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Research Article

Evaluating the Performance of a Diffusive Gradient in Thin Film Embedded with Montmorillonite for the Determination of Labile Cd, Pb, Mn, and Zn in Natural River Water

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Montmorillonite (MMT), a natural clay mineral with high ion-exchange capacity and trace metal adsorbability, has been demonstrated to be a suitable binding phase in the diffusive gradient in thin film (DGT) technique for the determination of labile trace metals in synthetic water samples. However, in situ working performance of DGT-MMT with natural river water has not yet been investigated. The present study examined the performance of a DGT containing montmorillonite (MMT) for the in situ isolation and determination of labile Cd, Pb, Mn, and Zn fractions in Lach Tray River water, North Vietnam. The repeatability and accuracy of the DGT-MMT probe were assessed on the basis of seven measurement replicates performed on Cd^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+} standard solutions. Then, the DGT-MMT probes were deployed in Lach Tray River water at different sampling sites to determine the labile metal fractions present in river water. By comparing the total and dissolved metal concentrations in the river water, the distributions of the four tested trace metals were constructed. The proportions of the dissolved fractions of Cd, Pb, Mn, and Zn were 46.7–73.7%, 38.5–63.9%, 36.4–41.6%, and 49.8–67.7%, respectively. The results also showed that the high accuracy and reproducibility of the DGT-MMT data were comparable with measurements obtained by the commonly used DGT-Chelex-100 method. In comparison with the data obtained from anodic stripping voltammetry (ASV), a traditional technique for the determination of non-in situ speciation of trace metals, labile metal concentrations measured by DGT-MMT were in similar ranges. These findings indicate that naturally available montmorillonite can be used as an alternative binding material in DGT probes for the in situ determination of labile metal concentrations in natural watercourses.

1. Introduction

Metals exist in aquatic environments as various species including dissolved ions, inorganic complexes, complexes with organic macromolecules (e.g., humic substances), and metals bound to suspended matter [1, 2]. Determination of the total concentration of heavy metals is not sufficient for precise predictions of metal toxicity because not all species will have a harmful impact [3, 4]. Depending on the existing species present, metals can show differences in bioavailability, especially the labile forms that can be bioaccumulated if separation occurs in the vicinity of cellular membranes [3, 5]. Moreover, the presence of heavy metal species in aquatic environments can vary significantly depending on the types of anthropogenic activities present within the study area. Therefore, speciation of heavy metals in aquatic environments, with a focus on the determination of labile forms, is always of high interest.

To determine the metal species present in aquatic environments, different types of trace metal speciation methods have been developed and applied, including (1) stripping electrochemical techniques (anodic stripping voltammetry (ASV), stripping chronopotentiometry (SSCP), and competitive ligand exchange adsorptive cathodic stripping voltammetry (CLE-AdCSV)), (2) gel-integrated microelectrode (GIME) voltammetry, (3) diffusive gradients in thin films (DGTs), and (4) isotopic dilution (ID) performed in isotopic exchange kinetic (IEK) mode [6]. Among these techniques, the most widely used tool for in situ speciation is the DGT method, as a result of its simplicity, the possibility of realizing in situ metal preconcentration, and the simultaneous accumulation of several metals [7, 8]. This technique, which functions on a cumulative basis, allows for in situ measurements of labile fractions of most cations, anions, and other hydrophilic compounds [9–12], thereby enabling improved predictions of biological effects in the ecological area of interest [13–15].

A DGT probe is composed of the following three layers: (1) a membrane filter for the separation of particulate matter, (2) a diffusive gel for controlling the metal flux , and (3) a metal binding layer for the accumulation of the diffused metal fraction [7, 16]. Among these components, the binding layer plays an important role in the accuracy of solute measurements because it determines the rapidity and irreversibility of solute accumulation on the binding material in the DGT probe [17]. Consequently, the concentration of the solute at the interface between the binding layer and diffusive layer is nearly zero, which supports additional solute diffusion from the bulk solution through the DGT apparatus, thus increasing the accuracy of the measurements [18]. To date, 46 binding layers have been developed and tested for use in the in situ speciation of labile species in aqueous environments. The components of these binding layers are mostly solid resins or powders embedded in a gel matrix, which forms a relatively homogeneous membrane [19–21]. Depending on the purpose of the research, numerous options are available for the selection of binding materials. Some typical binding materials are as follows. To measure trace metals, such as Cd, Cu, Co, Ni, Pb, and Zn, chelating ion-exchange resin Chelex-100 can be selected, while nonchelating ion-exchange resin AG50WX8 is more appropriate for the speciation of Cs and Sr [22]. Ferrihydrite (FeOOH) and MetSorb (based on TiO_2) are considered to be better binding materials for the accumulation of phosphorous and arsenic species [23–26], while silver iodide is the optimal material for the measurement of sulfide ions [27]. For research involving mercury and As(III), thiol-functionalized resins are a good choice for use during DGT speciation [28, 29]. Notably, the combination of different binding layers also has been reported to be a feasible approach to enlarge the application scope of the DGT method [30–33].

Among the recently reported binding layers, montmorillonite (MMT), the major constituent of the natural mineral smectitic clay, has been investigated for the speciation of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in synthetic natural waters [34]. The structure of montmorillonite consists of an octahedral alumina sheet sandwiched between two opposing tetrahedral silica sheets [35]. The weak bonding between the two silica sheets allows the water and exchangeable ions to enter, and this contributes to the swelling capacity [36]. This natural clay, in the form of sodium-MMT and calcium-MMT, has shown wide applicability as a potential adsorbent in heavy metal removal applications involving Pb(II), Cu(II), Co(II), Cd(II), Zn(II), Ag(I), Hg(I), and Cr(VI) in aqueous solutions [37, 38]. The adsorption process occurs mainly during the diffusion between the interlayers through the mechanisms of ion exchange and precipitation [39]. Therefore, MMT is considered to be a cost-effective, abundant, and naturally available potential binding material for application in DGT devices [34, 40, 41].

In our previous study [42], MMT K10 was impregnated in a polyacrylamide hydrogel and used as the binding phase in the DGT technique for the determination of Cd, Pb, Mn, and Zn in standard solutions. The results showed that the DGT modified with MMT as a new binding phase is suitable for the determination of labile trace metals in water samples, but its performance with natural water samples collected from real environments needs to be evaluated. Therefore, in this study, the DGT-MMT technique was applied to determine the labile metal fractions in Lach Tray River water (North Vietnam). The Lach Tray River (with a length of 23 km) is one of the major rivers that receives discharge from industrial areas in Haiphong City; it then flows to the sea through the Lach Tray estuary. The aim of this study was to evaluate the working performance of DGT-MMT probes for the determination of labile Cd, Pb, Mn, and Zn fractions in a real watercourse. Traditional DGT-Chelex-100 probes were also used in parallel for making comparisons. With the obtained data, a better understanding of the trace metal distribution in the Lach Tray River water was obtained.

2. Materials and Methods

2.1. Reagents and Materials. Chemicals and materials used for the preparation of the diffusive and binding membranes in the DGT devices included ammonium persulfate (APS) (99.99%, Merck), tetramethyl ethylenediamine (TEMED) (99.5%, Merck), acrylamide (99%, Merck) and Chelex-100 resins (Bio-Rad), agarose-derived cross-linker (DGT Research Ltd.), montmorillonite K10 (Sigma Aldrich), and 0.45 μm membrane filters (Whatman). The molds for assembling the DGT probes were supplied by DGT Research Ltd. All working chemicals and standard solutions for experiments were prepared by using water supplied by an ultrapure water purification system with a resistivity of 18.2 MΩ cm and TOC $<10\,\mu g \cdot L^{-1}$ (Barnstead). Individual $1000\,mg \cdot L^{-1}$ standard solutions of Cd^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+} were acquired from Merck.

Before use, montmorillonite was treated with HNO_3 acid (Pro Analysis, Merck) and then saturated with $NaNO_3$ (99.5%, Merck) as described in [42]. In brief, 10 g of MMT was soaked in 100 mL of HNO_3 ($1\,mol \cdot L^{-1}$) for 2 h, and then, it was centrifuged and washed with ultrapure water. This process was repeated twice before saturation with Na^+ by soaking the MMT in 100 mL of $NaNO_3$ ($1\,mol \cdot L^{-1}$) for 1 h. After the second round of saturation, the solid was rinsed thoroughly with ultrapure water and dried at 80°C for 3 h; then, it was ready for use.

2.2. Preparation of DGT-MMT and DGT-Chelex-100 Probes. The DGT-MMT and DGT-Chelex-100 probes were prepared based on the procedure described in detail in [7, 9]. Briefly, the procedure can be described as follows.

For the diffusive gels, 9.35 mL of 40% acrylamide (Bio-Rad), 3.25 mL of 2% agarose-derived cross-linker (DGT Research UK), and 11.9 mL of deionized water were mixed to form the monomer stock solution. Then, a mixture of 1 mL of monomer stock solution, 5 μL of N, N, N', N-tetramethylenediamine (TEMED), and 10 μL of 7% ammonium persulfate (APS) was polymerized at 45°C for 45 min to form gel sheets. In the next step, the gel sheets were saturated with deionized water for 24 h to obtain hydrogels. To obtain a good fit with the mold of the DGT assembly, hydrogels were cut into discs with a 2.5 cm diameter and stored in 0.01 M $NaNO_3$ solution at 4°C.

For binding membranes, similar procedures were applied, and 0.2 g of MMT or Chelex-100 was added to the mixture of gel solutions before polymerization.

For the DGT assembly, all membranes were arranged in the order of a binding membrane on the mold, then a diffusion membrane, and finally a microfilter membrane on the top. An upper lid with a window of 2.0 cm diameter was applied as a cover in the DGT devices [7].

The preparation of DGT blanks went through the whole procedure as for DGT samplers. All DGTs values in this study were corrected for the blank values of each binding phase and each eluent used.

2.3. Evaluation of the Working Performance of the DGT-MMT Probe. The metal scavenging capability of the DGT-MMT probe was investigated by using both Cd^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+} standard solutions (prepared from metal ion stock solutions and containing $NaNO_3$ at the concentration of 10^{-5} mol·L^{-1}) and river water spiked with the four targeted metal standard solutions. The DGT-MMT probes were deployed into solutions for 24 h. After that, the binding membranes were removed and soaked in 1 mol·L^{-1} nitric acid for another 24 h to extract the metal fractions bound to the binding phases. The extracts were then analyzed by using an inductively coupled plasma mass spectrometer (ICP-MS, model 7500ce, Agilent Technologies) with operating conditions set at a radiofrequency power of 1500 W, carrier gas flow rate of 0.9 L·min^{-1}, auxiliary gas flow rate of 0.22 L·min^{-1}, spray chamber temperature of 2°C, and peristaltic pump set to 0.1 rad·s^{-1}.

The labile metal concentrations in the investigated solutions, which were determined by the DGT device, were calculated with the following equation [7]:

$$c_{\mathrm{DGT}} = \frac{m\Delta_g}{\mathrm{DAt}}, \tag{1}$$

where CDGT is the concentration of the labile metal fraction in the tested solution (determined by DGT), m is the mass of metal bound to the binding phase (measured by acid extraction), Δg is the thickness of the diffusive membrane, D is the diffusion coefficient of the metal through the diffusive gel, A is the exposed surface area, and t is the deployment period.

By comparing C_{DGT} to the initial metal concentration in the solution (C_0), it is possible to calculate the working efficiency (H) of the DGT-MMT probe as follows:

$$H = \frac{C_{\mathrm{DGT}}}{C_0} \cdot 100\%. \tag{2}$$

2.4. Statistical Evaluation on the DGT-MMT Method of Analysis. The repeatability of the DGT-MMT probe was evaluated based on the standard deviation (SD) and relative standard deviation (RSD) of seven measurement replicates by using the following equations:

$$\begin{aligned} \mathrm{SD} &= \sqrt{\frac{\sum_{i=1}^{n}\left(C_i - C_{\mathrm{avg}}\right)}{n-1}}, \\ \mathrm{RSD} &= \frac{\mathrm{SD}}{C_{\mathrm{avg}}} \cdot 100\%, \end{aligned} \tag{3}$$

where C_i is the measured concentration of element i in the standard solutions, C_{avg} is the average concentration of replicates for element i, and n is the number of replicates.

The accuracy of the DGT-MMT probe for the determination of labile metal fractions was verified via the spiking method. River water samples were spiked with standard solutions containing 10 μg·L^{-1} Cd^{2+}, Pb^{2+}, Zn^{2+}, and Mn^{2+} ions. Quantification was then carried out based on the analyses of the original and spiked river water samples. The accuracy of the DGT-MMT probe was calculated by using the following equation:

$$X\,(\%) = \frac{C_0 - C_i}{C_0} \times 100\%, \tag{4}$$

where X (%) is the relative error, C_0 is the initial spiked concentration of element i, and C_i is the measured spiked concentration of element i, which is in turn calculated by the following equation:

$$C_i = C_{\mathrm{rs}} - C_{\mathrm{r}}, \tag{5}$$

where C_{rs} is the measured concentration of the spiked sample and C_{r} is the real concentration of river water before spiking.

Additionally, the recovery efficiency of DGT-MMT measurements was evaluated based on the data obtained from the following equation:

$$H\,(\%) = \frac{C_i}{C_0} \times 100\% = \frac{C_{\mathrm{rs}} - C_{\mathrm{r}}}{C_0} \times 100\% = 100\% - X\%. \tag{6}$$

2.5. Determination of Labile Metals in Lach Tray River Water Using DGT-MMT. The five sampling sites along the Lach Tray River are shown in Figure 1 and described in Table 1.

The first three sites were located around the Niem Bridge, downstream from the discharge point of a pulp

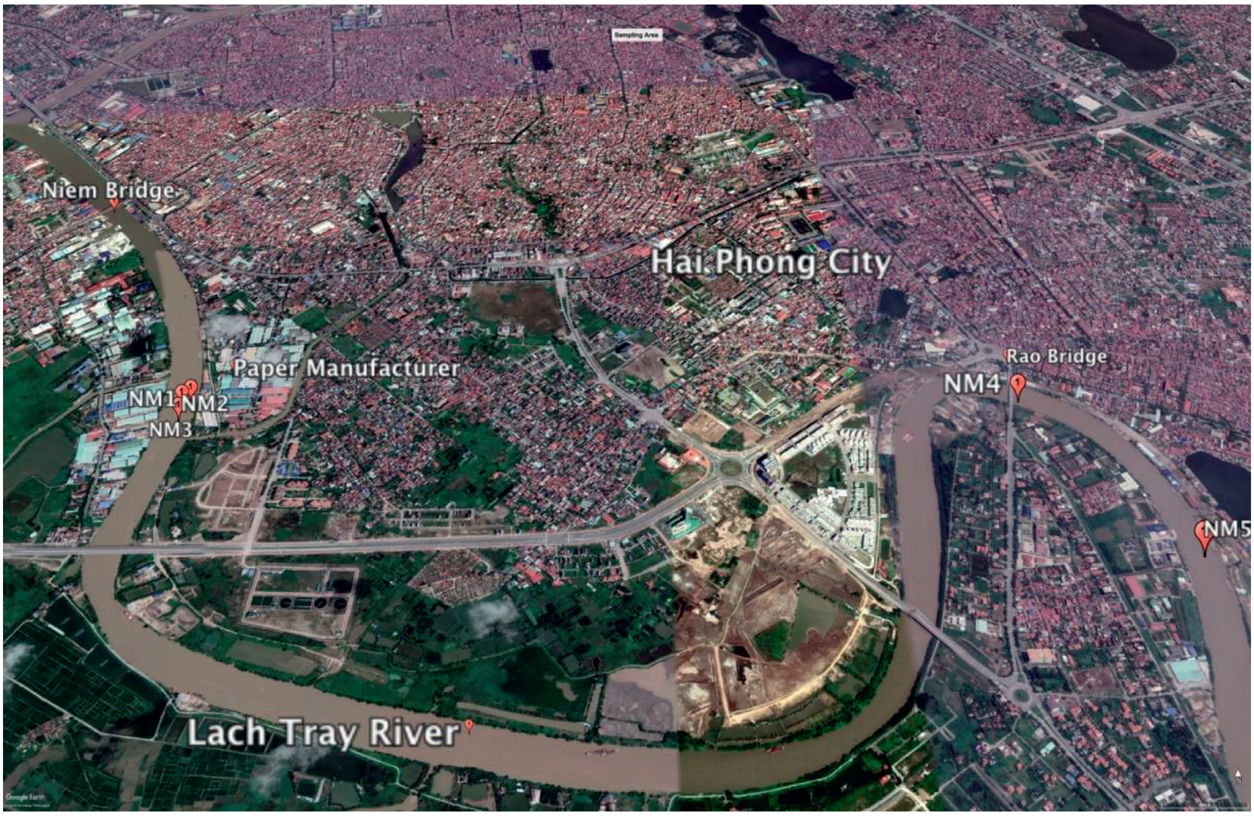


Figure 1: Sampling locations along the Lach Tray River.

Table 1: Location coordinates and descriptions of the water sampling sites along the Lach Tray River.

Sampling site	Location	Coordinates
NM1	5 m downstream from the sewage effluent site, near Niem Bridge	20°49′39.21″ N 106°40′13.97″ E
NM2	50 m downstream from the sewage effluent site, near Niem Bridge	20°49′38.42″ N 106°40′13.06″ E
NM3	100 m downstream from the sewage effluent site, near Niem Bridge	20°49′36.38″ N 106°40′13.23″ E
NM4	Rao Bridge	20°49′40.65″ N 106°42′0.08″ E
NM5	1 km downstream from Rao Bridge	20°49′17.55″ N 106°42′14.34″ E

manufacturer. The other two sites were close to a shipyard in the Rao Bridge area. At every sampling site, six DGT devices (three DGT-MMT and three DGT-Chelex-100 probes) were deployed 30 cm under the surface of the water. After 24 h, all DGT devices were removed and transferred to the laboratory. At the laboratory, labile metals accumulated in the binding phases were extracted with nitric acid and analyzed for the determination of labile Cd, Pb, Mn, and Zn with an ICP-MS using procedures similar to those described above.

To examine the differences between in situ determinations and non-in situ determinations of labile metals using a DGT-MMT probe, similar deployments were performed in the laboratory on 3 L of river water taken from each sampling site. For non-in situ testing, the river water samples were collected, stored in acid-washed low-density polyethylene bottles, kept on ice, and transferred to the laboratory.

To investigate the metal distribution trends in Lach Tray River site, total (metal concentration measured in unfiltered samples) and dissolved metal concentrations were also analyzed. In practice, 1 L of river water was taken at every sampling site, stored in acid-washed low-density polyethylene bottles, acidified to $pH < 2$ using HNO3 in accordance with the standard method ISO 5667-3 [43], and transferred to the laboratory. The total Cd, Pb, Mn, and Zn concentrations were determined by adding 5 mL of concentrated HNO3 to a 100 mL unfiltered water samples and heated for

30 min before the analysis using ICP-MS. For the analysis of dissolved metals, 100 mL of a river water sample was filtered through a 0.45 μm filter membrane, acidified by HNO3 (1 + 1) to pH < 2, and then analyzed using ICP-MS with similar conditions described in Section 2.3.

2.6. Anodic Stripping Voltammetry of Cd, Pb, Mn, and Zn. For the comparison and evaluation of labile metal determination using DGT-MMT probes, water samples taken from the five sampling sites were also analyzed by the conventional anodic stripping voltammetry (ASV) technique at the laboratory. All measurements were conducted on a PDV6000plus instrument (portable, digital voltammeter) equipped with a 3-electrode cell and plastic analysis vessel. The reference electrode was Ag/AgCl/1.0 M KCl and the auxiliary electrode was a platinum wire coil. For manganese measurement, the working electrode was a solid gold electrode, deposition potential $E = -1700$ mV, deposition time = 105 s, equilibration time = 15 s, and scan rate = 20 mV·s^{-1}. For Cd, Pb, and Zn measurements, the working electrode was Static Mercury Drop Electrode. The determination was carried out simultaneously for all three metals. The reductive accumulation of metals in the mercury drop electrode was performed at −800 mV for 600 s. After 15 s of equilibration, the anodic scan was applied from −750 mV to 20 mV in differential pulse mode. A pulse amplitude of 20 mV, a pulse duration of 0.040 s, and scan rate of 20 mV·s^{-1} were used in all measurements.

3. Results and Discussion

3.1. Repeatability and Accuracy of the DGT-MMT Probe. The repeatability of labile metal determinations when using the DGT-MMT probe was investigated based on seven measurement replicates performed on standard solutions containing Cd^{2+}, Pb^{2+}, Mn^{2+}, and Zn^{2+} (20 μg L^{-1} each). Similar experiments were performed on the DGT-Chelex-100 probe for comparative purposes. The statistical data obtained are presented in Table 2.

The results showed good repeatability in terms of the labile metal measurements for both DGT-MMT and DGT-Chelex-100 probes. The relative standard deviations of measurements were low and varied from 1.31 to 3.3% for the DGT-MMT probes and from 0.86 to 4.65% for the DGT-Chelex-100 probes. Depending on the metal, the recovery of labile metal fractions was comparable at high levels, with values ranging from 90.2 to 97.8% and from 90.0 to 96.9% for the DGT-MMT and DGT-Chelex-100 probes, respectively. The highest recovery efficiency (97%) was found for Cd^{2+}, and the lowest value (91%) was noted for Zn^{2+} and Mn^{2+}. In regard to the relative errors, the smallest value (2.2%) was found in the determination of labile lead using DGT-MMT probes, while the largest errors (up to 10%) were encountered in the measurements of labile zinc and manganese. Similar findings were obtained for the measurements using the DGT-Chelex-100 probes.

Thus, the experimental results confirmed that there was good repeatability of the measurements when using both DGT devices. The relative standard deviation of DGT-MMT measurements was within the accepted range for measurements when using the DGT technique and satisfied the requirements of quantitative analysis [44]. Importantly, the comparable working performance of the DGT-MMT to DGT-Chelex-100 probes revealed that there is high potential for the use of MMT as an alternative binding phase for Chelex-100 in the DGT technique to determine labile fractions of Cd, Pb, Mn, and Zn in water samples. These results coincide with the findings reported by Vanessa et al. [34].

3.2. In Situ Determination of Labile Metal Concentrations in Lach Tray River Water. Labile concentrations of Cd, Pb, Mn, and Zn in Lach Tray River water determined on-site using DGT-MMT and DGT-Chelex-100 probes are shown in Figure 2.

In situ determinations using the DGT-MMT probes showed that the labile Cd fraction in the Lach Tray River water ranged from 0.379 to 0.465 μg·L^{-1}, the labile Pb fraction ranged from 1.01 to 1.78 μg·L^{-1}, the labile Mn fraction ranged from 25.6 to 32.3 μg·L^{-1}, and the labile Zn fraction ranged from 30.5 to 35.7 μg·L^{-1}. The relative standard deviations of the three replicates were in the range of 2.23 to 8.42%, thus confirming the good working performance of DGT-MMT probes. For the in situ determinations using the DGT-Chelex-100 probes, the labile Cd fraction ranged from 0.367 to 0.442 μg·L^{-1}, the labile Pb fraction ranged from 1.08 to 1.69 μg·L^{-1}, the labile Mn fraction ranged from 28.1 to 31.2 μg·L^{-1}, and the labile Zn fraction ranged from 30.2 to 34.9 μg·L^{-1}. The relative standard deviations of the DGT-Chelex-100 probe measurements were in the range of 1.93 to 8.62%.

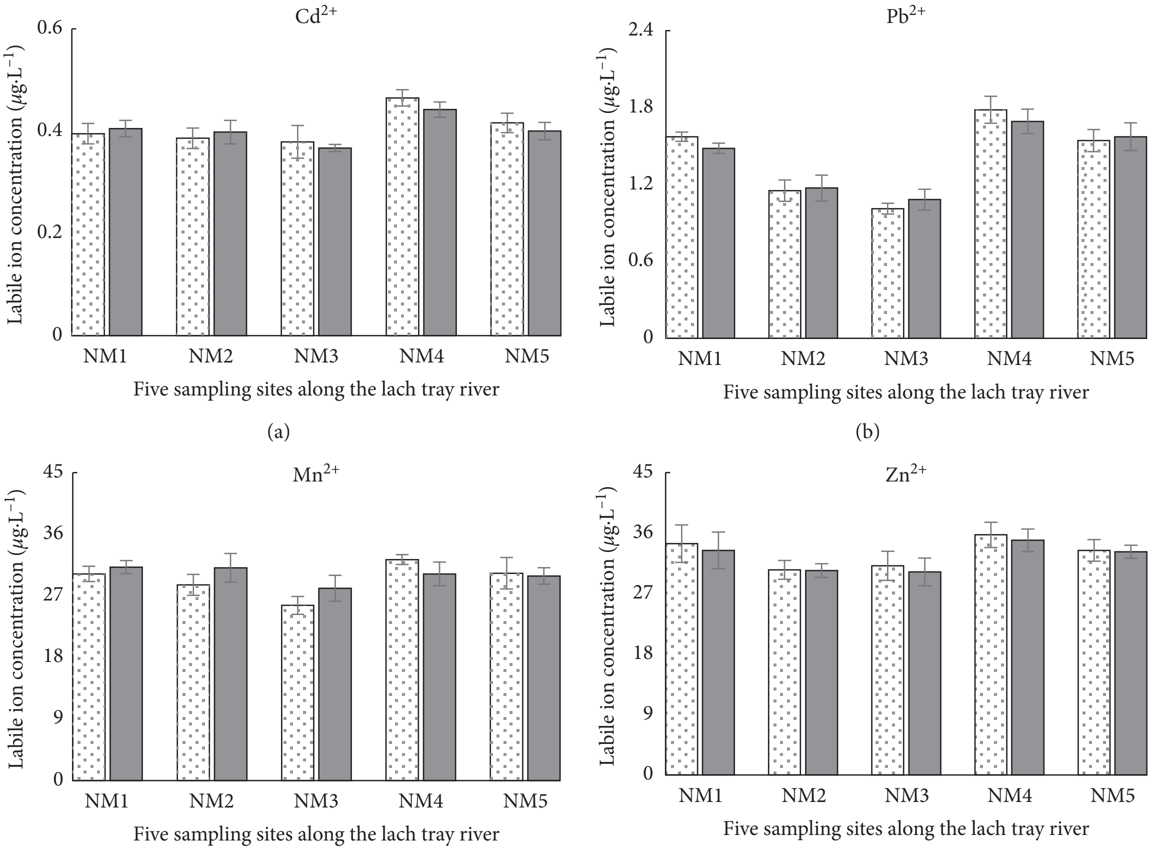
By comparing the results obtained by two DGT devices containing different binding phases, it can be recognized that both devices had an equally good working performance with an acceptable relative standard deviation (lower than 10%). This implies that MMT can be used as an alternative for Chelex-100 as the binding phase in DGT devices for the determination of labile Cd, Pb, Mn, and Zn fractions in river water.

3.3. Laboratory-Based Determination of Labile Metal Concentrations in Lach Tray River Water. The results obtained with DGT-Chelex-100 and DGT-MMT probes during the laboratory-based determinations of labile Cd, Pb, Mn, and Zn in river water samples taken from the five sampling sites are shown in Figure 3.

The analysis results indicated that the labile fractions of Cd, Pb, Mn, and Zn in the Lach Tray River water samples analyzed in the laboratory were 0.335–0.443 μg·L^{-1}, 0.924–1.657 μg·L^{-1}, 22.3–30.5 μg·L^{-1}, and 27.0–32.9 μg·L^{-1}, respectively. The relative standard deviations of three measurements ranged from 0.96 to 9.75% depending on the metal. Comparable results were found when DGT-Chelex-100 probes were used, where values for the labile fractions of Cd, Pb, Mn, and Zn were 0.338–0.412 μg·L^{-1}, 0.927–1.420 μg·L^{-1}, 25.6–29.7 μg·L^{-1}, and 26.0–30.5 μg·L^{-1},

Table 2: Average labile concentrations, standard deviations of the measurements, and recovery values for metals uptake by DGT-MMT and DGT-Chelex-100 ($n = 7$).

DGT device	DGT-MMT				DGT-Chelex-100			
	Cd^{2+}	Pb^{2+}	Zn^{2+}	Mn^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Mn^{2+}
Average labile metal concentration (C_{avg}), $\mu g\,L^{-1}$	19.2	19.6	18.1	18.0	19.0	19.4	18.0	18.1
Standard deviation (SD), $\mu g\,L^{-1}$	0.40	0.26	0.60	0.46	0.36	0.17	0.75	0.84
Relative standard deviation (RSD), %	2.10	1.31	3.30	2.53	1.88	0.86	4.15	4.65
Recovery (H), %	95.8	97.8	90.3	90.2	95.1	96.9	90.0	90.4
Relative error (X), %	4.2	2.2	9.7	9.8	4.9	3.1	10	9.6



(a) (b)

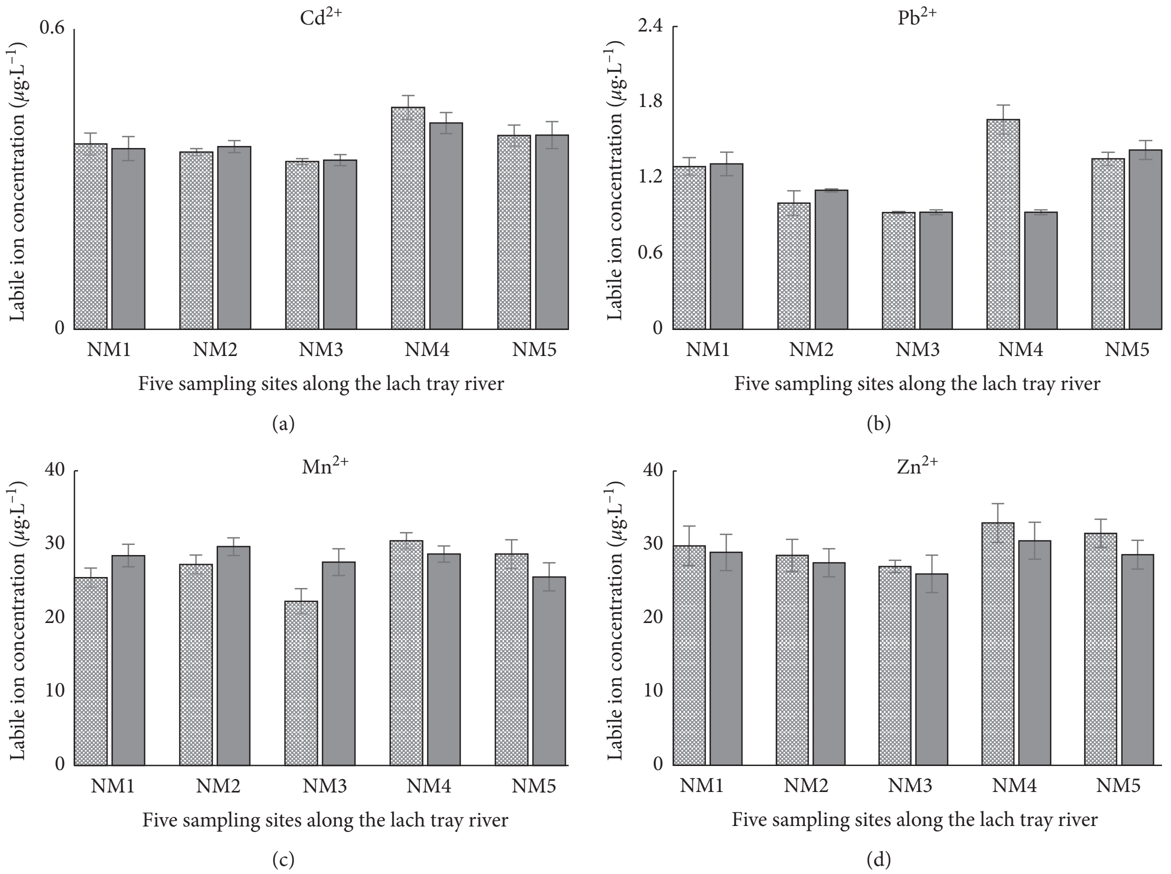
(c) (d)

Figure 2: In situ determination of labile metal fractions in Lach Tray River water using DGT-MMT (pattern fill) and DGT-Chelex-100 (solid fill).

respectively. The relative standard deviations of three replicates were lower than 10%, and the values ranged from 1.05 to 9.75%.

Compared to the data obtained on-site, the labile metal concentrations measured in the laboratory were slightly lower as a consequence of transformations among species during the sample transfer from the original sampling area to the laboratory. However, these differences were not significant, and the deviations were lower than 10% for all of the four tested elements owing to the short transportation duration of only 3 h.

One possibility that could be taken into account for these insignificant differences in labile metal concentrations measured by both experiments is the slow flow rate of river water at the sampling areas. The DGT-MMT probes were not deployed in the middle of the river, but at the distance of 1 m–1.5 m from the riverbank, where the flow rate of river water is the lowest. This may lead to unchanged or negligible



(a) (b) (c) (d)

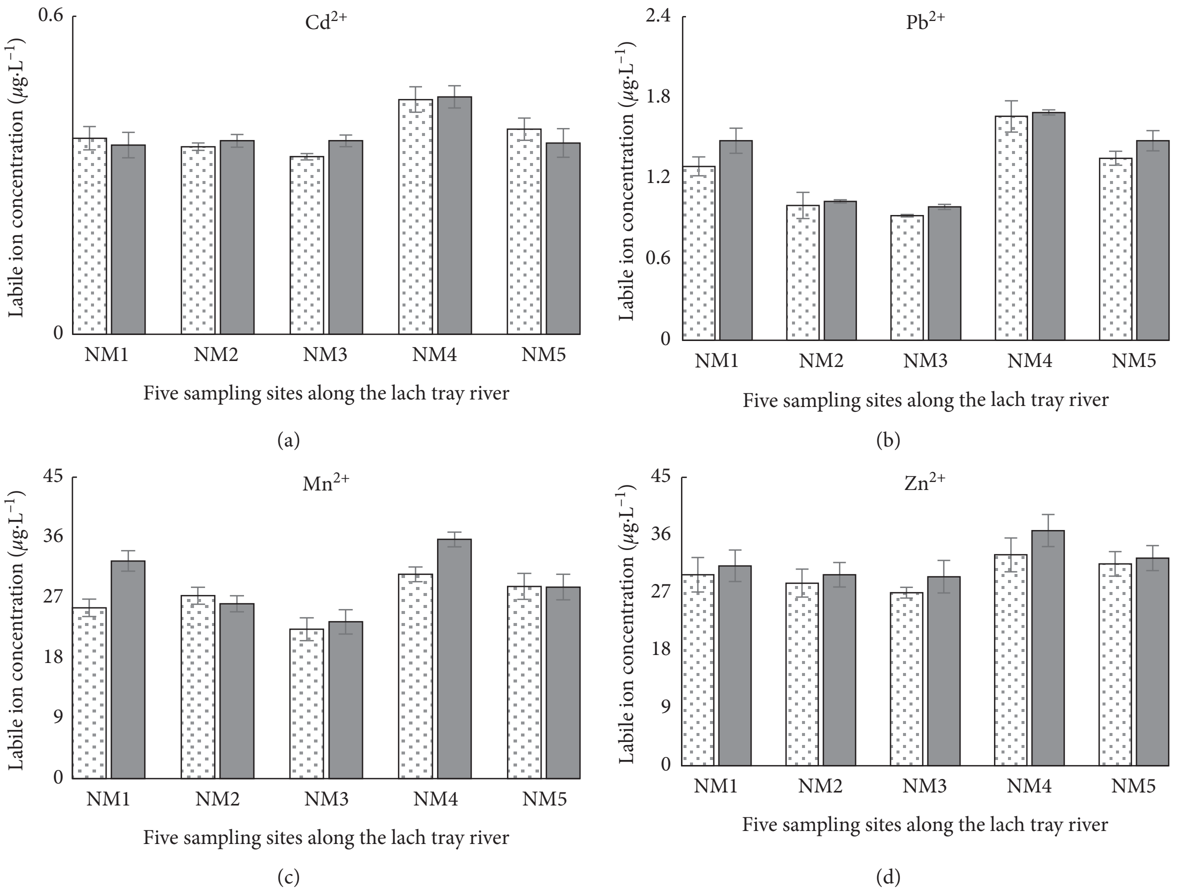
Figure 3: Laboratory-based determinations of labile metal fractions in Lach Tray River water using DGT-MMT (pattern fill) and DGT-Chelex-100 (solid fill).

variation in concentrations of labile metals in river water for a long time, at least during the deployment period. As a result, DGT devices might be exposed to similar hydrodynamic conditions in river and in lab-based performance as observed.

3.4. Comparison between DGT and the Anodic Stripping Voltammetry (ASV) Technique. According to [45], anodic stripping voltammetry (ASV) has been widely recognized as a powerful tool for the analysis of metal ions and certain organic compounds in solutions. Therefore, in order to compare the results of labile metal concentrations determined using DGT-MMT probes with data obtained by ASV technique, water samples taken from different sampling sites along the Lach Tray River were also analyzed by using a portable voltammeter (PDV6000plus). The labile metal fractions in river water samples measured by both techniques are shown in Figure 4.

As can be seen from Figure 4, labile Cd, Pb, Mn, and Zn concentrations in the river water were 0.357–0.448 μg·L^{-1}, 0.989–1.69 μg·L^{-1}, 23.4–35.7 μg·L^{-1}, and 29.5–36.7 μg·L^{-1}, respectively, according to the ASV technique. Insignificant differences (less than 10%) in the labile metal concentrations measured by using DGT-MMT probes and ASV technique were obtained.

According to [46, 47], the metal accumulation mechanisms of these techniques are similar, but different in kinetic window (time-scale). Therefore, similar information related to distribution of labile metal species in the same water environment is expected, but lower labile metal fractions measured by ASV are generally observed due to the shorter kinetic window. Zhang and Davison [48] stated that, for the ASV, the diffusion layer thickness is 10 μm and effective time of the measurement is around 0.1 s. Meanwhile, the diffusion layer thickness is 0.9 mm, and the effective measurement time is 13.5 min for DGT. However, complexing capability of metals to organic ligands present in water environment may affect the measurements by both techniques. Different observations have been reported when results obtained by DGT were compared with the data from ASV. For examples, Cindríc et al. [49] found that ASV-labile concentration was 35% lower than that of the DGT labile during analysis of labile Cu in estuarine water, whereas Zhang and Davison [48] reported higher ASV concentrations compared to the DGT data when labile Cu was determined in natural water containing humic substances. Those significant differences in the labile Cu fraction measured by DGT and ASV might



(a) (b) (c) (d)

Figure 4: Labile metal fractions in Lach Tray River water determined using DGT-MMT (pattern fill) and ASV (solid fill) techniques.

be originated from the slow dissociation kinetics of very strong complexes of Cu with organic ligands [49, 50]. However, for the cases of Mn, Zn, Pb, and Cd, their weak complexes with organic matters may not highly affect the measurement of ASV [49, 51]. This may explain the equivalent results measured by DGT and ASV in the present study as observed.

Apart from the complexation, other possibilities could be proposed for this discrepancy, including (1) unsuitable conditions for the ASV measurement, (2) overestimation of the measurement by DGT, and (3) high proportion of complexed metal fraction with low diffusion coefficients [50]. More research should be done in the future for clarification of this matter. Within the framework of present study, obtained results again confirm the applicability of MMT as a binding phase in the DGT technique for the determination of labile Cd, Pb, Mn, and Zn in natural water systems.

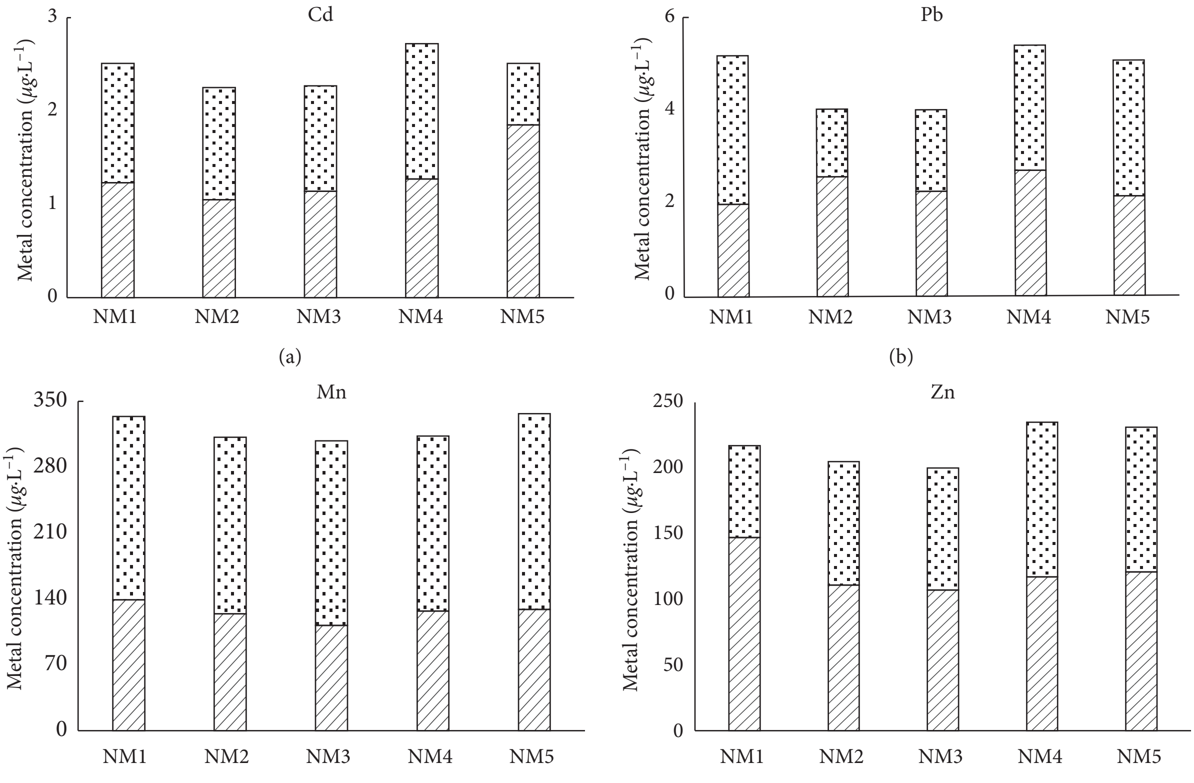
3.5. Distribution of Metal Fractions in Lach Tray River Water.

To determine the distribution of Cd, Pb, Zn, and Mn species in Lach Tray River water, the total and dissolved concentrations of these metals were analyzed, and these results are illustrated in Figure 5. The particulate metal proportions were determined from the difference between the total and dissolved metal concentrations.

The results showed that the total Cd varied from 2.27 to 2.51 μg·L^{-1}, while the dissolved fraction ranged from 1.05 to 1.85 μg·L^{-1}. The percentage of dissolved Cd compared to total Cd varied from 46.7 to 73.7% depending on the sampling site. In the case of Pb, the proportion of dissolved species also fluctuated from 38.5 to 63.9% at the level of 1.99–2.69 μg·L^{-1}, while the total Pb concentrations ranged from 4 to 5.37 μg·L^{-1}. In contrast to the low concentrations of Cd and Pb, higher levels of Mn and Zn were observed. The total Mn concentrations ranged from 308 to 334 μg·L^{-1}, while the dissolved fraction concentrations ranged from 112 to 139 μg·L^{-1}, which amounted to 36.4–41.6%. Total Zn concentrations ranged from 200 to 235 μg·L^{-1}, while the dissolved fraction concentrations ranged from 107 to 147 μg·L^{-1}, which amounted to 49.8–67.7%. No significant differences in the proportions of dissolved species within the sampling area were observed, except for Cd at NM5 and Zn at NM1.

To determine the distributions of metal species in Lach Tray River water, the proportions of labile metal species, nonlabile metal species (in dissolved fractions), and metals bound to particulate matter were calculated, and these data are illustrated in Figure 6.

As shown in Figure 6, the ratios of labile to nonlabile species in nonparticulate fractions for the four targeted metals varied largely depending on the metal. The highest ratio of the labile fraction was found for Pb species at



(a) (b)

(c) (d)

Figure 5: Proportions of dissolved (diagonal pattern fill) and particulate (dot pattern fill) metal concentrations in Lach Tray River water.

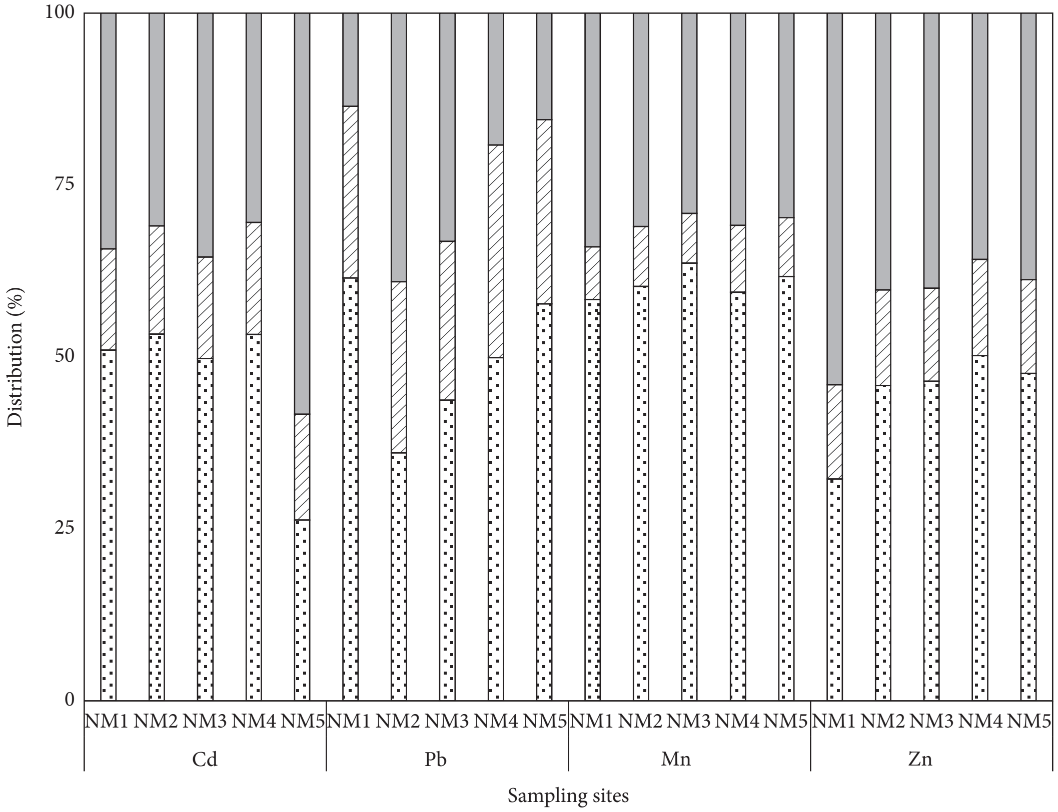


Figure 6: Proportions of nonlabile (solid fill), labile (diagonal pattern fill), and particulate (dot pattern fill) metal concentrations in Lach Tray River water.

percentages of 38.9–64.8%, while lower ratios of 20.9–34.9% were observed for Cd, followed by decreasing values of 18.3%–24.0% for Mn and 20.3–28.1% for Zn. Additionally, it was observed that the distribution of labile to dissolved concentrations changed from site to site along the Lach Tray River. In particular, higher labile metal concentrations were observed closer to the sewage sites. The highest labile metal proportions in Lach Tray River water were detected at the NM4 sampling site (near the discharge point of the shipyard), and the lowest proportions were detected at NM3. In the downstream area of the river, the percentage of metals associated with particulates increased likely as a result of the cumulative higher discharges amounts to the river. Among the tested metals, the relatively high labile fractions of Pb at all of the sampling sites were of most concern for the potential risk of metal bioaccumulation in the study area.

4. Conclusions

Extensive testing was carried out to determine if DGT-MMT probes can be used for the quantification of labile Cd, Pb, Mn, and Zn concentrations in aquatic environments and natural water samples. Statistical data based on seven measurement replicates demonstrated that the DGT-MMT probe data have high repeatability, good accuracy, and low relative standard deviations. The values of labile metal fractions measured by DGT-MMT probes were comparable to the measurements derived by using conventional DGT-Chelex-100 devices. In applications involving the determination of trace metals in Lach Tray River water, consistency in the labile fractions of the four targeted metals obtained by both DGT tools was observed, thus implying good working performance of the DGT-MMT devices. In comparison with traditional analyses using the ASV technique, the relative deviation of labile metal concentrations between the DGT and ASV techniques was smaller than 10%.

For the determinations of labile metals in Lach Tray River water using DGT-MMT probes, the labile metal fractions increased in the order of Cd < Pb < Mn < Zn, with the highest concentration being $37\,\mu g{\cdot}L^{-1}$. Again, the relative standard deviation between measurements was lower than 10%, thus confirming the good repeatability of the DGT-MMT data. The largest proportions of labile metals in the nonparticulate fraction were observed for Pb (40%–65%), followed by Cd (21%–35%) and Zn (20%–28%), while the lowest proportions were found for Mn (18%–24%); these data varied somewhat based on the sampling position along the river. The relatively high-lability Pb fractions at all sampling sites in the Lach Tray River are of concern in relation to risks for biological impacts from this heavy metal in the research basin. Concerning the geographic distribution of labile fractions in the Lach Tray River, the highest labile metal concentrations were usually detected at NM4 near the discharges of industrial shipyard areas.

In summary, the good working performance of DGT-MMT probes revealed that there is high potential for the use of low-cost and naturally available MMT as an alternative binding phase for synthetic Chelex-100 resins in the DGT method to determine labile fractions of Cd, Pb, Mn, and Zn in natural water samples.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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