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## Comparison of Chelex Based Resins in Diffusive Gradients in Thin-Film for High Resolution Assessment of Metals

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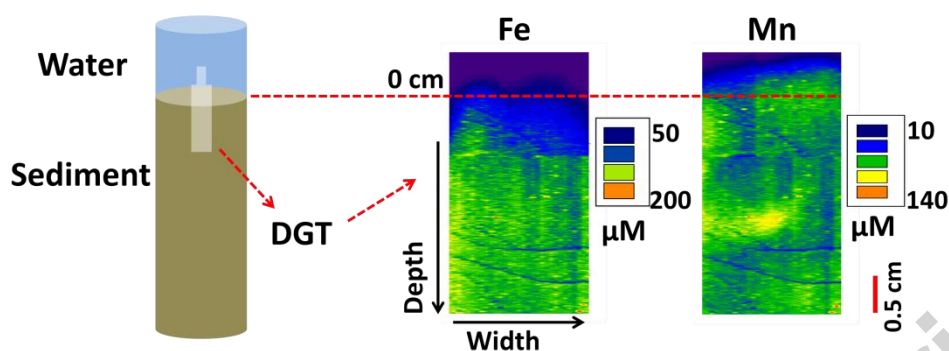
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### Abstract

The passive sampling technique of diffusive gradients in thin-film (DGT) is widely used to determine 1D profiles (using Chelex-100 resin) and 2D images (using suspended particulate reagent-iminodiacetate resin, abbreviated as SPR-IDA resin) of metals in sediment pore waters and in oxic/anoxic soils. However, when deployed in anoxic sediments with high metal concentrations, Fe and Mn concentrations determined with the Chelex-100 resin gel were ~5 times higher than concentrations measured with the SPR-IDA resin gel. This discrepancy suggests that the SPR-IDA resin gel is saturated faster than the Chelex-100 resin gel. Here, we tested the adsorption capacity of the SPR-IDA resin gel and compared it to the Chelex-100 resin gel. Fe and Mn binding capacities on a SPR-IDA gel disc are less than 0.1  $\mu$ moles, which means that they are far below those on a Chelex-100 gel disc (around 3.2  $\mu$ moles), while competition with stronger binding metals such as Cu and Cd further lowers Fe and Mn capacities. This restricts the SPR-IDA resin gel to be used in contaminated marine sediments. We propose the use of a ground Chelex-100 resin, which is prepared by grinding Chelex-100 resin in a ball-mill prior to gel preparation. The capacities of Fe and Mn on a ground Chelex-100 resin gel disc are around 1.6  $\mu$ moles, more than 16 times higher than the capacity on SPR-IDA gel

disc. In addition, the bead size of the ground Chelex-100 resin is small enough ( $\sim 10\ \mu\text{m}$ ) to allow high resolution LA-ICP-MS imaging of Fe, Mn and trace metals in sediment pore waters as well as soils.

#### Graphical Abstract:



(5 × 13 cm, resolution 150 dpi)

**Keywords:** Diffusive Gradients in Thin-Film (DGT), Chelex-100, SPR-IDA, capacity, ground Chelex-100, high resolution

#### Introduction

Metals behavior in sediments is regulated by precipitation/dissolution, oxidation/reduction and adsorption/desorption, with some of these processes occurring in combination [1–3]. During organic matter mineralization, iron and manganese oxides are reduced, releasing Fe(II) and Mn(II) in the pore water [4, 5]. The resulting reduced Fe and Mn species are much more soluble than their oxidized forms, but in anoxic environments sulfides or carbonates will again precipitate the reduced metal species [6–8]. These Fe/Mn dissolution/precipitation reactions also control the

mobilization/immobilization of co-existing trace metals, e.g. by co-precipitation with sulfide minerals like iron mono-sulfide (FeS) or pyrite (FeS<sub>2</sub>) [9]. The concentration of Fe and Mn can reach millimolar levels in contaminated sediments [5, 8, 10], which is much higher than the level of trace metals, which are typically 3 – 6 orders of magnitude lower. Sediments are heterogeneous, and pore water concentration gradients exhibit three dimensional features. Traditionally, pore water concentrations were determined by vertical slicing, extraction of the pore water and subsequent analysis [11, 12]. This technique generates one dimensional profiles but at a low resolution (typically at cm level), leading to a loss of information with respect to the fine spatial heterogeneity that is typical for marine sediments. With the development of diffusive gradients in thin-film (DGT) technique, simultaneous imaging of multi-analytes in soils and sediments is achieved, providing more detailed information about the behavior of these analytes [13–15].

A DGT sampler consists of three stacked layers; a filter membrane (0.45 µm) at the top, a diffusive gel and a resin gel at the bottom. The resin that is commonly used for metal analysis in sediment pore waters is Chelex-100 (abbreviated as CH, bead size 100 µm) with iminodiacetate as the functional group. The routine treatment of the resin gel after deployment is slicing it into 5 mm strips, eluting the gel strips with 1 M HNO<sub>3</sub> and analyzing this eluate [16]. This procedure results in one dimensional, vertical profiles of solutes at mm resolution. The use of a new binding agent, suspended particulate reagent-iminodiacetate (abbreviated as SPR-IDA, bead size 0.2 µm) in combination with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), enhances the resolution to 100 µm, which is 10 times higher than with the CH resin. This improvement makes the technique very promising for the investigation of trace metal distribution and mobilization in sediments or soils at ultra-small scale and in two dimensions [17, 18].

The key limiting parameter for widespread application of this gel technique is the binding capacity of the resin gel. However, very few studies have documented the capacity of the SPR-IDA gel disc. Warnken et al. [19] reported that the capacity of Cd is around 2.3 µmoles per SPR-IDA gel disc and around 5.6 µmoles per CH gel disc, which infers that the capacities of Fe and Mn are both also

around 2.3  $\mu\text{moles}$  on a SPR-IDA gel disc. However, a recent study addressing the pollution in the Zenne river, a contaminated tributary of the Scheldt river, revealed that the Fe and Mn concentrations in sediment pore water obtained from the CH DGT probe were about a factor 5 to 10 higher than those observed from the SPR-IDA DGT probe (Figure S1), despite both resins contain the same functional groups. This discrepancy suggested that the SPR-IDA resin was not suited for measurement of high dissolved metal concentrations.

Here, we present an in-depth study of the binding capacities of CH and SPR-IDA gel disc for Fe and Mn. We also experimentally determined the influence of competing elements such as Cu and Cd (single and as a mixture) on the Fe and Mn binding characteristics of both resins. From these results, we could conclude that the SPR-IDA gel disc has a low binding capacity and cannot be used in highly enriched pore waters. A ground Chelex-100 (GCH) gel disc was therefore developed, characterized, validated and applied in pore waters for high resolution, 2D imaging of dissolved Fe, Mn, Co and Ni.

## Materials and methods

### *2.1 DGT piston and probe assembly*

All DGT gels, pistons and probes were prepared according to the method described previously [20, 21] and are detailed in supplementary information.

### *2.2 Elution factors for the GCH resin and SPR-IDA resin gels*

Elution factors ( $f_e$ ) for Fe, Mn, Cd, Co, Cu and Ni from GCH and SPR-IDA resin gels were determined. Six resin gel discs were immersed in a solution containing 5  $\mu\text{g L}^{-1}$  of all metals at a pH of 6 for 2 days. In parallel, control experiments without resin gel discs in the metal solution were run. At the start and the end of the experiments, sub-samples of the solution were taken, and metal concentrations were analyzed by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, Thermo Element 2). Three blanks of each type of resin gel followed the same procedure except the immersion. After deployment, all resin gels were eluted in 1 mL 1 M  $\text{HNO}_3$  and analyzed by HR-ICP-

MS. The elution factor ( $f_e$ ) was determined as the ratio of the experimental eluted mass ( $M_e$ ) and the theoretical accumulated mass ( $M_t$ )

$$f_e = M_e / M_t \quad (1)$$

where  $M_t$  is the amount of metal removed from solution during the deployment (corrected for metal adsorption on the container walls) and  $M_e$  is the amount of metal eluted with 1 M  $\text{HNO}_3$  from the deployed resin gel disc (corrected for the blank discs).

### 2.3 Calculation of the metal concentration in deployed solution

The DGT metal concentration ( $C_{dgt}$ ), which equals to the metal concentration in a well-mixed deployed solution ( $C_s$ ), as long as the resin does not reach its saturation point [22], can be calculated as

$$C_s = C_{dgt} = M (\Delta g + \delta) / D t A \quad (2)$$

where  $\Delta g$  is the thickness of diffusive layer (0.094 cm),  $\delta$  is the thickness of diffusive boundary layer (DBL),  $M$  is the mass of metal on the resin,  $D$  is the diffusion coefficient of the metal ( $T = 20^\circ\text{C}$ ) [23],  $t$  is the DGT deployment time and  $A$  is the exposure area of a DGT piston ( $r = 1$  cm). When a typical 0.8-mm diffusive gel is used in a well-stirred or rapidly flowing solution, the DBL can be ignored and the geometric exposure area ( $3.14 \text{ cm}^2$ ) can be used [24, 25]. So the thickness of DBL was omitted in the concentration calculations of this study.

### 2.4 Spiking test

To determine whether there is a difference between CH gel disc and SPR-IDA gel disc towards the metal binding efficiency, a simple test was done in the laboratory. 10 L of tap groundwater (The physicochemical parameters of this groundwater are reported in Table S1 in Supplementary Information of this paper) was sampled in the laboratory and spiked with  $1700 \mu\text{M}$  of Fe and Mn and  $0.3$ ,  $0.5$ ,  $0.5$  and  $0.6 \mu\text{M}$  of Cd, Co, Cu and Ni respectively.

Three SPR-IDA DGT and three CH DGT pistons were deployed in each of the spiked solution, which was continuously mixed by a magnetic stirrer (stirring rate > 300 rpm) for 5 h at room temperature (~20°C). Afterwards these pistons were removed from the solution and the resin gels were peeled off and eluted with 1 mL 1 M HNO<sub>3</sub>, the gel eluents were then analyzed by high resolution - inductively coupled plasma - mass spectrometry (HR-ICP-MS; Thermo Scientific Element 2) after dilution with Milli-Q water containing 1% HNO<sub>3</sub>. Indium (2.5 µg L<sup>-1</sup>) containing 2% HNO<sub>3</sub> was injected simultaneously with the samples as an internal standard.

#### *2.5 Capacity and affinity tests of Fe and Mn on CH and SPR-IDA gel disc*

1000 mg L<sup>-1</sup> metal stock solutions of FeCl<sub>2</sub>, MnCl<sub>2</sub>, CdCl<sub>2</sub> and CuCl<sub>2</sub> were prepared in Eppendorf vessels (polypropylene, PP) in an oxygen free atmosphere and kept in the refrigerator at 4°C. Standard solutions were prepared freshly under oxygen free condition before each new experiment. In order to verify the capacity and affinity of Fe and Mn on CH and SPR-IDA gel disc, 3 CH and 3 SPR-IDA DGT pistons were mounted in the same plastic rack holder and the whole rack including DGT pistons was then placed in a polypropylene container filled with solutions containing different concentrations of Fe, Mn, Cd and Cu (Table 1). All prepared solutions containing 0.03 M NaNO<sub>3</sub> were well mixed during the experiment with a magnetic stir bar. Three DGT piston blanks for each type of resin were followed the same procedure except for the deployment. The whole experiment lasted 4 hours and was performed under an oxygen free condition in a glove bag by purging with N<sub>2</sub> flow. After the deployment, the resin gels including the blanks were eluted with 1 mL 1 M HNO<sub>3</sub>. Sub-samples of the immersion solutions were taken before and after the experiments under oxygen free condition. The solution and gel eluents were analyzed by HR-ICP-MS, as described above.

#### *2.6 Preparation of GCH resin and capacity tests of Fe and Mn on GCH gel disc*

A former study on Zenne River sediments showed that the application of SPR-IDA is limited by its capacity, while CH is limited by its resolution (due to its large bead size of 100 µm). As an alternative to both resins, we ground the CH resin beads and embedded them into a gel matrix in the same way



as for the SPR-IDA resin [21], details can be found in Supplementary Information. Two grams of freeze-dried CH resin beads were put into a metal-free Polytetrafluoroethylene (PTFE) jar (25 mL), which is equipped with a PTFE coated metal ball, and was then fixed onto a Mixer Mill (MM200, Retsch®). After 20 minutes vibration at a frequency of 20 Hz, the ground CH resin, hereafter named GCH resin, was transferred into a 50 mL centrifuge tube. 20 mL Milli-Q water was added into the tube which was then vigorously agitated until the GCH resin was homogeneously suspended in water. To make a resin gel, the GCH resin beads were evenly dispersed on the gel surface using the same method as for the SPR-IDA resin. The GCH resin gel was dried using BioRad gel dryer (BioRad, Germany) and then scanned by scanning electron microscopy (SEM, IT300, JEOL®) to check the uniformity and to measure the real bead size after milling (SEM was operated under high vacuum mode and the accelerating voltage is 5.0 kV).

The capacity of Fe and Mn on GCH gel disc was tested in the same fashion as for the CH and SPR-IDA gel disc. The GCH DGT pistons were deployed for 4 h in 2 L well-stirred solutions containing a range of concentrations of Fe between 1 and 1500  $\mu\text{M}$  at pH 5. The same procedure was followed for testing the capacity of Mn.

### *2.7 Field application of the GCH DGT probe*

The true strength of the SPR-IDA resin gel lies in its ability to achieve high resolution, 2D images of trace metals in soil and sediment pore waters. To provide a proof-of-concept of our novel developed GCH resin gel, we deployed the GCH DGT probe in sediment, collected with a sediment trap, from the Belgian Coastal Zone. The sediment displayed distinct layers and consisted of clay minerals [26], which is well suited for DGT application due to the vertical heterogeneity of the sediment layers.

Two DGT probes, CH DGT and GCH DGT, were deoxygenated prior to the deployment by purging  $\text{N}_2$  for 24 h in 0.03 M NaCl solution. These probes were arranged back to back and vertically inserted into the sediment trap. After 10 h deployment, two probes were retrieved and the surface of the DGT probe were rinsed thoroughly with MQ water. For CH probe, the CH resin gel was peeled from

the probe and sliced at a resolution of 0.5 cm. Each slice was eluted in 1 ml of 1 M HNO<sub>3</sub> solution for at least 24 h and the eluate was subsequently analyzed by HR-ICP-MS. For GCH probe, the GCH resin gel was peeled off and placed onto a clean filter membrane and dried at 60°C for at least 24 h in the gel dryer (BioRad, Germany). The dry GCH gel was placed on a glass plate under the laminar hood in the clean lab and analyzed by LA-ICP-MS (Thermo Elemental X-Series II ICP-MS connected to an ESI 193FX LA system) using line scan mode.

Details about the operating parameters of LA-ICP-MS are presented in Supplementary Information. Calibration was done using the GCH DGT pistons deployed in multi-metals standard solutions. The whole procedure and the calibration curve results are described in the Supplementary Information.

## Results and discussion

### *3.1 Elution factors ( $f_e$ ) of metals for SPR-IDA and GCH resin gels*

Elution factors are expressed as the ratio of the amount of metals eluted from the resin to the total amount of metals initially adsorbed onto the resin. In the control solutions, the difference between final and initial masses was smaller than 3% for all elements, implying that mass losses onto the container wall were negligible. Even though this amount was very low, it has been taken into account for the elution factor calculations. The accumulated mass of each element on the SPR-IDA and GCH resin gel was calculated using the difference in the immersing solution before and after gel deployment. Elution factor values (Table 2) for SPR-IDA and GCH resin gels are similar, while most of them are slightly higher than the values for CH resin gel. These values were used, each of them for the corresponding resin gel, in further calculations (Table 2).

### *3.2 Comparison between CH and SPR-IDA gel disc in spiked tap groundwater*

CH and SPR-IDA DGT pistons were deployed in a tap groundwater sample (relevant physicochemical parameters are present in Table S1), spiked with a known mixture of metals. Orange-brown aggregates became immediately visible in this solution most likely due to the formation of Fe-oxy-

hydroxides. Although the spiked concentrations of Fe and Mn to the tap groundwater were both 1700  $\mu\text{M}$ , the values measured by CH DGT piston were around 5  $\mu\text{M}$  for Fe and 360  $\mu\text{M}$  for Mn respectively, thus 340 and 5 times lower than the spiked concentration, confirming the precipitation of Fe (Figure 1). Similarly, the measured concentrations of Cu and Cd by CH DGT piston were 40 and 150 times lower than the spiked concentrations (0.5 and 0.3  $\mu\text{M}$  respectively). This can be explained by the co-precipitation with Fe oxyhydroxides which can adsorb large fractions of these metal cations [27]. No significant difference was observed between the concentrations of Co, Ni, Cd and Fe measured by CH and SPR-IDA DGT pistons and a difference ( $p = 0.04$ ) was obtained for Cu according to the independent t-test in SigmaPlot software. However, 4 times higher values were measured for Mn by the CH DGT than by the SPR-IDA DGT piston ( $p < 0.01$ , Figure 1). This is consistent with previous results obtained by two types of DGT probe deployed in the sediments of Zenne River (Figure S1), where Mn concentrations measured by CH probe were 5 to 10 times higher than those measured by SPR-IDA probe. These results suggested that there was a problem related to a difference in capacity levels of CH and SPR-IDA gel discs that needed to be further tested.

### *3.3 Capacity tests of Fe and Mn on CH and SPR-IDA gel disc*

Capacities of Fe and Mn on CH and SPR-IDA gel disc were tested at concentrations covering 3 orders of magnitude (1 - 2400  $\mu\text{M}$ ). Figure 2A shows the amount of Fe accumulated on the SPR-IDA gel disc (black circle) and the CH gel disc (red triangle), respectively. The amount accumulated on the SPR-IDA gel disc was equal to the theoretical value as long as the solution concentration was lower than 30  $\mu\text{M}$  (Magnified area in Figure 2A). But at higher deployment concentrations it gradually deviated from that theoretical line, suggesting that the capacity of Fe on SPR-IDA gel disc is only around 0.08  $\mu\text{moles}$ . The amount of Fe accumulated on the CH gel disc was equal to the theoretical value as long as the accumulated amount was below 3.2  $\mu\text{moles}$ , but deviated from that theoretical line at higher amounts. These results suggest that the capacity of Fe on CH gel disc is about 30 times higher than that on SPR-IDA gel disc (Figure 2A).

Manganese exhibits a similar behavior as Fe (Figure 2B). The amount accumulated on SPR-IDA gel disc deviated from the theoretical line after around 0.05  $\mu\text{moles}$ , while the amount on CH gel disc was equal to the value on the theoretical line even up to 3.2  $\mu\text{moles}$ . Clearly, the capacity difference between the two types of gel is the cause of the difference in observed concentrations during deployment in Zenne river and spiked tap groundwater.

### 3.4 Competition effect of Cu and Cd on Fe accumulation on CH and SPR-IDA gel disc

The low capacity of the SPR-IDA gel disc for Fe and Mn could be also reduced when stronger competing cations are present. The approximate affinity order for metals binding on Chelex-100 resin is as follows:  $\text{Cu}^{2+} \gg \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+} \gg \text{Na}^+$  [28]. This selectivity sequence shows that  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  have a lower affinity with this type of resin compared to cations such as  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . Therefore, the competition between  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  (the strongest binding cation) and between  $\text{Fe}^{2+}$  and  $\text{Cd}^{2+}$  (slightly stronger binding than Fe) to bind on the SPR-IDA gel disc was studied. Five concentration levels of Cd (10 to 45  $\mu\text{M}$ ) were added to 45  $\mu\text{M}$  of Fe solution. On the SPR-IDA gel disc, the increase of Cd concentration in the solution (from 10 to 35  $\mu\text{M}$ ) led to a slight decrease of Fe accumulated on the resin (0.1 to 0.06  $\mu\text{moles}$ ; black triangles, Figure 3A), whereas Cd accumulation increased from 0.03 to 0.05  $\mu\text{moles}$  (black circles, Figure 3A). It is obviously that Cd competes with Fe to bind on the SPR-IDA gel disc. At higher concentration levels in the solution, no further accumulation of Cd occurs, which is probably due to the reaching of the SPR-IDA gel disc capacity limit ( $\sim 0.1$   $\mu\text{moles}$ ).

Fe accumulation on CH gel disc is less affected by the competition with Cd, the amount stays at 0.13  $\mu\text{moles}$  (red triangles, Figure 3B) despite the increase of Cd concentration in solution. Cd accumulation on CH gel disc increased linearly along with the rise of Cd concentration in solution (red circles, Figure 3B), with the highest Cd accumulation (0.18  $\mu\text{moles}$ ) at a concentration of 45  $\mu\text{M}$ , which is almost 4 times higher than on the SPR-IDA gel disc. The accumulation of Cd on the SPR-IDA gel disc reaches quickly a steady value of 0.05  $\mu\text{moles}$ . CH gel disc has a much larger binding capacity

than the SPR-IDA gel disc towards Fe and Mn, and most likely also towards other metals such as Cd, in contradiction with literature data [19, 29]. Moreover, these tests show the competing effect of Cd, that has only a slightly higher affinity, on the Fe and Mn accumulation on the SPR-IDA gel disc, but not on the CH gel because of its higher capacity.

In the selectivity list, Cu shows the highest affinity with Chelex-100 resin. Five concentration levels of Cu (20 to 90  $\mu\text{M}$ ) were added to a mixture of 45  $\mu\text{M}$  of Fe and 12  $\mu\text{M}$  of Cd solution. On the SPR-IDA gel disc, an increase of Cu concentration in the solution led to a decrease of Fe accumulation on the resin from 0.06 to 0.04  $\mu\text{moles}$ , and also a big drop for Cd (Figure 3C). The Cu accumulation on SPR-IDA gel disc increased up to 0.2  $\mu\text{moles}$  for a concentration in solution of 70  $\mu\text{M}$ . It confirms that Cu severely competes with Fe and even Cd to bind on the SPR-IDA resin. The higher accumulation of Cu on SPR-IDA gel disc (0.2  $\mu\text{moles}$ ) suggests that there is may be a capacity difference between metals.

Fe and Cd accumulation on the CH gel disc were not affected by the competition of Cu, the amount of the two metals remained around 0.12 and 0.04  $\mu\text{moles}$  respectively (Figure 3D). Cu accumulation showed a continuously increasing trend with the rise of concentration in solution. The highest accumulation amount is 0.32  $\mu\text{moles}$  at a Cu concentration of 90  $\mu\text{M}$  in solution, which is 1.6 times higher than the largest accumulated amount on SPR-IDA gel disc (0.2  $\mu\text{moles}$ ). Obviously, the Fe and Mn binding capacity on SPR-IDA gel disc can be further reduced by the competition of Cu and Cd, which have a stronger affinity on iminodiacetate based chelating resins.

### 3.5 Characterization of GCH resin gel

The previous results show that the differences observed for Fe and Mn between CH and SPR-IDA gel disc, are due to the lower capacity of the SPR-IDA resin, amplified by the competition of Fe and Mn with stronger binding cations such as Cd and Cu. Therefore, we developed a new ground Chelex-100 (GCH) resin, which combines the high capacity of the CH resin, and the small bead size of the SPR-IDA resin.

The Fe and Mn capacities on GCH gel disc were tested identically as for the CH and SPR-IDA resins.

The accumulation of both Fe and Mn on the GCH gel disc was increasing linearly with rising concentration in solution (Figure 2A, B). The accumulation of both Fe and Mn around 1.6  $\mu\text{moles}$  starts to deviate from the theoretical line when the concentration in solution reaches 800  $\mu\text{M}$ . Thus the capacities of Fe and Mn on GCH gel disc are 16 times higher than those on SPR-IDA gel disc.

The amounts of dried resin beads per gel disc are around 4 mg for CH, 2.5 mg for GCH and 0.5 mg for SPR-IDA, which results in the following capacity values for Fe and Mn per mg resin: 0.80  $\mu\text{moles}$  Fe or Mn/mg CH; 0.64  $\mu\text{moles}$  Fe or Mn/ mg GCH; 0.16  $\mu\text{moles}$  Fe/mg SPR-IDA and 0.10  $\mu\text{moles}$  Mn/mg SPR-IDA. This means that CH gel disc has the highest capacity, that GCH gel disc has a little lower capacity than CH, while SPR-IDA gel disc has still the lowest capacity even when the same amount of resin is considered.

According to Xu et al. [30], the capacity of Fe on CH gel disc is 45  $\mu\text{g cm}^{-2}$ , equals to 2.5  $\mu\text{moles}$  Fe per gel disc or 0.63  $\mu\text{moles}$  Fe/mg CH. This capacity value is slightly lower than the one we observed on CH gel disc but similar to the one found for GCH gel disc. According to Mason et al. [31], the capacity of Mn on Mixed Binding Layer (MBL) gel disc (made by mixing 3 g ferrihydrite and 1.5 g CH resin in 10 mL gel solution) is 0.72  $\mu\text{moles}$  Mn per gel disc. Considering 2.6 times lower amount of CH resin was used than in our study, the capacity equals then 0.48  $\mu\text{moles}$  Mn/mg CH, which is somewhat lower than what we observed on CH gel disc and also on GCH gel disc. There is no information available on the capacities of Fe and Mn on SPR-IDA resin gel disc in literature.

After verifying the capacity of GCH gel disc, the uniformity and bead size of each of the resin gels were checked by scanning the surface of dried gels using SEM. CH resin beads were unevenly dispersed on the gel surface and had a diameter of  $\sim 100 \mu\text{m}$  (Figure 4a), which was much larger than the GCH resin beads with a diameter of  $\sim 10 \mu\text{m}$  (Figure 4b,d). The SPR-IDA resin beads were still smaller than the GCH resin beads (Figure 4c, e). The GCH DGT can thus achieve higher resolutions

than the CH DGT (Details are presented in Supplementary Information), while having a very similar binding capacity.

### 3.6 *In situ* application of the GCH DGT probe

The CH resin can resolve vertical, millimeter-scale profiles, while the SPR-IDA resin allows imaging of metals at 100  $\mu\text{m}$  resolution using LA-ICP-MS [17]. To demonstrate the capability of GCH DGT probe in real environmental studies, it was arranged back to back with a CH DGT probe and deployed in the sediment core collected with a sediment trap in the Belgian Coastal Zone. According to the literature [32–34], the CH and GCH resin gels accumulate less  $\text{Mn}^{2+}$  in seawater than in fresh water due to competition effects from Mg and Ca. Additional experiments of  $\text{Mn}^{2+}$  accumulation on CH and GCH resin gels in salt water (0.6 M NaCl) with and without Ca and Mg showed a decrease of 60 % in the amount of Mn accumulated on the resins when Ca and Mg were present at seawater concentrations (10 mM Ca and 53 mM Mg). The concentrations of  $\text{Mn}^{2+}$  assessed with both DGT probes in seawater and calculated according equation (2), were therefore multiplied with a factor 2.5 (Figures 5 and 6). The vertical Fe, Mn, Co and Ni profiles obtained with the CH and the GCH probe were very similar (Figure 5). Fe, Mn and Co concentrations increased sharply across the water-sediment interface (SWI) and stayed relatively constant afterwards. In contrast, Ni concentrations peaked (24 nM) at the SWI, followed by a decrease to 15 nM at -3 cm depth. The smaller bead size of the GCH resin allowed, however, a 2D mapping of the trace metals in the pore water (Figure 6). For Mn, a hotspot was observed at -1.5 cm depth (maximum concentration 120  $\mu\text{M}$ ). The concentration of Co peaked in the vicinity of 0 cm (up to 20 nM), followed by a decrease. The 2D image of Ni shows an obvious hotspot at -1.0 cm depth (maximum concentration 50 nM).

Clearly, the newly developed GCH resin combines the advantage of a high capacity from the CH resin, with the enhanced resolution of the SPR-IDA resin. This makes it a promising tool for *in situ*, high resolution imaging of trace metals, which can extend the research into micro-scale biogeochemistry processes in sediment.

## Conclusion

For the determination of high resolution 2D images of trace metals in sediment pore waters with LA-ICP-MS, the use of SPR-IDA gel disc was previously a prerequisite. However, serious capacity problems with SPR-IDA gel disc were encountered. The SPR-IDA gel disc shows a much lower capacity for Fe and Mn than CH gel disc. In addition, other competing ions like Cd and Cu which have higher affinities than Fe and Mn in natural aquatic systems can further lower their binding capacity. Hence a fast saturation of SPR-IDA resin gel should be always considered when it is used in pore waters which are enriched in metals.

To solve this problem, we developed a new DGT with GCH instead of SPR-IDA as the resin phase. This GCH resin not only performs as effective as the CH resin but is also suitable for high resolution analysis (at 100  $\mu\text{m}$  and eventually 75  $\mu\text{m}$  resolution) with LA-ICP-MS. Further studies can now make use of this GCH DGT probe to unravel and better understand biogeochemical processes of metals in marine sediment pore waters at high resolution scale.

## Supplementary Information

Preparation of the gels; DGT piston and probe assembly; Calibration curves of metals on GCH resin gel to be used by LA-ICP-MS; LA-ICP-MS analyses at high resolution on GCH resin gel.

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Figure 1. Metal concentrations measured in spiked tap groundwater by Chelex-100 (CH) and SPR-IDA DGT pistons. The data are shown as the mean  $\pm$  SD (n=3). \* There is a statistically significant difference between two types of resin gels (T-test: \*P < 0.05 and \*\* P < 0.01).

Figure 2. Accumulated amount ( $\mu$ moles) of Fe and Mn on Chelex-100 (CH) (red triangles), Ground Chelex-100 (GCH) (blue rectangles) and SPR-IDA (black circles) gel discs deployed for 4 hours in solutions containing Fe or Mn in a concentration range of 1 to 2400  $\mu$ M. The solid line is the theoretical mass of Fe and Mn on each of the three types of resin gel. The embedded graphs in panel A and B are the amplified figures from the red frame areas.

Figure 3. Competition effect of Cd and Cu on Fe accumulation on SPR-IDA and Chelex-100 (CH) gel disc.

Figure 4. SEM images of Chelex-100 (CH) (A), Ground Chelex-100 (GCH) (B) and SPR-IDA (C) resin gel at 100  $\mu$ m scale, and the amplified images of GCH (D) and SPR-IDA (E) resin gel at 10  $\mu$ m scale. The red line appearing in image D represents a length of 10  $\mu$ m which is roughly similar as the diameter of the GCH resin bead.

Figure 5. Vertical concentration changes of Fe, Mn, Co and Ni in sediment pore water (red lines were obtained with Chelex-100 (CH) probe, black lines were obtained with Ground Chelex-100 (GCH) probe).

Figure 6. Two-dimensional concentration images of Fe, Mn, Co and Ni across water-sediment interface (0 cm depth) at high resolution obtained with Ground Chelex-100 (GCH) probe.

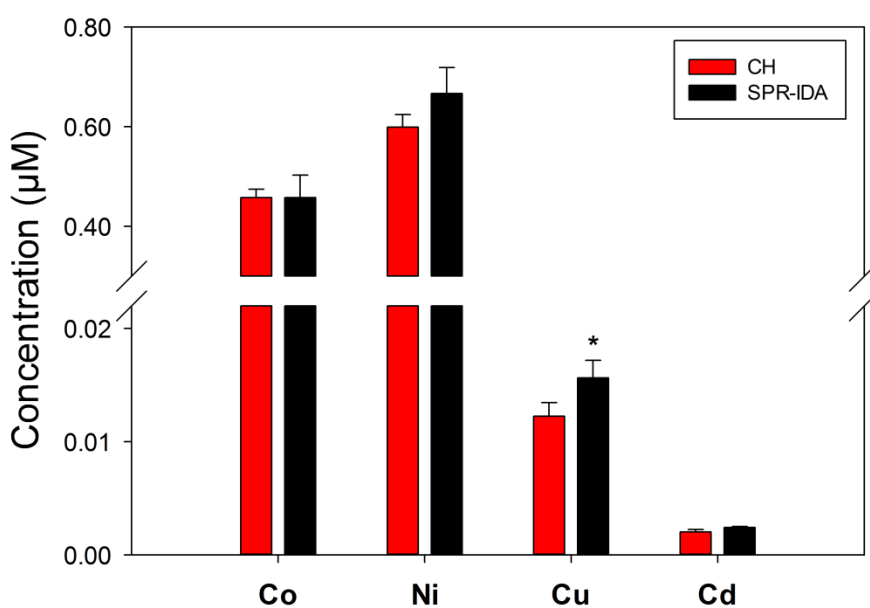
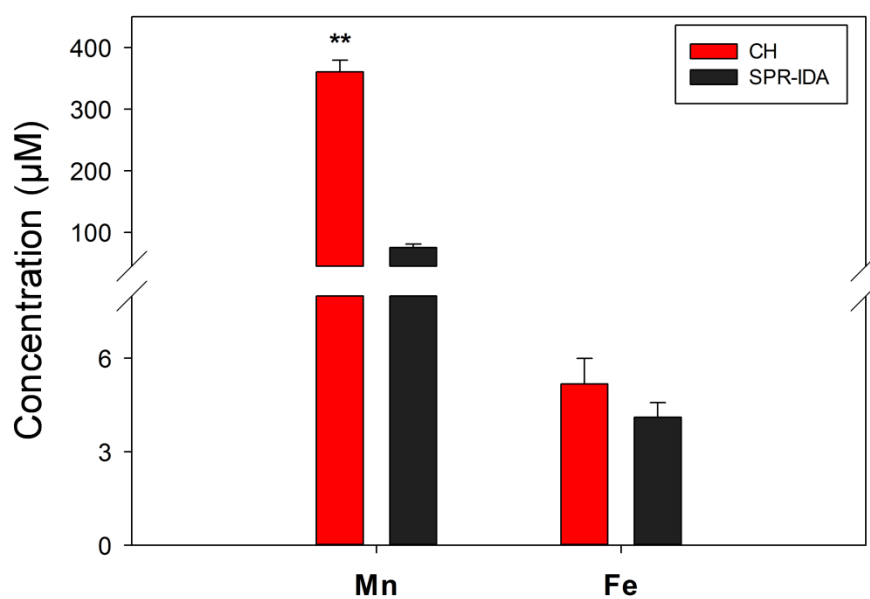


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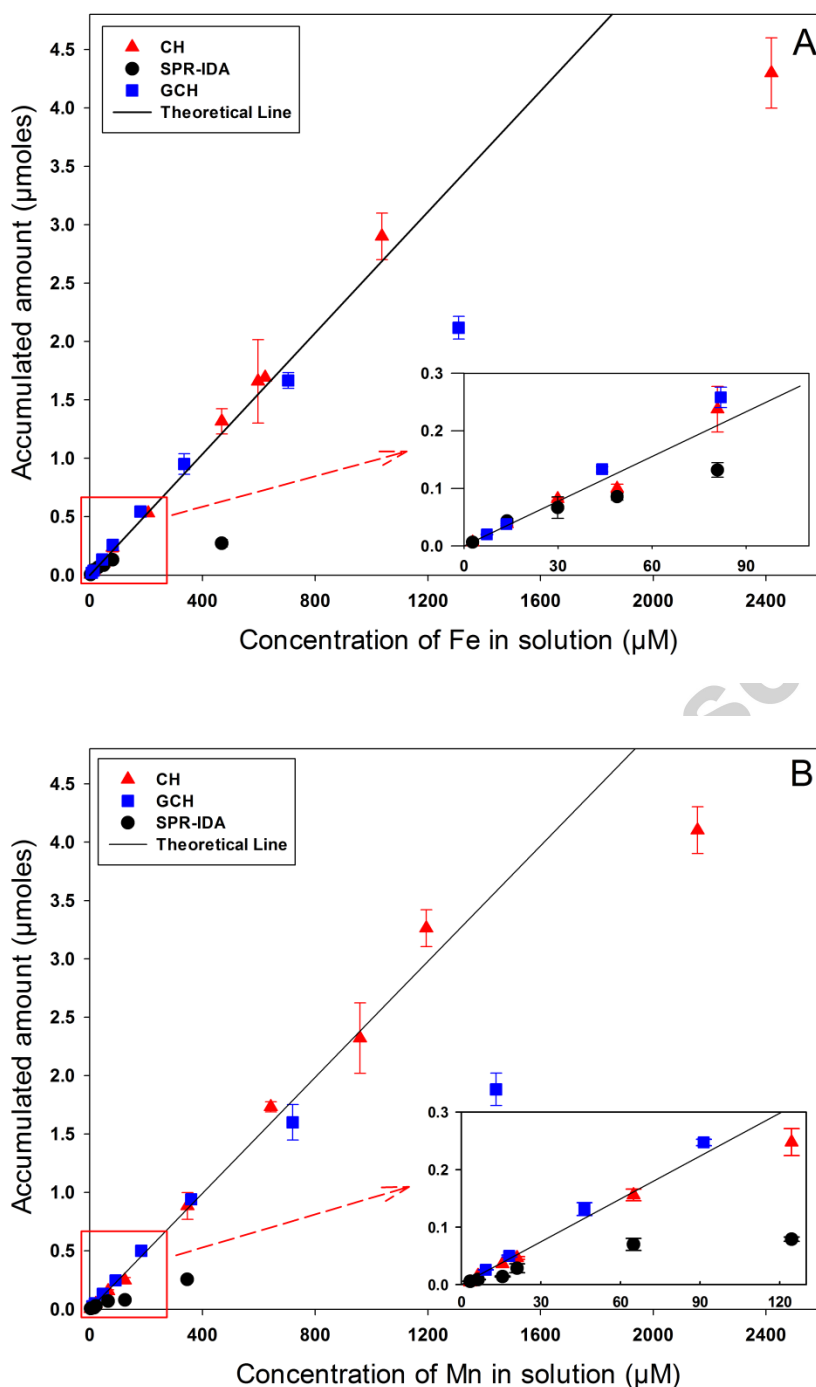


Figure 2. Accumulated amount ( $\mu\text{moles}$ ) of Fe and Mn on Chelex-100 (CH) (red triangle), Ground Chelex-100 (GCH) (blue rectangle) and SPR-IDA (black circle) gel disc deployed for 4 hours in solutions containing Fe or Mn in a concentration range of 1 to 2400  $\mu\text{M}$ . The solid line is the theoretical mass of Fe and Mn on each of the three types of resin gel. The embedded graphs in panel A and B are the amplified figures from the red frame areas.

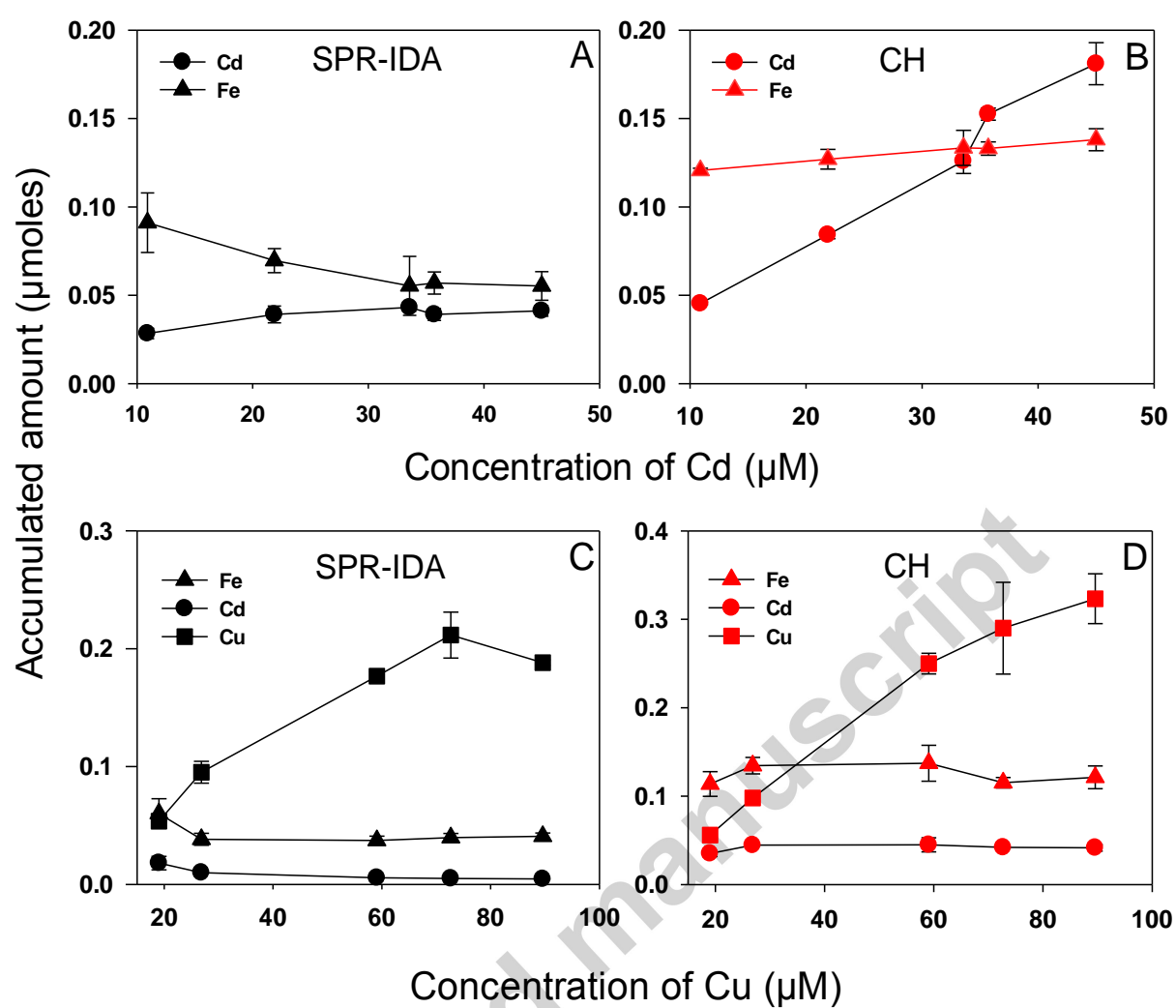


Figure 3. Competition effect of Cd and Cu on Fe accumulation on SPR-IDA and Chelex-100 (CH) gel disc.



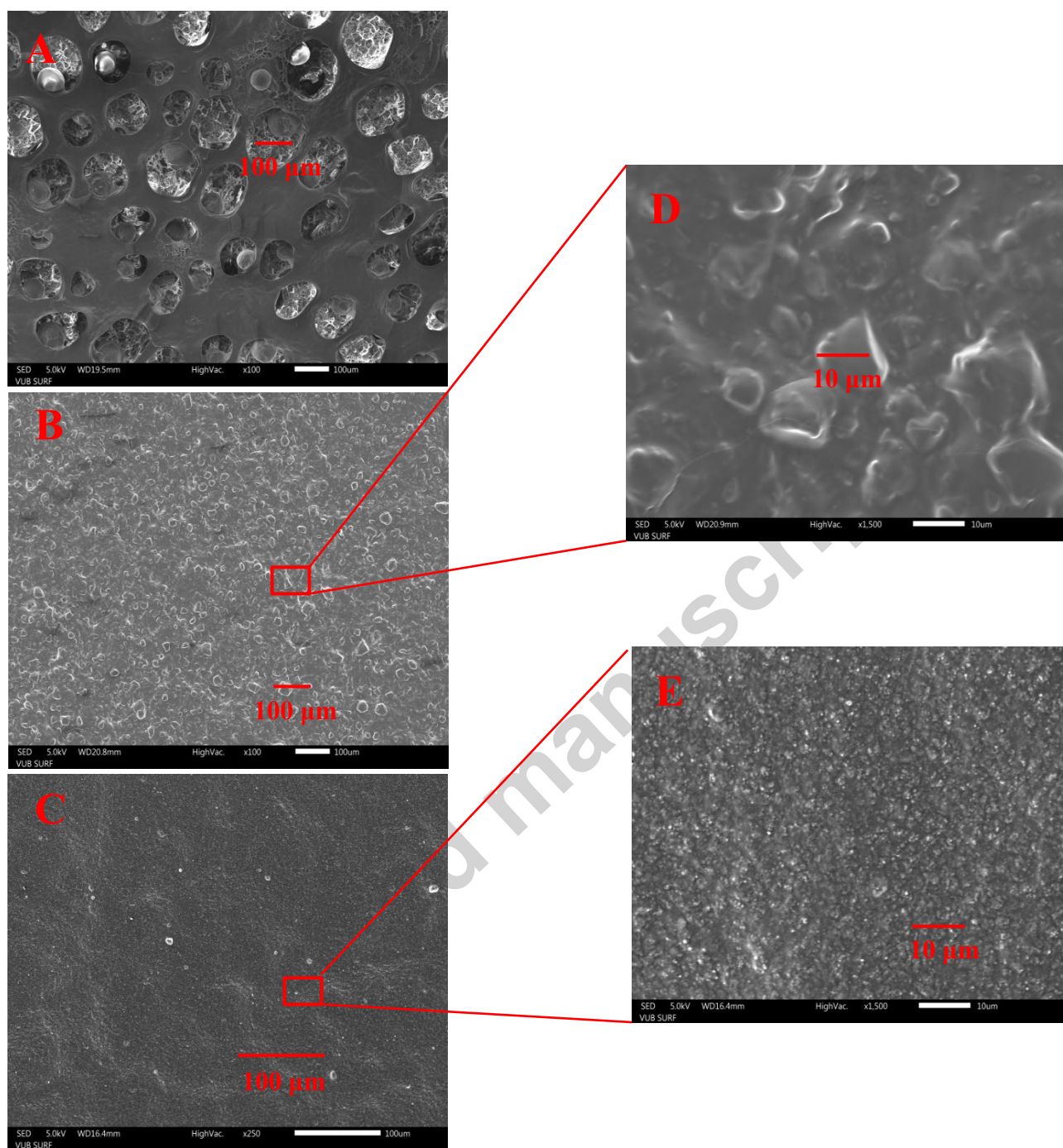


Figure 4. SEM images of Chelex-100 (CH) (A), Ground Chelex-100 (GCH) (B) and SPR-IDA (C) resin gel at 100 μm scale, and the amplified images of GCH (D) and SPR-IDA (E) resin gel at 10 μm scale. The red line appearing in image D represents a length of 10 μm which is roughly similar as the diameter of the GCH resin bead.

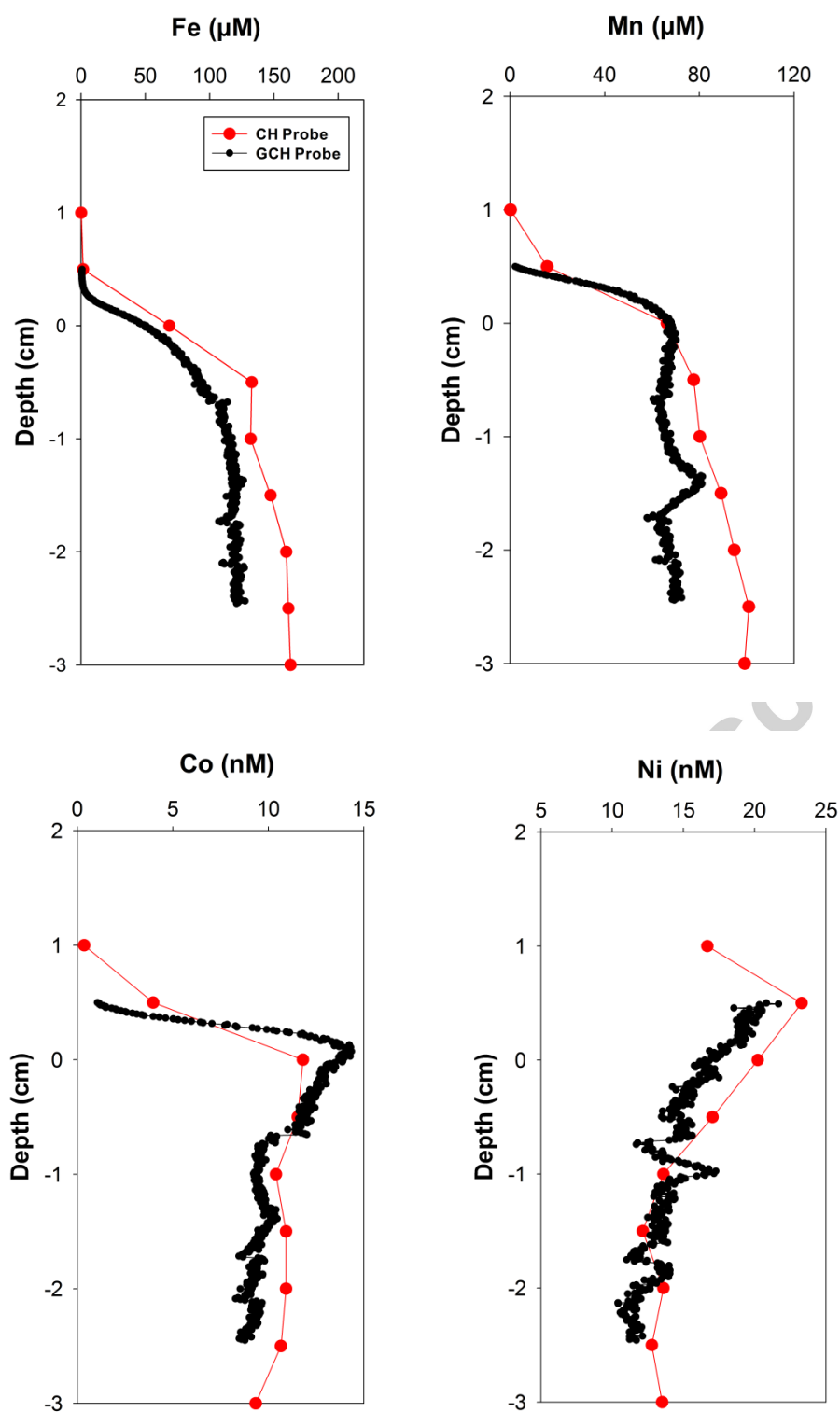


Figure 5. Vertical concentration changes of Fe, Mn, Co and Ni in sediment pore water (red lines were obtained with Chelex-100 (CH) probe, black lines were obtained with Ground Chelex-100 (GCH) probe).

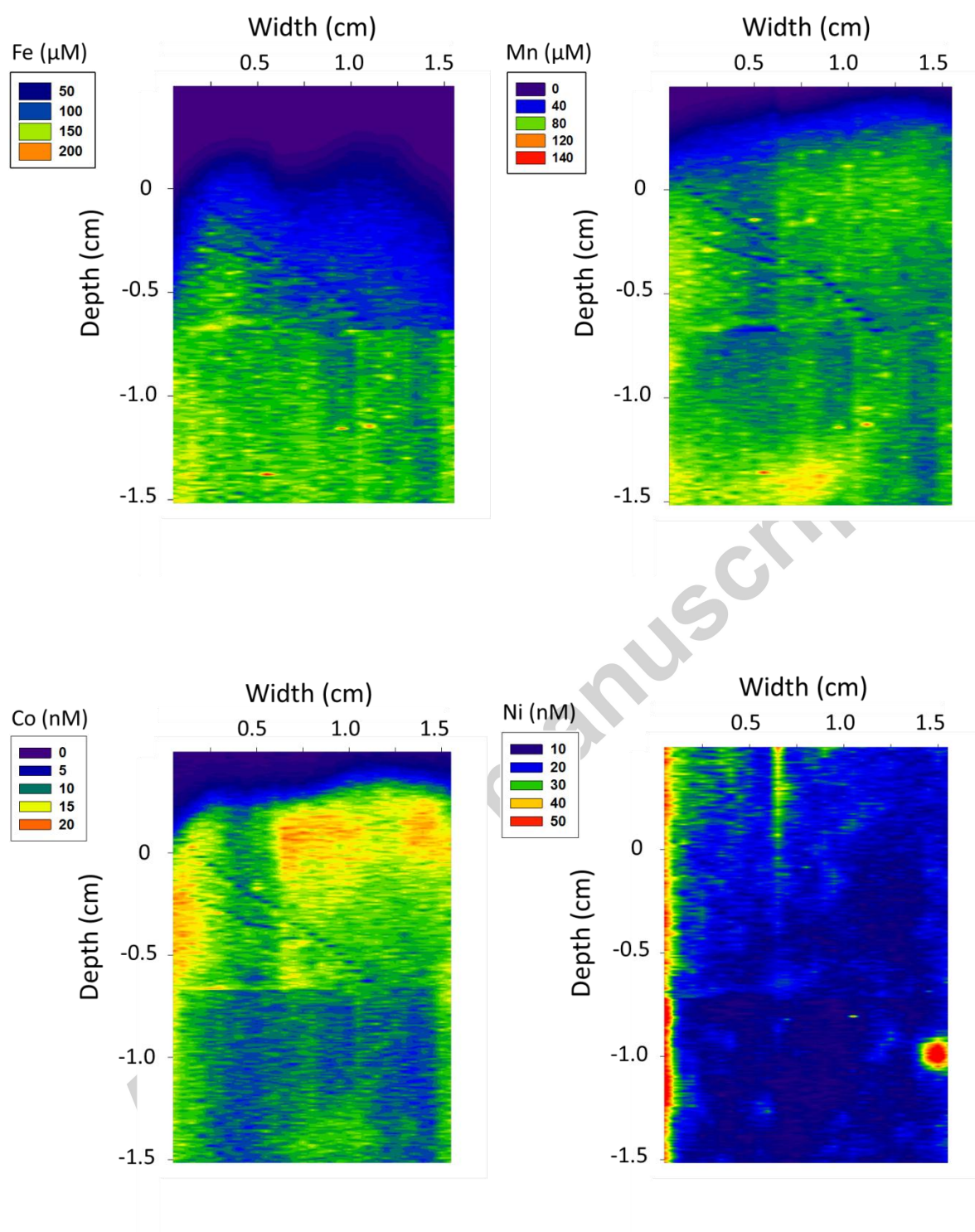


Figure 6. Two-dimensional concentration images of Fe, Mn, Co and Ni across water-sediment interface (0 cm depth) at high resolution obtained with Ground Chelex-100 (GCH) probe.

Table 1. Solutions (A, B, C and D) prepared for capacity and affinity tests of Fe and Mn on Chelex-100 (CH) and SPR-IDA gel disc.

Concentration ( $\mu\text{M}$ )	Capacity test		Affinity test	
	A	B	C	D
<b>Fe</b>	1 to 2400	/	45	45
<b>Mn</b>	/	1 to 2400	/	/
<b>Cd</b>	/	/	10 to 45	12
<b>Cu</b>	/	/	/	20 to 90

Table 2. Elution factors for different metals from SPR-IDA, Ground Chelex-100 (GCH) and Chelex-100 (CH) resin gels using 1 M  $\text{HNO}_3$ .

Elution factors	Type of resin gels		
	SPR-IDA	GCH	CH
<b>Fe</b>	$0.93 \pm 0.03$	$0.90 \pm 0.06$	$0.70 \pm 0.05^a$
<b>Mn</b>	$0.94 \pm 0.01$	$0.93 \pm 0.04$	$0.81 \pm 0.02^a$
<b>Cd</b>	$0.82 \pm 0.02$	$0.91 \pm 0.03$	$0.84 \pm 0.03^a$
<b>Co</b>	$0.86 \pm 0.02$	$0.88 \pm 0.03$	/
<b>Ni</b>	$0.87 \pm 0.03$	$0.93 \pm 0.03$	$0.82 \pm 0.07^a$
<b>Cu</b>	$0.84 \pm 0.03$	$0.91 \pm 0.04$	$0.79 \pm 0.06^a$

<sup>a</sup> Zhang & Davison [22]

**Highlights**

1. Erroneous SPR-IDA DGT results were observed in contaminated sediments
2. SPR-IDA resin gel disc has a much lower adsorption capacity than chelex-100
3. Chelex-100 resin was grinded to produce fine particles to replace SPR-IDA resin
4. The ground Chelex-100 gel disc has a similar capacity as the Chelex-100 gel disc
5. 2D, high resolution image of metals in sediment was obtained by ground Chelex-100 DGT

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