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Metal measurement in aquatic environments by passive sampling methods: Lessons learning from an *in situ* intercomparison exercise



A. Dabrin ^{a,*}, J.-P. Ghestem ^b, E. Uher ^c, J.-L. Gonzalez ^d, I.J. Allan ^e, M. Schintu ^f,
N. Montero ^g, J. Balaam ^h, E. Peinerud ⁱ, C. Miège ^a, M. Coquery ^a

^a Irstea, UR MALY, Freshwater Systems, Ecology and Pollution Research Unit, 5 rue de la Doua, CS 70077, F-69626, Villeurbanne, France

^b BRGM, 3 Avenue C. Guillemin, BP 36009, Orléans Cedex 2, France

^c Irstea, UR HBAN, F-92163, Antony, France

^d Ifremer, Département Biogéochimie et Ecotoxicologie, B.P. 330 Zone Portuaire de Brégaillon, 83507, La Seyne/mer cedex, France

^e Norwegian Institute for Water Research (NIVA), Gaustalleen 21, O349, Oslo, Norway

^f Università degli Studi di Cagliari, Cagliari, Italy

^g AZTI-Tecnalia, Marine Research Division, Herrera kai, Portualdea z/g, Pasaia, 20110, Spain

^h Cefas, Centre for the Environment, Fisheries and Aquaculture Science, Lowestoft Laboratory, Lowestoft, United Kingdom

ⁱ ALS Scandinavia, Box 511, SE-183 25, Taby, Sweden

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ABSTRACT

Passive sampling devices (PS) are widely used for pollutant monitoring in water, but estimation of measurement uncertainties by PS has seldom been undertaken. The aim of this work was to identify key parameters governing PS measurements of metals and their dispersion. We report the results of an *in situ* intercomparison exercise on diffusive gradient in thin films (DGT) in surface waters. Interlaboratory uncertainties of time-weighted average (TWA) concentrations were satisfactory (from 28% to 112%) given the number of participating laboratories (10) and ultra-trace metal concentrations involved. Data dispersion of TWA concentrations was mainly explained by uncertainties generated during DGT handling and analytical procedure steps. We highlight that DGT handling is critical for metals such as Cd, Cr and Zn, implying that DGT assembly/dismantling should be performed in very clean conditions. Using a unique dataset, we demonstrated that DGT markedly lowered the LOQ in comparison to spot sampling and stressed the need for accurate data calculation.

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1. Introduction

Reliable chemical monitoring of surface waters has become a crucial issue, especially in the context of the Water Framework Directive (WFD). In particular, there is an emerging need to find cheap and easy alternatives to spot sampling taking into account temporal variability (e.g. flood events, seasons). Several tools have been developed over the years to address this challenge, including bioassays/biosensors, biomonitors, chemical sensor probes and passive samplers (PS).

The last 20 years have seen a surge in the development of PS to enable measurements of a wide range of contaminants in surface waters (e.g. Vrana et al., 2014). PS tools carry many advantages, as

they (i) provide an integrated measure of the contamination over the period of deployment, (ii) preconcentrate contaminants, which enables a lower limit of quantification (LOQ) than classical analysis in spot samples and (iii) simplify the matrix of the sample. Allan et al. (2006) showed that time-weighted average (TWA) concentrations estimated by PS could be used to monitor long-term trends, to screen contaminants at very low concentrations, and to identify sources of pollution. For metals, diffusive gradients in thin films (DGT) and Chemcatcher[®] are the main PS devices used for monitoring surface waters (Allan et al., 2008). The DGT device consists in a plastic piston loaded with a diffusive gel layer backed by an ion-exchange resin gel (Chelex-100). The diffusive gel of the DGT allows to measure metals in ionic form and weakly bound to small inorganic and organic complexes, which represent a fraction of the total metal dissolved concentration (<0.45 μm), commonly called the “labile” fraction. Metal accumulation in the resin is governed by the concentration gradient established in the diffusive

* Corresponding author.

E-mail address: aymeric.dabrin@irstea.fr (A. Dabrin).

gel between the media and the resin. The TWA concentration of the metal present in water over the period of exposure may be estimated as follows:

$$TWAC = \frac{m \cdot \Delta g}{D \cdot t \cdot A} \quad (1)$$

where m is the mass of metal accumulated in the receiving phase of the DGT (ng), Δg is the thickness of the diffusive gel/filter (cm), D is the diffusion coefficient of the ionic metal in the diffusive gel ($\text{cm}^2 \text{s}^{-1}$), t is the period of deployment (s), and A is the surface area (cm^2) of DGT. For this calculation, only m has to be determined by the analytical step, as Δg , D , t and A are generally known (DGT supplier and field data). The Chemcatcher[®] is constituted by a standardized body combining a cellulose acetate membrane with a 47 mm Empore[™] chelating disk for metals measurement. The uptake rates needed to calculate TWA concentrations are less well known for Chemcatcher than the diffusive coefficient determined for DGT (DGT Lancaster), and require element-specific uptake rate estimations in field conditions (Neziri et al., 2011).

The DGT has a rapid response to fluctuating concentrations of Cd, Cu, Ni, Pb and Zn during the period of deployment (Allan et al., 2007). For Cu, Zn and Pb, TWA concentrations were in agreement with the filtered or ultrafiltered fractions obtained in spot samples and with predicted inorganic and inorganic-fulvic acid associated metal fraction according to the visual MINTEQ programme (Allan et al., 2007). Thus, DGT has been widely used as a speciation tool for metals in freshwaters (Roig et al., 2011), coastal waters (Schintu et al., 2008), and sediments (Dabrin et al., 2012). Several studies have focused on the applicability of DGT for monitoring metals in freshwaters. Montero et al. (2012) reported that DGT gave reproducible TWA concentrations for Cd, Cu, Ni and Zn in highly-fluctuating systems such as estuaries. However, Buzier et al. (2014) reported that DGT monitoring of Cu, Cd, Ni and As in surface waters requires stringent procedures to avoid DGT contamination and biases in the TWA concentration estimation. Allan et al. (2008) also assessed Chemcatcher performances for measuring Cd, Cu, Ni, Pb and Zn in surface waters. They reported that DGT and Chemcatcher gave similar Cd and Zn concentrations to filtered samples, but both PS consistently underestimated Cu and Ni concentrations and carried high measurement uncertainty for Pb due to low sampler accumulation for this metal. Moreover, to improve validity of Chemcatcher TWA concentrations, a performance reference compounds procedure was needed to account for *in situ* turbulence, biofouling and temperature (Allan et al., 2008).

The upshot is that while both DGT and Chemcatcher are widely used for monitoring metals in waters, there has been little effort to assess the uncertainty of their measurements. To date, only one study has reported global results of an *in situ* intercomparison exercise on several PS for priority pollutants (polycyclic aromatic hydrocarbons, pesticides and metals) in surface waters (Miège et al., 2012). This first trial allowed to evaluate the representativeness of PS for *in situ* monitoring and showed that despite the very low concentration levels, the variety of tools and the different exposure and analytical strategies, global interlaboratory dispersion was relatively low (relative standard deviation, $\text{RSD} < 100\%$). Nevertheless, this work needed further investigations of results on metals measurements by DGT, particularly to scrutinize sources of TWA concentration uncertainties, such as analytical and data treatment steps.

2. Strategy of the intercomparison exercise

Ten laboratories with previous expertise in PS deployment participated in this intercomparison exercise, i.e. ALS Scandinavia

(SW), AZTI (SP), BRGM (FR), Cefas (UK), Irstea Paris (FR), Irstea Lyon (FR), EDF R&D/LNHE (FR), IFREMER Toulon (FR), NIVA (NO) and University of Cagliari (IT). Ten and 6 laboratories participated in the exercise for metals at Ternay (France) and Thau (France), respectively. Each laboratory was asked to provide its own samplers and apply its own methodology and strategy for PS assembly/deployment, PS analytical treatment and TWA concentration calculation.

Field campaigns were led on two contrasted environments: one continental (Rhône River, Ternay, France) and one coastal (Thau Lagoon, Hérault, France). All PS were deployed 7 days at Ternay (17–24 June 2010) and 9 days at Thau (27 April–5 May 2010). Details of the exercise strategy are available in Miège et al. (2012).

Since some laboratories (3 at Ternay and 1 at Thau) exposed two types of PS for metals, each laboratory code corresponds to the association of one laboratory and one tool. The exposed PS were represented by DGT with open pores (OP) or restrictive pores (RP), while only one Chemcatcher[®] was deployed at the Ternay site (Table 1). For each laboratory, PS were exposed in triplicate together with one field blank (i.e. brought to the field but not exposed in waters). Results from PS blanks (DGT/Chemcatcher laboratory blank) and from the acid used for resin elution (acid blank) were also provided by each participant. Each laboratory was asked to analyze 8 metals, i.e. Cd, Pb and Ni (priority substances of the WFD; EC, 2013), Cr, Cu and Zn (substances on the French ecological status list; MEEDDM, 2010), Mn and Co; and to provide information related to analytical performances (Table 2), diffusion coefficients used (Table 3), resin elution, analytical procedure and calculation steps (Table 3).

In order to evaluate the accuracy and uncertainty of the analytical step, all participants were provided with a reference solution (QC solution) that had to be analyzed in triplicate ($n = 3$) at the same time as PS eluate. The reference values for the QC solution were obtained by isotope dilution coupled with inductively-coupled plasma mass spectrometry (ICP-MS). Since Mn and Co have only one isotope, a standard addition method was used.

In order to compare TWA concentrations against total dissolved metal concentrations, surface water samples were collected at the start, during and at the end of PS deployment. Samples were collected in polypropylene bottles, immediately kept at 4 °C, then filtered with polyvinylidene difluoride (PVDF) filters (0.45 μm) previously cleaned in HNO_3 10% (v/v). At the Ternay site, filtrates were acidified with ultra-pure HNO_3 (0.5% v/v). At the Thau site, due to the saline matrix, samples were preconcentrated by liquid–liquid extraction prior to analysis (Danielsson et al., 1982). All samples were then analyzed by ICP-MS (Thermo X7, Series 1^l).

A robust mean value and associated uncertainty was calculated for the QC solution and the field-exposed PS according to ISO standard method 5725-5 (1994); Miège et al. (2012).

3. Results and discussion

3.1. The analytical step: the need for a clean room to avoid contaminations

In order to identify which step(s) could affect the dispersion of TWA concentrations obtained by PS, a thorough evaluation of the analytical step was performed. Fig. 1 displays results of QC data from each laboratory with robust means and reference values of the QC solution. The ratio between robust mean and reference value (expressed in percentage) varied from 91% for Ni to 123% for Zn. Clearly, there was a lack of accuracy for Zn, since there was no overlap between the reference value \pm uncertainty of the QC solution ($1.030 \pm 0.036 \mu\text{g/L}$) and the robust mean ($1.263 \pm 0.130 \mu\text{g/L}$). This is not surprising, since Zn is known to be one of the most critical metals to analyze at low levels due to sample contamination

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