

Scientific paper

Determination of Dissolved Iron Redox Species in Freshwater Sediment using DGT Technique Coupled to BDS

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Abstract

In this work we have developed a novel method for determination of iron redox species by the use of diffusive gradients in thin-film (DGT) technique coupled to photothermal beam deflection spectroscopy (BDS). The combination of both methods achieved low limit of detection (LOD) of 0.14 μM for Fe (II) ions. The total Fe concentration determined in the Vrtojba river sediment (Slovenia, Rožna Dolina, 5000 Nova Gorica) was 49.3 μgL^{-1} . The Fe (II) and Fe (III) concentration amounted to 12.8 μgL^{-1} and 39.9 μgL^{-1} , respectively. Such an approach opens new opportunities for monitoring the content of iron species in natural waters and sediments and provides highly sensitive chemical analysis and an accurate qualitative and quantitative characteristic of the materials under study.

Keywords: Beam deflection spectroscopy; diffusive gradients in thin-film technique; iron redox species; photothermal techniques; sediment

1. Introduction

Metals in trace amounts are natural components of the environment, but at high concentrations they can become toxic to living organisms since they act as conservative pollutants. All trace elements (including iron, Fe) that are essential for supporting various life processes have a fairly narrow “concentration window” between their biogenic and toxic levels. Iron is a vital constituent of plant life since it is essential for photosynthetic and respiratory electron transport, nitrate reduction, chlorophyll synthesis, and detoxification of reactive oxygen species.¹ At low concentrations, Fe plays an important role in metabolic and fermentation processes, as an enzyme activator, stabilizer and functional component of proteins, and may be limiting for growth of organisms. Its redox state will also have influence on being available for the uptake.

Human populations in areas contaminated by iron and other heavy metals could be significantly exposed to

these contaminants due to their bioaccumulation properties. They can accumulate in bone, hair and in some soft tissues, such as the liver, kidney and lungs. Prolonged exposure and high concentration levels can lead to heart disease, the development of cancer, as well as other complications such as arthritis, diabetes or liver disease.²

As a result of these health concerns various methods have been developed for determination of iron concentration in the environmental samples, including UV-Vis spectrophotometry,³ atomic absorption spectrometry,⁴ ion chromatography⁵ and high-performance liquid chromatography.⁶ Unfortunately, the information about the bioavailable fraction content of its redox species is very difficult to measure and is in most cases lacking, although it is very important for understanding Fe toxicity.^{7,8} This is partly due to complex Fe geochemistry; either of the two redox states (Fe(II), Fe(III)) may be present in various

complexes and size fractions (e.g. as truly dissolved, in soluble coordination complexes with inorganic ligands and organic ligands, or in a variety of colloidal and/or particulate forms). Investigation of the fractions accessible to biota (bioavailable) is often hampered by their extremely low environmental concentrations, which requires the use of contamination-prone detection methods (e.g. voltammetry and potentiometry).^{9–11} Studying Fe cycling in the environment is further complicated also because the distribution of its chemical species often changes during sampling and storage. Since the above methods are not sensitive enough to satisfy the requirements associated with detection of ultra-trace amounts of Fe, thus, there is need to develop new sensitive techniques that provide reliable measurement of Fe redox species in natural environments.

Diffusive gradients in thin-film (DGT) technique has been increasingly used for monitoring of environmental pollution due to its robustness, versatility, precision and capacity of pre-concentrating trace-level metal pollutants. In the uptake process, metals diffuse from natural waters through the diffusive layer to the binding layer (commonly Chelex-100 resin), which is selective to transition metals and their species,^{12,13} such as Fe(II) and Fe(III). It is important to point out that DGT technique advantage is capability of pre-concentrating Fe species from the dissolved phase. It samples labile fraction passively, which is without external pressures, sample manipulation, transport, derivations, etc. It provides also a time-average of environmental species concentrations during the deployment time.

In contrast to the above enumerated methods, optothermal methods provide high-sensitivity measurements for spectroscopic characterization and detection of low-absorption transparent samples.^{14–17} The high sensitivity of the optothermal methods has already been repeatedly improved by combining with other methods.^{18–22} In this work the detection of iron species strongly bound in the resin gel was performed by the photothermal beam deflection spectroscopy (BDS).

In the theoretical approach to the coupled DGT-DBS method, an intensity modulated beam of light illuminates (excitation beam EB) the absorbing sample with iron species. As a result of nonradiative deexcitation processes, thermal waves are generated. They diffuse into the sample and the adjacent medium inducing the thermal oscillations (TOs) called the temperature field. Causing the intensity change of another light beam (probe beam PB) passing through the samples adjacent medium and grazing its surface.^{23,24} Intensity changes are correlated to the iron concentration bonded in the examined gel.²⁵ Presumably, the BDS technique would provide a highly sensitive chemical analysis, will be non-invasive and will retain optical and structural characteristics of the sample, thus, offering new possibilities for determination of iron species in natural water environments.

The goal of this work was therefore to couple DGT and BDS methods, and to determine dissolved Fe redox species concentration as well as the amount of dissolved total Fe in the river sediments.

2. Experimental

2. 1. Solutions and Reagents

The solution of 3 mM 1.10-phenanthroline (PHN) was prepared by adding 2.61 g of PHN (Merck) to 5.0 mL of 6 M HCl and dissolving both in 500 mL of double-deionized water (18 MΩ m⁻¹, NANOPURE), then diluted 10-times in 100 mL flasks. While 6 M of hydrochloric acid (HCl) solution was prepared by dissolving 5.9 mL of 32% pure HCl (Sigma-Aldrich) in 10 mL of double-deionized water.

The solution of 5.1 mM of L-ascorbic acid (Sigma-Aldrich) was prepared in 100 mL flask by dissolution of 9 mg of solid L-ascorbic acid in 0.1 M acetic acid. While 0.1 M acetic acid solution was prepared by dissolving 0.6 mL of 99.8% pure acetic acid (Merck) in 100 mL flask and diluted with double-deionized water.

Working solutions of Fe(II) and Fe(III) to construct the calibration curves were prepared using concentrations of 4, 8, 12, 16 and 20 μmol L⁻¹ in 25 mL flasks by proper dilution of stock solution in the double-deionized water (18 MΩ m⁻¹, NANOPURE).

The Fe(II) stock solution was prepared by dissolving 695 mg of ferrous sulphate heptahydrate (FeSO₄ 7H₂O) reagent (Merck) in 250 mL of 0.1 M HCl solutions (Sigma-Aldrich). The Fe(II) concentration of stock solution was than 10 mmol L⁻¹. While the 0.1 M of HCl prepared by dissolving 4.9 mL of 32% HCl in 500 mL of double-deionized H₂O.

The Fe(III) stock solution was prepared by dissolving 677.6 mg of Iron (III) chloride hexahydrate (FeCl₃ 6H₂O) reagent (Riedel de Haen) in 250 mL of 0.1 M HCl solutions. The Fe(III) concentration of stock solution was than 10 mmol L⁻¹.

All reagents and solvents were used as purchased without further purification.

2. 2. Preparation of DGT

The procedure for DGT probe preparation is in depth described elsewhere.²⁶ Briefly, the probe base was overlaid in the following order with 1) ground Chelex-100 resin gel, 2) polyacrylamide diffusive gel (APA, 0.8 mm final thickness) and 3) acid-precleaned 0.45 μm HVLP filter (Millipore). The layers were secured by the probe cover with a fixed-area window for diffusion (Figure 1).

To avoid contamination of the samplers, all used equipment, as well as DGT sediment probes were pre-cleaned in 5% HNO₃. Before assembling DGT sampler, its parts were thoroughly washed with double-deionized wa-

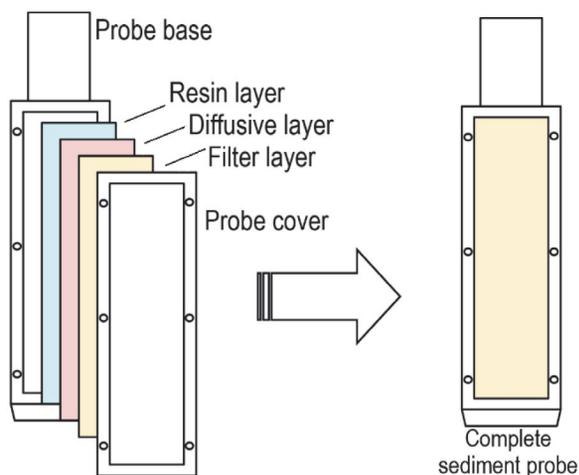


Figure 1. The components and assembled DGT probe for sediment deployment.

ter ($18 \text{ M}\Omega \text{ m}^{-1}$, NANOPURE) to protect from acid coming into contact with the gels. Both polyacrylamide gel and Chelex-100 resin were stored in closed plastic vials in double-deionized water before use to prevent them from drying. The gels were cut with Teflon-covered blade to fit the sediment probe.

One day before field work, the assembled DGT probe was inserted into a bottle filled with double-deionized water and purged with nitrogen to expel oxygen, which could affect redox speciation. Immediately before sampling, the bottle was tightly closed and transferred to the sampling site, where the sampler was inserted into the sediment.

2. 3. Field Work

DGT sediment probes were used for accumulation and pre-concentration of the Fe redox species *in situ* in the Vrtojbica River sediment. Vrtojbica flows through an anthropogenically-impacted environment of the city of Nova Gorica and its sedimentary Fe content is expected to be sufficiently high for reliable analysis. Two assembled DGT sediment probes were placed back-to-back in the river sediment for 5 days (from 18.07.2018 to 23.07.2018), reaching approximately 7.5 cm deep. The water temperature recorded at the beginning and the end of the experiment ranged between $23.5 \text{ }^{\circ}\text{C}$ and $24.5 \text{ }^{\circ}\text{C}$.

After sampling, the DGT probes were carefully recuperated from the sediment, rinsed with a double-deionized water, inserted into the plastic bag and transferred to the laboratory.

2. 4. Laboratory Analysis

In the laboratory the diffusive layer and filter were discarded, and resin layer was transferred into clean vial with double-deionized water until analysis. One probe gel was

used to determine the dissolved Fe(II) concentration, whereas the second one to determine the total dissolved amount of iron. Fe(III) was calculated as the difference between dissolved total and Fe(II) values. The procedure for total Fe determination was the same as described below (see 2.3).

After determination of Fe redox values in the gel, DGT equation was applied to calculate the concentration of Fe species (C) in the sediment pore waters:

$$C = \frac{M \Delta d}{D A t}, \quad (1)$$

where M is the mass of accumulated Fe species, t is the time of exposure, A is the area of exposed surface ($A = 0.15 \times 10^{-3} \text{ m}^2$), Δd is the diffusive layer thickness and D is the diffusive coefficient of the labile Fe species ($D = 5.9 \times 10^{-6} \text{ m}^2/\text{s}$).

The determination of Fe redox species is based on colorimetric reaction of the Fe(II) and PHN, accompanied by the formation of a stable orange complex, named Ferroin ($[\text{Fe}(\text{phen})_3]^{2+}$), with high absorptivity at 508 nm (Figure 2). For the total iron content, the Fe(III) was reduced to Fe(II) with L-ascorbic acid, followed by determination of total Fe as Fe(II).

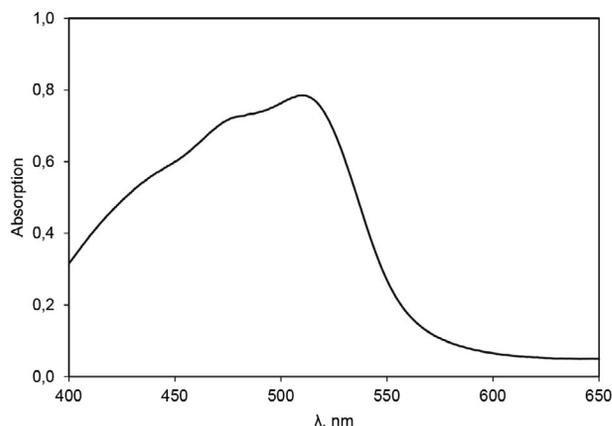


Figure 2. The Ferroin complex absorption spectrum.

For a comprehensive understanding of how Fe ions are distributed in the aqueous phase of the sediments using of the sampler described above, the binding gel was cut into smaller pieces vertically and horizontally by Teflon-covered blade. They were then separately, piece by piece, immersed directly in the 3 mM solution of PHN for the formation of a coloured complex. Before immersing in the PHN solution the pieces of gel from the second sampler were enriched by 5.1 mM L-ascorbic acid for reduction reaction of Fe(III) to Fe(II) for determination of the total Fe content. After 24 hours of soaking in the PHN solution, the gels were dried between clean glass layers for another 24 hours before performing the BDS measurements.

2. 5. Experimental Setup for BDS Method

For determination of Fe concentration, the dried gels on glass support was placed on the sample's holder in BDS system (Figure 3, 4).

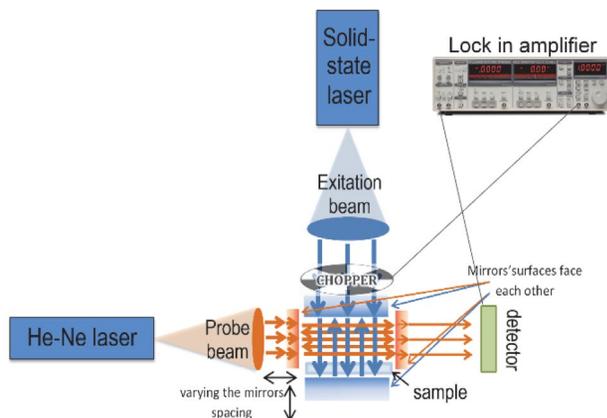


Figure 3. Experimental setup of BDS system.

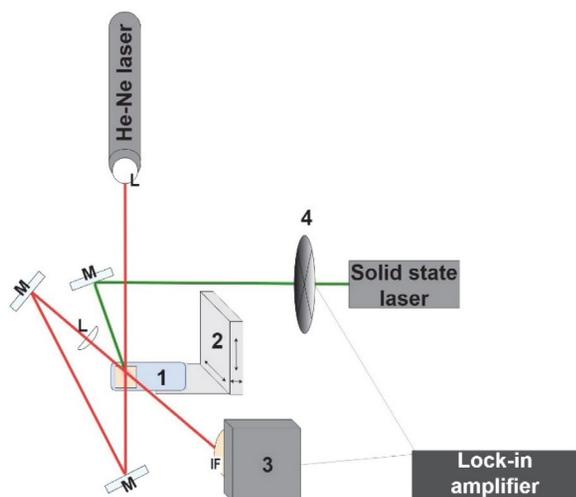


Figure 4. The scheme of BDS system with view from above, where: 1 - glass layer with a sample; 2 - 3D translation stage; 3 - detector; M - mirror; IF- interference filter; L - lens.

As EB (excitation beam) was chosen a solid-state laser at 532 nm output wavelength because the absorption maximum of Ferriin complex is close to it (508 nm), and 30 mW output power (CST-H-532nm-1000 MW). He-Ne laser (Uniphase, Model 1103P) was used as PB (probe beam) source at 633 nm output wavelength and 3 mW output power since this wavelength is not absorbed by Ferriin complex. Both beams were focused by a set of lenses (Bi-Convex, AR Coated: 350–700 nm, EDMUND OPTICS). A variable-speed mechanical chopper (SCIENTIC INSTRUMENTS, Control unit model 300C, chopping head model 300CD, chopping disks model 300H) at frequency of 3.0 Hz was used to modulate the EB. The used frequency range was chosen to ensure the TOs penetration only within the sample (the thickness of the dried gel is

0.04 mm) to get the information only from it without the influence of the support. The sensitivity of the BDS system was improved by using additional mirrors (400–750 nm, Thorlabs) that directed PB through the TOs to increase its intensity change and thus enhance the BDS signal. The intensity change of PB was measured by a quadrant photodiode (RBM-R. Braumann GmbH, Model C30846E) equipped with an interference filter (633 nm, Edmund Optics) and connected to the lock-in amplifier (Stanford research instruments, Model SR830 DSP). The examined sample was placed on a 3D translation stage (CVI, Model 2480M/2488) to vary its position in x, y and z direction and optimize the experimental configuration.

3. Results and Discussion

3. 1. Determination of Fe(II) Content

The calibration curve obtained for the Chelex-100 resin spiked with different concentration of Fe(II) including best fit equation is shown on the Figure 5. After immersing the gels in the Fe(II) solution for 5 days, the gels were transferred to the PHN solution for 1 day to form a coloured Ferriin complex, then transferred to the glass layers for drying. The achieved limit of detection was 0.14 $\mu\text{mol L}^{-1}$.

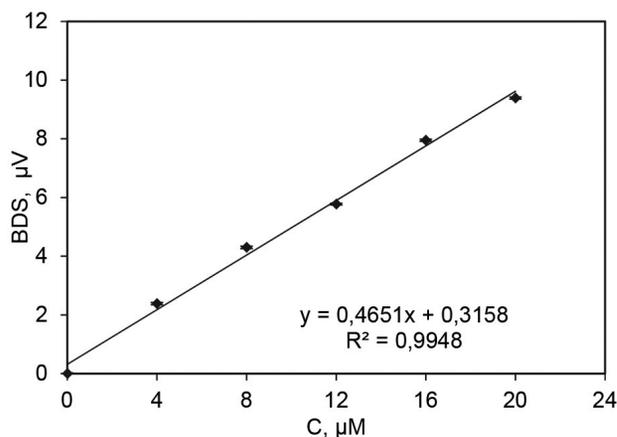


Figure 5. Calibration curve for Fe(II) determination.

A linear relationship between Fe concentration and BDS signal was obtained between 0 and 20 μM of Fe(II). All our samples fit in this concentration range.

To determine the 2D distribution of Fe redox species in the gels, the binding gel was cut into 4 parts horizontally and into 3 parts vertically. In each part, Fe(II) concentration was determined. The gel concentrations from Vrtojba River sediment are presented in Table 1 and Figure 7a.

The lower horizontal part was damaged during the deployment, so the data for Fe (II) (respectively for Fe (III) also) in this layer at the depth 7.5 cm is not available.

Table 1. Concentrations of the Fe(II) ions in the Chelex-100 resin. (The “–” sign indicates data lower than the LOD.)

Vertical position in the sample, cm	Horizontal position in the sample, cm			Average, $\mu\text{mol L}^{-1}$
	0.6	1.2	1.8	
0	2.1±0.2	1.9±0.4	1.9±0.4	2.0±0.3
–2.5	2.3±0.2	–	–	2.3±0.2
–5.0	2.5±0.4	1.5±0.4	–	2.0±0.3
Average, $\mu\text{mol L}^{-1}$	2.3±0.3	1.7±0.4	1.9±0.4	2.0±0.3

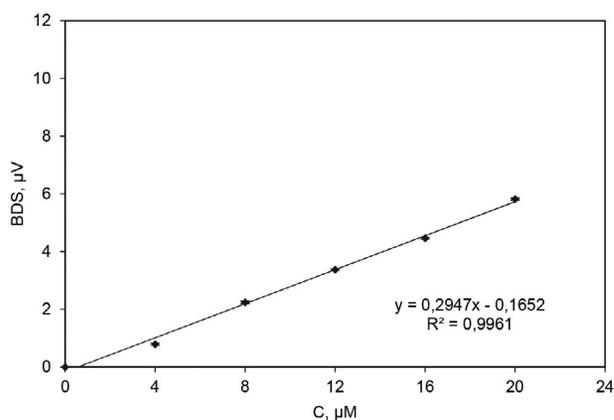
The obtained data indicate that the concentrations of Fe(II) do not vary much in the sediment pore waters. Generally, the absence of Fe(II) indicates oxidative environment and the presence implies reductive conditions. There is an increase on the left side of the investigated area, which could imply more reductive localized condition during the time of the sampling. Considering that DGT binds the dissolved and labile fractions of total Fe(II), our data suggest there was a constant amount of Fe(II) available for geochemical transformations and as well for organisms. Surprisingly, no decrease in Fe(II) concentrations were observed at the sediment-water interface (SWI), suggesting that there might be a loss of this species to the water. Also interestingly and somewhat contrary to general behaviour of reduced metals species, the values around –2.5 and –5 cm were below LOD on the right side of the gel. Usually, in the sediments the anoxia begins somewhere below SWI and extends in the interior of the sediment, where the reduced species dominate²⁶. The Vrtojba River however, is a quickly flowing stream of water, hence the absence of Fe(II) in the part of the sediment of might represent a well aerated sediment.

3. 2. Determination of Total Fe Content

Dissolved total Fe was determined by conversion of the Fe (III) to Fe (II) with L-ascorbic acid as a reducing agent, using this method previously described in the literature for photothermal techniques.^{18–19}

The calibration curve obtained for the Chelex-100 resin spiked with different concentration of Fe(III) re-

duced into Fe(II) including best fit equation is shown in the Figure 6. The achieved limit of detection in this case was $0.21 \mu\text{mol L}^{-1}$.

**Figure 6.** Calibration curve for total Fe determination.

Using a linear equation of the calibration curve the total Fe concentrations in river water and sediment were calculated. The results are presented in Table 2 and its distribution in the gels in Figure 7b.

The distribution of the total dissolved Fe in the sediment of the Vrtojba River is quite uniform. This suggests stable conditions during the deployment, and also a stable pool of labile, dissolved Fe species that was continuously present in the sediment during the time of the sampling.

Table 2. Concentrations of total Fe in the Chelex-100 resin.

Vertical position in the sample, cm	Horizontal position in the sample, cm			Average, $\mu\text{mol L}^{-1}$
	0.6	1.2	1.8	
0	3.0±0.4	8.4±0.3	2.3±0.0	4.6±0.2
–2.5	10.1±0.0	10.8±0.2	7.8±0.1	9.6±0.1
–5.0	9.8±0.3	8.3±0.3	8.4±0.2	8.8±0.3
–7.5	8.5±0.1	6.9±0.1	9.7±0.2	8.3±0.1
Average, $\mu\text{mol L}^{-1}$	7.9±0.2	8.6±0.2	7.0±0.2	7.8±0.2

At the SWI, the concentration of total dissolved Fe species is lower than inside of the sediments, clearly indicating general loss to the water of both redox species. The increase of dissolved species in the sediment interior is associated with dissolved Fe(III) increase (see 3.3).

3.3. Determination of Fe(III) Content

One of the goals of the study was to determine the concentration of Fe(III) ions in the sediment since it is one of the species in which iron as essential metal appears in the nature. Numerous factors contribute to the environmental ratios of Fe(II) and Fe(III), e.g. pH, temperature and reductive-oxidative environmental conditions, presence of sulphide ions, ammonia and oxygen. Furthermore, the ratio is also dependant on geological features of the river sediment.

The content of Fe(III) was calculated as a difference between the total Fe content (Table 2) and Fe (II) (Table 1). The results are given in the Table 3 and presented in the Figure 7c.

Generally, the distribution of the Fe(III) in the sediment follows the distribution of total dissolved Fe. There is an increase of Fe(III) below the SWI at the depth of ap-

proximately 2.5 – 5 cm in the centre of the gel. This might indicate a geological source dissolving and releasing Fe(I-II) into the pore waters, or a local oxidation hotspot that would oxidize any Fe(II) to Fe(III). The oxidation source might be geochemical or microbial. Very likely this feature indicates sediment heterogeneity, which we were able to observe as a result of the newly developed method.

The coupling of DGT and BDS methods enables the determination of the distribution of Fe redox species in two dimensions. While Fe(III) is present over all investigated area and occurs simultaneously with Fe(II), Fe(III) is exclusively present on the right side of the gel. Combined with the Fe(II) results, this part of the sediment appears to be fully oxygenated and/or excludes formation of Fe(II), at least during the sampling period. As the DGT technique reports time-average values, this indicates very stable conditions in the time of the sampling.

The DGT-BDS method does not require intensive manipulation after the sampling, which renders the possibility of transport or storage artefacts that could influence Fe speciation less likely and increases the reliability of the obtained results. Therefore, the observed patterns of Fe redox species likely accurately represent the sedimentary conditions. To summarize the data obtained in Figure 7

Table 3. Concentrations of the Fe (III) ions in the Chelex-100 resin.

Vertical position in the sample, cm	Horizontal position in the sample, cm			Average, $\mu\text{mol L}^{-1}$
	0.6	1.2	1.8	
0	1.0±0.3	6.5±0.3	0.4±0.2	2.6±0.3
-2.5	7.8±0.1	10.8±0.3	7.8±0.2	8.8±0.2
-5.0	7.3±0.4	6.9±0.4	8.4±0.2	7.5±0.3
Average, $\mu\text{mol L}^{-1}$	5.3±0.3	8.1±0.3	5.5±0.2	6.3±0.3

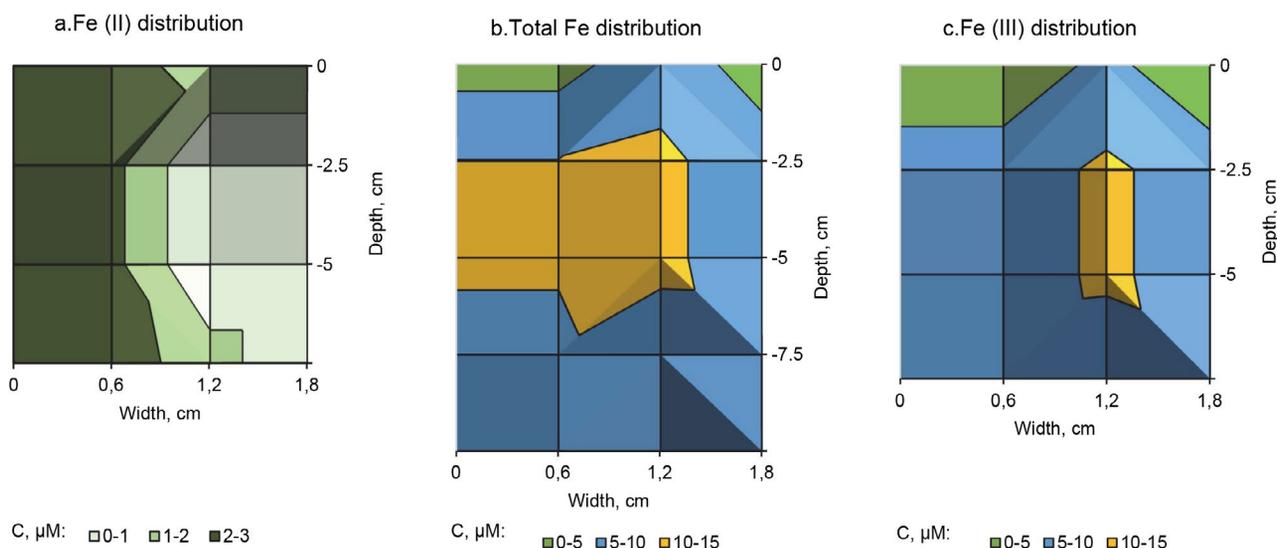


Figure 7. Graphical presentation of Fe redox species distribution in the Chelex-100 resin.

presents the Fe (II), total Fe and Fe (III) distribution in the Chelex-100 resin, respectively.

Although our preliminary results are not accompanied with a suite of other geochemical parameters, they clearly demonstrate the potential and applicability of the newly developed method to be used for two-dimensional imaging of dissolved, bioavailable Fe redox species in natural environments.

3. 4. Concentrations of the Fe Redox Species in the River Sediment

Using the equation (1) we calculated the concentration of Fe species in the sediment pore waters (Table 4).

Although not much data exist for comparison of DGT-derived Fe redox species concentrations, our data fit in the range of the published results for pristine environments.¹⁸ Total concentrations obtained from polluted or strongly impacted river sediments are higher for factor of 10 or 100.^{28–30} Nonetheless, the distribution of dissolved, labile and potentially bioavailable fraction of Fe redox species in the Vrtojba River indicates a dynamic sediment system. As observed before, the low values at SWI indicate sediments are a source of both Fe redox species to the river water. The observed increases in dissolved Fe(II) and dissolved total Fe in the sediment interior could be attributable either to geochemical and microbial interactions with Fe-rich minerals, or both. Since these are the first data on iron speciation in this system, it cannot be said with cer-

tainty if the concentrations are representative of this particular environment. However, despite its city location, Vrtojba river sediment is far from polluted and not likely to increase river water Fe concentration to above WHO guidelines on Fe in drinking water (0.3 mg/L). Together with low SWI concentration our data suggests that anthropogenic activity might have not affected the river and that the sediment does not act as a sink for Fe. Simultaneously, however, it is also yet unclear which factors have highest influence on the redox state of dissolved Fe in the sediment.

4. Conclusions

We report for the first time the dissolved Fe redox species distribution in freshwater sediments measured by coupled DGT technique and BDS method.

The average total iron concentration in the Vrtojba River river sediment was found to be 49.3 $\mu\text{g/L}^{-1}$. The average amount of Fe(III) was 3 times higher than the average Fe(II) concentration and reached the value of 39.9 $\mu\text{g/L}^{-1}$ and 12.8 $\mu\text{g/L}^{-1}$, respectively.

The obtained results show the potential of using DGT method coupled to BDS technique for monitoring biologically relevant Fe species at environmental concentrations in natural waters and sediments. The information received from the newly coupled method will advance our understanding of the basic biogeochemical processes gov-

Table 4. Concentrations of the Fe redox species in the Vrtojba sediment.

Vertical position in the sample, cm	Horizontal position in the sample, cm			Average, $\mu\text{g/L}$
	0.6	1.2	1.8	
	Fe(II) in pore waters, $\mu\text{g/L}$			
0	13.2±1.3	12.0±2.5	12.0±2.5	12.4±2.1
-2.5	14.5±1.3			14.5±1.3
-5.0	15.7±2.5	9.4±2.5		12.6±2.5
Average	14.5±1.7	10.7±2.5	12.0±2.5	12.8±2.1
	Total Fe in pore waters, $\mu\text{g/L}$			
0	18.9±2.5	52.9±1.9	14.5±0.0	28.7±1.5
-2.5	63.6±0.0	68.0±1.3	49.1±0.6	60.2±0.6
-5.0	61.7±1.9	52.2±1.9	52.9±1.3	55.6±1.7
-7.5	53.5±0.6	43.4±0.6	61.0±1.3	52.7±0.8
Average	49.4±1.3	54.1±1.4	44.4±0.8	49.3±2.0
	Fe(III) in pore waters, $\mu\text{g/L}$			
0	6.3±1.9	40.9±1.9	2.5±1.3	16.6±1.7
-2.5	49.1±0.6	68.6±1.9	49.1±1.3	55.6±1.3
-5.0	45.9±2.5	43.4±1.9	52.9±1.3	47.4±1.9
Average, $\mu\text{g/L}$	33.8±1.7	51.0±1.9	34.8±1.3	39.9±2.2

erning trace metal behaviour in pristine and anthropogenically-impacted environments. Its results may be well incorporated in the existing mathematical models, which are currently based primarily on one-dimensional profiles, thereby increasing reliability of the model predictions. Further development, application and testing of the DGT-BDS is warranted, since it is reliable, precise, resistant to contamination, inexpensive, and time-saving analytical method.

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Povzetek

V tem delu je predstavljena nova metoda za določanje železovih redoks specij z uporabo tehnike difuznega gradienta v tankem filmu (DGT) povezane s spektroskopijo na optotermični odklon (BDS). S povezavo obeh metod smo dosegli nizko mejo detekcije (LOD) 0.14 μM za Fe (II) ione. Celotna koncentracija železa, ki smo jo določili v sedimentih reke Vrtojbe (Slovenija, Rožna Dolina, 5000 Nova Gorica) je znašala 49.3 μgL^{-1} , pri čemer je bila koncentracija Fe (II) ionov 12.8 μgL^{-1} in koncentracija Fe (III) ionov 39.9 μgL^{-1} . Razviti pristop odpira nove možnosti monitoringa vsebnosti železovih specij v površinskih vodah ter sedimentih, saj omogoča visoko občutljivo kemično analizo ter natančno kvalitativno in kvantitativno karakterizacijo preučevanih materialov.