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Determination of the long-term release of metal(loid)s from construction materials using DGTs

A. Schmukat, L. Duester*, D. Ecker, P. Heininger, T.A. Ternes

Federal Institute of Hydrology, Department of Aquatic Chemistry, Am Mainzer Tor 1, 56068 Koblenz, Germany

HIGHLIGHTS

- DGTs are very useful in long-term leaching experiments.
- Release mechanisms of metal(loid)s can be studied with DGTs.
- Secondary mineral formation and sorption processes can be studied with DGTs.
- Sulphides are the main source for the release of some metals from copper slags.
- Pb can be measured with Fe-binding layers in DGTs.

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ABSTRACT

Long-term leaching experiments are crucial to estimate the potential release of dangerous substances from construction materials. The application of Diffuse Gradients in Thin film (DGT) in static-batch experiments was tested to study the long-term release of metal(loid)s from construction materials for hydraulic engineering, for half a year. Long-term release experiments are essential to improve calculations of the life-time release for this materials. DGTs in batch experiments were found to be a space and labour efficient application, which enabled (i) to study, in a non-invasive manner, the total release of nine metal(loid)s for half a year, (ii) to differentiate between release mechanisms and (iii) to study mechanisms which were contrary to the release or caused experimental artefacts in the batch experiments. For copper slag (test material) it was found that eight metal(loid)s were released over the whole time period of 184 d. Cu, Ni and Pb were found to be released, predominantly caused by (the) weathering of sulphide minerals. Only for Zn a surface depletion mechanism was identified. The results from the long-term batch experiments deliver new information on the release of metal(loid)s during the life cycle of construction materials with regard to river basin management objectives.

1. Introduction

Long-term leaching experiments are crucial to estimate the potential release of dangerous substances from construction materials [1]. Recently, the European Committee for Standardisation developed new testing framework recommendations for construction materials. These intend to evaluate the influence of intrinsic release parameters (e.g., the diffusion coefficient), to predict surface wash-off effects and to assess the long-term behaviour in the aquatic environment (e.g., mineral transformation [2]). However, the current long-term tank tests have certain limitations: (i) the maximum time scale is only 60 days, (ii) they are labour intensive and need a relative large work space and (iii) they are based on the exchange of the eluent. The renewal of the eluent includes an unaffordable abrupt change of the experimental conditions and of the accompanying parameters. If the eluent is not replaced, the total release potential of metal(loid)s might be underestimated [3]. This is, due to the formation of solution equilibriums between aqueous and solid phase. Since it is known that under submerged conditions certain construction materials release continuously significant quantities of pollutants over time, it is urgent to estimate the total release potential of priority pollutants (e.g., Cd) into the surface water. To facilitate calculations on the release during their life cycle in water construction, time scales of half a year or longer need to be investigated [4].

To enable constant experimental conditions, Diffuse Gradients in Thin films (DGTs) were applied to elucidate the release of metal(loid)s from construction materials. DGT is an in situ method developed for the measurement of metal(loid)s in water, sediments and soils [5]. In principle, the metal(loid)s diffuse from a solution through a diffusion layer to a binding layer, where they are accumulated, which prevent the establishment of solution equilibriums of

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* Corresponding author. Tel.: +49 261 1306 5275; fax: +49 261 1306 5363.
E-mail address: duester@bafg.de (L. Duester).

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metal(loid)s during the long-term experiments. The DGT technique has already been used to elaborate the behaviour of trace elements in a variety of environmental matrices [5–7].

Worldwide, construction materials are used in rivers and streams for river bank reinforcement to maintain the desired shipping and transportation conditions as well as to protect the shores and the surrounding land. As a simplification, in this study construction materials for hydraulic engineering are named as water construction materials. For instance, several million tonnes of copper slags (CUS) have already been applied in Germany as water construction material [8]. In this study, CUS (product name: iron-silicate stone) was used as a model material to elucidate the release of metal(loid)s into the water phase. The main mineral phases are fayalite, oxides, glasses and sulphides [9]. A specific property of CUS is their elevated Fe(II) content. Fe(II) is likely to be released into the surrounding water phase. After oxidation to Fe(III), further elements may be co-precipitated or absorbed due to the formation of iron (hydr)oxide colloids. The colloid formation in leaching experiments may cause misleading interpretations of eluent analyses. In addition to the high Fe(II) content, CUS contains significant quantities of metal(loid)s, exceeding significantly the total content of natural stones [9].

In addition to the release of the metal(loid)s, leaching experiments enable to investigate release mechanisms. In this study As, Sb and Mo were chosen as representatives for (hydr)oxide forming elements, while Cd, Co, Cu, Ni, Pb and Zn are studied as representatives for elements that form cationic species after the release into the water phase. Fe was included to study potential colloid formation during the leaching experiments. Since Mn is not bound as sulphide, it was measured in the sulphide leaching experiments.

The aim of this study was (i) to test the applicability of DGTs in long-term batch experiments to quantify the release of metal(loid)s from construction materials for at least half a year, (ii) to assess the capability of this method to identify significant metal(loid) release mechanisms and to (iii) transfer the results of the experiments to an exemplary field emission scenario for the tested model material. The over all goal was to improve life-cycle predictions of water construction materials.

2. Methods

2.1. Test material and leaching experiments

CUS stones were sampled close to the city of Wedel at the river Elbe (Germany). The stones were crushed (<5 mm) by a jaw crusher (Chemisch Technisches Laboratorium Heinrich Hart, Germany) and divided into sub-samples of 25 g using a rotary divider (Laborette 27, Fritsch, Germany). The specific surface area of the sub-samples was determined by the method of the Brunauer, Emmett and Teller theory (TriStar II 3020 V1.03, Micromeritics, Germany) as described elsewhere [10].

Static leaching batch experiments were used without adjusting the pH of the eluent. The experimental setup is shown in Fig. SI 1. Three different experiments were carried out for leaching periods between 48 h and 184 d (Table SI 1): (i) without DGT, (ii) with $\text{DGT}_{\text{Chelex}}$ (DGT with a Chelex 100 binding layer for cations) and (iii) with $\text{DGT}_{\text{Fe-oxide}}$ (DGT with a Fe-oxide binding layer for anions). All experiments were performed in triplicate. Additionally, one blank sample was added in each series (Fig. SI 1). The slag sub-samples (0–5 mm, 25 g) were leached with 0.25 l (liquid/solid ratio 10:1) of ultra pure water (Purelab Plus, USF ELGA, Germany) and stored in the dark with an average temperature of $22.9 \pm 0.8\,^{\circ}\text{C}$. After different leaching periods the experiments were sacrificed and the eluent was filtered (nitrogen pressure filtration, 0.45 μm and 8 μm cut-off cellulose nitrate membrane filters, Sartorius, Germany). In total, 156 batch experiments were carried out. The difference in concentration of metal(loid)s in the eluent between 0.45 μm and 8 μm cut-off were used as an indicator for the colloid formation. Therefore, the concentrations of the analytes after the filtration with 8 μm were only used for the results of the colloid formation. All samples were immediately acidified by adding HNO_3 to a percentage of 1% (subboiled, dst-1000, savillex, USA).

The metal(loid) concentrations were quantified by means of Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP-QMS, Agilent 7700 series ICP – MS, Agilent technologies, Japan) and Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES, JY 238 Ultratrace, Horiba Jobin Yvon, Germany). Limits of detection are listed in Table SI 2. Statistica 10 (Statsoft, Germany) was used for the statistical processing and evaluation of the data. All chemicals were per analysis grade or higher quality. Furthermore, all vessels were rinsed prior to use with 10% or 1% HNO_3.

2.2. DGT measurements

DGT units were purchased from DGT Research Inc. (UK). Detailed information is available in the Supporting Information (page 2). The DGT units were fixed on the bottom of the bottles with a mounting tape (3 M, Scotch, USA). After the leaching periods, the DGT units were thoroughly washed with ultra-pure water. The diffusion layer and the filter membrane (0.45 μm, Sartorius, Germany) were peeled off and the binding layer was placed in a cleaned 15 ml polypropylene tube (VWR, Germany). A 2 ml aliquot of 1 M HNO_3 was added to the tube to extract the metal(loid)s from the binding layer. After an extraction period of 24 h the concentrations of the metal(loid)s within the extraction solution were measured by ICP-QMS/OES. The analyte mass (M) can be calculated with Equation 1 [6].

$$M = \frac{C_e(V_g + V_e)}{f_e} \tag{1}$$

C_e: measured extraction concentration [μg/l], V_g: volume of the extraction solution [l]. V_e: volume of the binding layer [l]; f_e: elution factor.

Several binding layers are available for a variety of elements. While many of the cationic metal ions (e.g., Cu, Zn) accumulate onto the Chelex layers, the anionic and neutral species of As, Sb and Mo do not bind. However, the anionic species show high affinities to Fe-oxide layers [11–13]. Therefore, the metalloids accumulated in Fe-oxide binding layers. Due to the diffusion through the diffusion layer, the accumulation of the metal(loid)s is slow and the physicochemical conditions of the eluent do not change abruptly in the course of the experiments.

2.3. Elution factors for Fe-oxide binding layers

The elution factors for the extraction with 1 ml 1 M HNO_3 of the Chelex binding layer were already reported by Zhang [14]. Preliminary experiments indicated that significant Cu and Pb quantities are also present in the Fe-oxide binding layers (data not shown). However, neither the accumulation of Cu and Pb in Fe-oxide binding layers nor the respective elution factors are reported in literature. Therefore, in this study the elution factors for the accumulated metal(loid)s were determined empirically by application of two methods. In the first approach, the elution factors were determined by loading the binding layers with a known mass of metal(loid)s [15]. For that, three Fe-oxide binding layers were placed in 10 ml of standard solution (SI page 3) and shaken for 24 h. Subsequently, the Fe-oxide gel was extracted with 2 ml of 1 M HNO_3 for 24 h. In a second experiment 6 DGT units with a Fe-oxide binding layer were placed in a solution of the respective metal(loid)s prepared from CUS (SI page 3) and shaken for 72 h. Since the properties