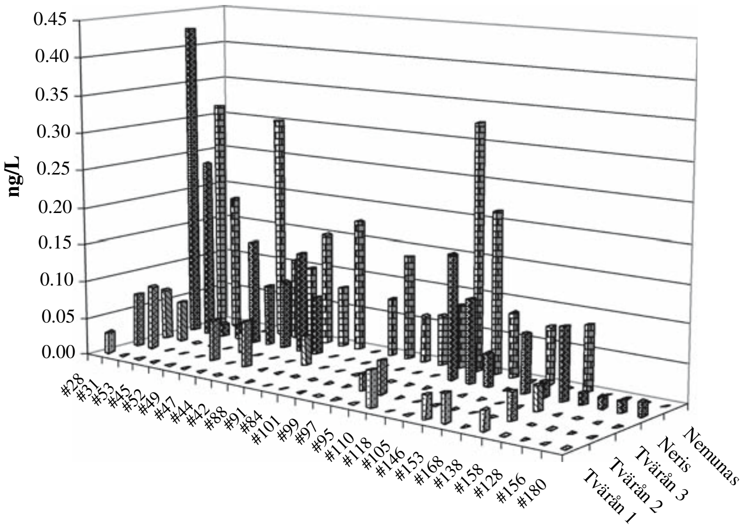


Fig. 1 Dissolved water concentrations of polychlorinated biphenyl (PCB) congeners found in the Lithuanian (rivers Neris and Nemunas) and Swedish (Tvärån stream) surface waters

ration and their relatively high solubility and transport rates). Since the concentrations of PCBs #28 and #31 were found to be higher than those of the more heavily chlorinated congeners, the pollution in the river Neris may be of recent origin, consisting of fresh PCBs and/or the site may be close to a continuing source (see Fig. 1). Another factor that may contribute to such a PCB pattern is the tendency of highly chlorinated PCB congeners to bind to dissolved organic matter and suspended particulate material within the water column, thereby reducing their availability for membrane uptake. Similar amounts of sum PCB$_{27}$ (i.e. the total level of 27 congeners) have previously been detected upstream of our investigated site, e.g. 0.02–0.08 μg/ml SPMD triolein (Södergren et al., 1996), while at our studied site sum PCB$_{27}$ amounted to 0.05 μg/ml SPMD triolein.

The PCB profiles in the rivers Neris and Nemunas included elevated levels of the highly (penta-)chlorinated congeners PCB #110 and PCB #118, indicating that there may have been an additional source of highly chlorinated PCBs. Usually the #110 and #118 peaks are smaller than those of some of the other penta-chlorinated biphenyls, but in these samples #110 and #118 were most abundant. Together with the tri-chlorinated biphenyl data, these findings suggest that there were both recent and older sources (the latter contributing highly chlorinated species) of PCBs upstream of the sampling points.

Three sampling sites along the stream Tvärån were chosen to assess the influence of an industrial area on the PCB levels, at various distances, in the stream. The industrial facilities consist mainly of scrap metal works and transportation companies, but it is difficult to define all of the potential sources in this industrial estate, comprised of a range of small-scale businesses. PCB congeners were mainly detected at sites Tvärån 2 and Tvärån 3 (PCBs #28, #31, #44, #49, #97, #95, #138, and #110), where concentrations of the individual congeners ranged from 0.022 ng/L to 0.085 ng/L. Only limited amounts of dissolved hexa-PCBs were present in water samples from both Tvärån 2 and Nemunas. The sampling site Tvärån 1 was located upstream of the industrial area and most PCB congeners were present at concentrations below their respective detection limits. These results indicate that some activities within the industrial area may be sources of PCB contamination, but further studies would be required to identify the exact source(s). At the last site (Tvärån 3) PCB concentrations decreased and levels of some PCB congeners were again below their respective detection limits. The reduction in concentrations may be partly attributable to the tendency of PCBs (especially highly chlorinated PCBs) to bind to sediment particles and then settle out before the dam located immediately upstream of the Tvärån 3 site. Such sedimentation may be enhanced by PCBs binding to additional particles entering the stream from roads before the Tvärån 3 site. A third possible contributory factor is dilution, since more water (stormwater and groundwater) enters the stream after the Tvärån 2 site. Figures 2 and 3 show selected ion monitoring (SIM) chromatograms of five homolog groups of PCBs obtained from samples from the Nemunas and Tvärån 2 sites, which provide additional information about the samples. Notably, several large, unidentified peaks were located close to identified PCB peaks. Unfortunately, whole SIM chromatograms are often not scrutinized in pollutant analyses, although they can provide valuable additional information regarding the samples, even in relatively specific SIM analyses.

Tri-PCBs are masked in the chromatogram for sampling site Tvärån 2 by a large peak due to the presence of unknown compounds with a retention time of 18.58 min, but

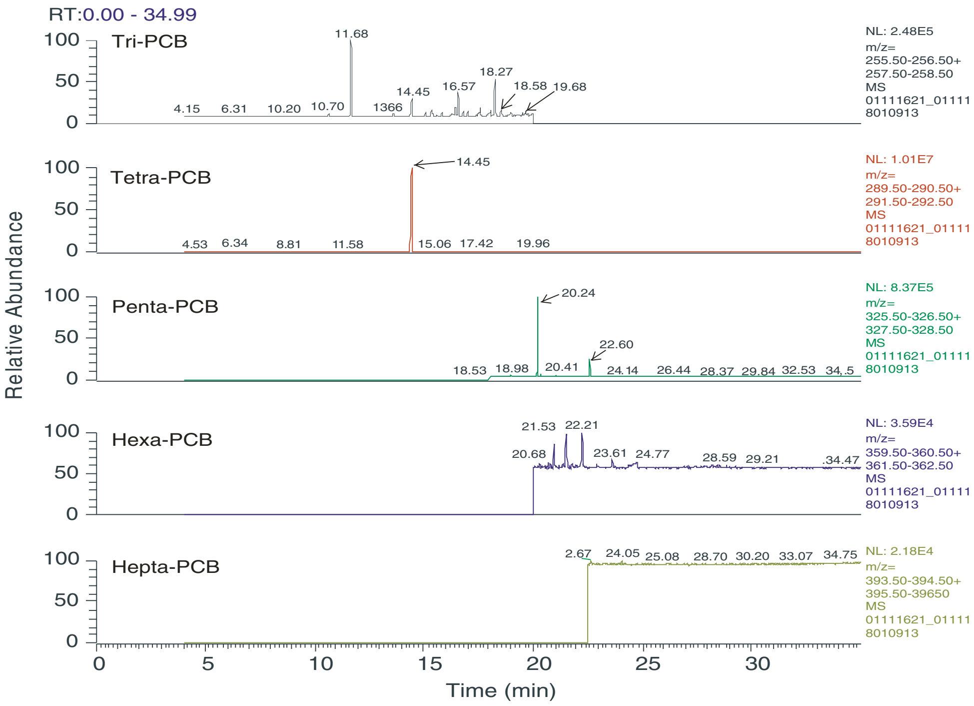


Fig. 2 Selected ion monitoring (SIM) chromatograms of five homolog groups of polychlorinated biphenyls (PCBs) from the Nemunas sampling site

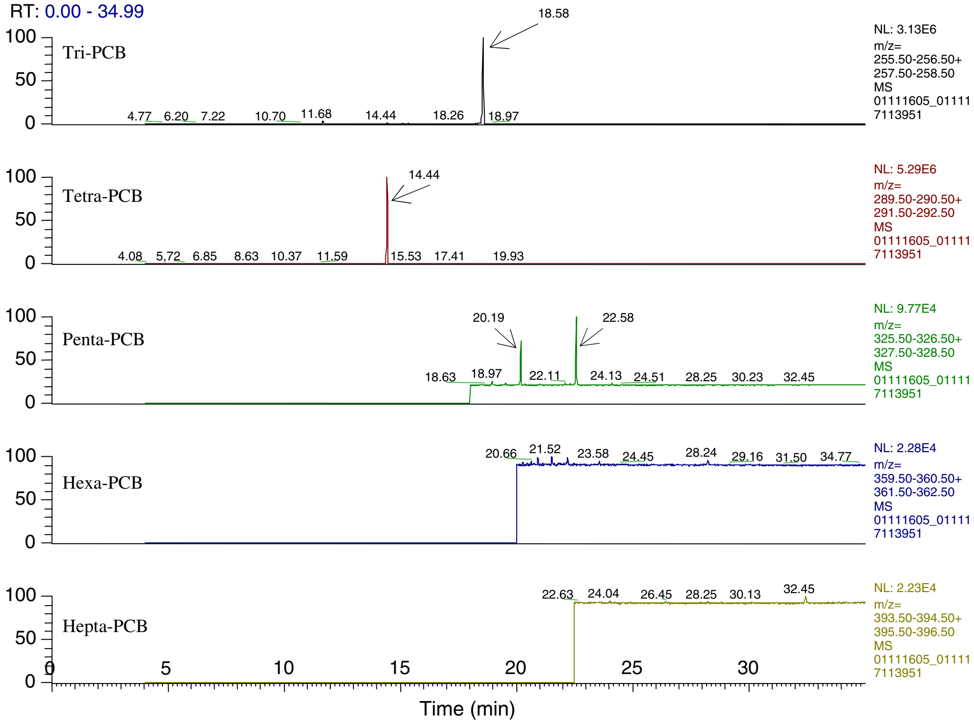
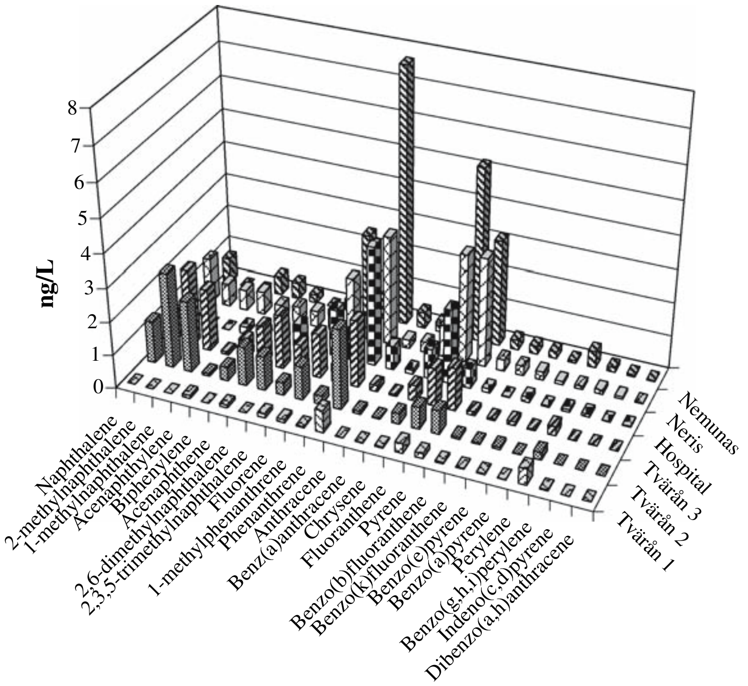


Fig. 3 Selected ion monitoring (SIM) chromatograms of five homolog groups of polychlorinated biphenyls (PCBs) from the Tvärån 2 site

not in the chromatogram for the Nemunas sample in which the unknown compounds appear to be absent or present at sub-detectable levels. The tetra-PCB pattern is not visible in either chromatogram due to the presence of a large unknown peak, with retention times of 14.44 and 14.45 min, respectively. Penta-PCB was very close to the detection limit in the Tvärån 2 sample, but some penta-PCB peaks can be seen in the Nemunas chromatogram, in addition to two common, large peaks attributable to unknown substances at 20,19/20,24 and 22,58/22,60, respectively. Hexa- and hepta-PCB peaks were easily identified in samples from both sites. These features of the chromatograms

Fig. 4 Dissolved water concentrations of polycyclic aromatic hydrocarbons (PAHs) found in the Lithuanian (rivers Neris and Nemunas) and Swedish (Tvärån stream) (plus site Hospital) waters



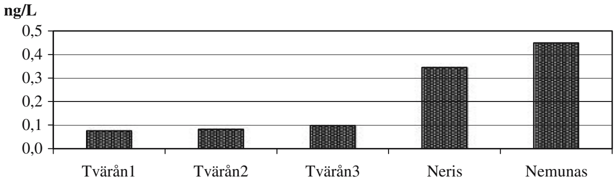


Fig. 5 Hexachlorobenzene (HCBz) concentrations in the Lithuanian (Neris and Nemunas rivers) and Swedish (Tvärån stream) surface waters

suggest that at least one unknown substance were present in the stream Tvärån at relatively high levels, but not in the river Nemunas. In addition, at least three other larger peaks could be located in samples that were found in both areas. Therefore, efforts should be made to identify these four substances, which were not specifically targeted, since they seem to be location-specific compounds with a currently unknown source.

All 24 targeted polyaromatic hydrocarbons were detected in the rivers Nemunas and Neris as can be seen in Fig. 2. Generally the smaller PAH substances were lower and the medium size molecules were higher in dissolved concentration in the Lithuanian samples compared to the Swedish samples. The compound that was present at the highest concentration was phenanthrene (7.7 ng/L, 10 times higher than at the background site, Tvärån 1). The estimated concentrations of less water-soluble compounds such as fluoranthene and pyrene (5.2 and 3.2 ng/L, respectively) were slightly lower. Earlier studies (Södergren et al., 1996) upstream of the sampling point in Neris have also found a predominance of phenantrene, fluoranthene and pyrene. Concentrations of fluoranthene and pyrene were up to 20 times higher than those at the background site. Acenaphthylene and fluorene, which are difficult to detect using grab samples (Crunkilton et al., 1997), were detected in all samples. Concentrations of fluorene were also about 20 times higher at the Neris and Nemunas sites than at the background site Tvärån 1. The dissolved water concentrations of more water-soluble compounds in the stream Tvärån showed the same tendency to increase after the industrial area as phenanthrene. PAH compounds are very common in vehicle exhaust gases and oil products, which could be the reason why they were found at all studied sites downstream of industrial and urban areas. Increased partitioning of these compounds into the dissolved phase with increasing distance from their sources may also contribute (Bennett et al., 1996). Benzo(a)pyrene and benzo(b+k)fluoranthene, both of which were detected in the rivers Neris and Nemunas, are among the 10 most hazardous substances. The concentrations of benzo(b+k)fluoranthene were an order of magnitude higher in the river Neris than at the background site.

Hexachlorobenzene (HCBz) was detected in all samples examined, but the concentrations were generally higher at the Lithuanian sites than at the Swedish sites. The concentrations of HCBz in the Lithuanian rivers Neris and Nemunas were 0.35 and 0.45 ng/L, respectively. At the Tvärån 1, 2 and 3 sites the corresponding concentrations were 0.076, 0.082 and 0.098 ng/L, respectively. The concentration of HCBz in the stream Tvärån was not influenced by the industrial catchment area, being the same at the background site as at the other investigated sites. The identities, concentrations, and distribution of selected POPs that have not previously been monitored in Lithuania were determined. The results illustrate the utility of SPMDs for comparing the extent of pollution and pollution profiles at multiple sampling sites within either a single country or more than one country and thus, for global or regional monitoring of POPs.

References

Alvarez DA, Petty JD, Huckins JN, Jones-Lepp TL, Getting DT, Goddard JP, Manahan SE (2004) Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environ Toxicol Chem 23 (7):1640–1648

Bennett ER, Metcalfe TL, Metcalfe CD (1996) Semi-permeable membrane devices (SPMDs) for monitoring organic contaminants in the Otonabee river, Ontario. Chemosphere 33 (3):363–375

Bergqvist P-A, Augulytė L, Jurjonienė V (2006) PAH and PCB removal efficiencies in Umeå (Sweden) and Šiauliai (Lithuania) municipal wastewater treatment plants. Water Air Soil Pollut 175:291–303

Crunkilton LR, de Vita WM (1997) Determination of aqueous concentrations of polycyclic aromatic hydrocarbons (PAHs) in an urban stream. Chemosphere 35 (7):1447–1463

Petty JD, Orazio CE, Huckins JN, Gale RW, Lebo JA (2000) Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants. J Chromatogr A 879 (1):83–95

Petty JD, Huckins JN, Alvarez DA, Brumbaugh WG, Cranor WL, Gale RW, Rastall AC, Jones-Lepp TL, Leiker TJ, Rostad CE, Furlong ET (2004) A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants. Chemosphere 54 (6):695–705

Söderström HS, Bergqvist P-A (2003) Polycyclic aromatic hydrocarbons in a semipermeable membrane device exposed to air in Thailand. Environ Sci Technol 37 (1):47–52

Södergren A, Sabaliūnas D (1996) Semipermeable Membranes in Environmental Analysis: a review. Environ Res Engin and Management 2 (3):1392–1649

Strandberg B, Wågman N, Bergqvist P-A, Haglund P, Rappe C (1997) Semipermeable membrane devices as passive samplers to determine organochlorine pollutants in compost. Environ Sci Technol 31:2960–2965

Strandberg B (1998) The use of semipermeable membrane devices in studies of concentrations, distribution and fate of organochlorine compounds in the environment. Thesis, Inst of Environ Chemistry, Umeå University. Sweden

Twinning project No. LI99/IB/EN/01 (2001). Strengthening of environmental monitoring capacities in Lithuania. Natl environ research institute, Denmark

Zhang H, Davison W (2000) Direct in situ measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films. Anal Chem 72 (18):4447–4457