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6.1 • ANALYTICAL AND BIO-ANALYTICAL METHODS FOR QUANTIFYING PERSISTENT CHEMICALS

Suitability of using diffusive gradients in thin films (DGT) to study metal bioavailability in mine tailings: possibilities and constraints

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Abstract

Background, aim, and scope Diffusive gradients in thin films (DGT) have been recognized as a suitable tool to assess in situ metal bioavailability in soils. Mine tailings have some singular characteristics such as high heavy-metal concentrations, low pH, or absence of water retention capacity that may compromise the correct application of this technique whose applicability is known to be pH dependent. The goal of this study was to determine the response of DGT devices in heavy-metal-polluted mine tailings with different pH. In addition some experiments were performed in order to determine the effect of acidic pH and dissolved ions on the binding properties of the chelating resin.

Materials and methods We tested DGT devices on three different mine tailings: acid pH3, acid tailing limed to pH 5.5, and neutral pH7.2. The tailings showed high metal concentrations, e.g., 7,000 mg kg⁻¹ Pb, 9,000 mg kg⁻¹ Zn, and 380 mg kg⁻¹ Cu. Diffusive and Chelex resin gels were prepared according to previously published methods. Two chelating resins and diffusive gels thicknesses (0.4 and 0.7 mm) were tested. Four DGT devices of each type were placed during 24 h in pots (one device per pot) containing 1 kg mine tailings in a climate chamber with humidity (50–

90%) and controlled temperature conditions (night 16°C and day 23°C). Pots were irrigated with deionized water to field capacity, and then two different experiments were performed: (a) allowing free drainage and (b) maintaining the water saturation. In addition, we tested DGT devices in solutions at pH3 with similar properties to the soil solution measured in the acid tailing. Eluted Zn, Cd, Pb, and Cu from the chelating resins were measured using inductively coupled plasma–optical emission spectrometer (ICP–OES; Vista-MPX Varian).

Results and discussion The metal concentrations taken up by the DGT devices were affected by the different pH values of the tailings. The highest metal concentrations measured with DGT (C_{DGT}) were obtained in the pH3 treatments (both saturated and free drainage). Significant differences for C_{DGT} were observed between water-saturated and free drainage treatments in the acid pH3 tailing. When limed pH5.5 tailing and neutral pH7 tailing were considered, these differences were lower and not significant. In pH3 tailings low values for $C_{DGT}/C_{soil\ solution}$ were obtained (<0.06), indicating that these soils have a low capacity to resupply depleted metals to the solution. The limed acid tailing and the neutral tailing showed values between 0.05 and 0.94 indicating a much more rapid resupply from the solid phase. Deployment under water-saturated conditions yielded much higher C_{DGT} values than under free drainage, indicating the importance to adequately control the moisture content in these soils with poor water retention capacity. In solutions with pH3 mimicking the soil solution composition of the tailings, a loss of the binding capacity of the resin of 50–60% and 60–80% for Zn in 0.7-mm DGT and 0.4-mm DGT devices, respectively, was observed. As a consequence, 0.7-mm DGT devices had better reliability to carry out in situ determinations in solutions with high metal concentrations and low pH.

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Conclusions The use of DGT in mining soils can be a promising tool to study bioavailable metals concentrations in mine tailings but it has to be used carefully under acidic pH. Competition with other cations that are present at very high concentrations may hinder the accumulation of metals by the chelating resins, which should be tested under the conditions of the particular mine tailing.

Keywords DGT · Mine tailings · Acid pH · Metal bioavailability

1 Background, aim, and scope

The assessment of metal toxicity in soils and sediments is considered an important issue in heavy-metal-polluted ecosystems. Traditionally, these studies have been based on the determination of the total concentration, avoiding aspects related with the speciation or bioavailability (McGrath et al. 1999; Degryse et al. 2003). However, in the last decades the majority of researchers that work in the field of soil contamination have assumed that using total metal concentrations in environmental risk assessment studies is not a suitable tool, because a large fraction of the total metal content is not bioavailable (Zhang et al. 2001). In this sense speciation studies using weak extractants have been proposed as a more accurate tool (Planquart et al. 1999). These procedures represent a better approach to the environmental behavior of metals, but still they are limited since they are generally applied on disturbed soil samples that have been previously dried and thus metal speciation has been affected (Wang et al. 2002), and there is a separation of the solid phase from the soil solution (that may affect the physical–chemical equilibrium; Zhang et al. 1998). In this sense and in order to avoid these problems, the technique diffusive gradient in thin films (DGT) was proposed to study *in situ* the bioavailability of metals in soils. This technique has been applied successfully in waters (Davison and Zhang 1994), sediments (Zhang et al. 1995), and soils (Zhang et al. 1998). In the last years it has also been applied in the study of metal-polluted soils (Degryse et al. 2003; Nowack et al. 2004). DGT is based on the diffusion of metals from the soil solution to a chelating resin through a diffusion gel layer, causing a decrease in the metal concentration of the soil solution and potentially inducing the resupply of metals from the solid phase.

The mining industry has many injurious effects on the environment. Among the most important are the generation of effluents and solid wastes with high concentrations of heavy metals. The DGT technique is a promising tool to assess the environmental risk of these wastes in a better way than the conventional techniques. However, the mining wastes present some singular characteristics such as high

heavy metal concentrations, low pH, or absence of water retention capacity that may compromise the correct application of this technique. DGT is limited to the pH range of five to nine for most of the metals and from two to 11 for Cu (INAP 2002), and does not work under dry conditions (studies at field capacity conditions are necessary), and also saturation of the chelating resin may occur at high metal concentrations. Some previous studies have focused on acid mine drainage samples, using a correction factor when pH was low (Sondergaard 2007). In this sense much more work has to be carried out to improve the use of DGT in mining soils since saturation conditions and the presence of high concentrations of different ions may affect the binding properties of the chelating resin.

The goal of this study was to determine the response of DGT devices in heavy-metal-polluted mine tailings with different pH. In addition some studies were done in order to determine the effect of acidic pH and dissolved ions on the binding properties of the chelating resin.

2 Materials and methods

2.1 Soil analyses

The soil was sampled from two mine tailings (“Belleza” and “El Gorguel”) situated in Southeast Spain. Both tailings were extensively characterized by Conesa et al. (2006) and have pH values of 3 and 7, respectively, and high metal concentrations, e.g., 7,900 mg kg⁻¹ Pb, 7,700 mg kg⁻¹ Zn, and 530 mg kg⁻¹ Cu for acid pH tailing and 5,600 mg kg⁻¹ Pb, 12,000 mg kg⁻¹ Zn, and 94 mg kg⁻¹ Cu for neutral pH tailing. Tailing samples were taken from the upper 40 cm of 15 separate soil pits that were dug at regular intervals, at least 8 m apart, on each tailing pile. All samples of a tailing were mixed to give one homogenized composite sample per mine tailing. The composite samples were air-dried, sieved to <2 mm, and stored in plastic bags prior to the experiment. A third tailing material was prepared by liming the acid tailing with 25 g CaCO₃ (Merck) kg⁻¹ soil. The limed tailing mixture went through several wetting–drying cycles (with deionized water) during the 2 weeks preparation period. Soil solution from the three tailings soils was extracted at field capacity using Rhizon Flex soil moisture samplers (Rhizosphere Research Products, Wageningen, Netherlands). Results of the characterization of the soil solutions are shown in Table 1.

2.2 DGT

Diffusive and resin gels were prepared according to Zhang and Davison (1995) from acrylamide (Fluka, Switzerland) with cross-linker (supplied by DGT Research Ltd, Lancaster,

Table 1 Soil solution composition according to Conesa et al. (2007a, 2007b)

Parameter		Tailing		
		Acid (N=5)	Acid limed (N=3)	Neutral (N=8)
pH		2.9 (<0.1)	5.6 (0.2)	7.1 (<0.1)
EC (dS m ⁻¹)		25 (3)	4 (1)	11 (2.7)
Cations (mg L ⁻¹)	Na	7.5 (1.5)	9.0 (3.0)	1,400 (440)
	Mg	3,800 (850)	600 (460)	850 (220)
	K	0.5 (0.3)	1.5 (1.0)	38 (6)
	Ca	71 (45)	460 (40)	520 (67)
	Cu	16 (1.1)	<0.1	<0.1
	Zn	3,100 (1200)	1.1 (0.6)	0.47 (0.06)
	Cd	17 (3.0)	<0.1	<0.1
	Pb	4.5 (0.2)	<0.1	<0.1
	SO ₄ ²⁻	36,000 (6,600)	3,100 (770)	4,900 (2,100)
Anions (mg L ⁻¹)	Cl ⁻	130 (23)	140 (88)	2,600 (1,500)

Values between parentheses correspond to the standard deviation
EC electrical conductivity

UK). Two thicknesses of diffusive and resin gels of 0.4 and 0.7 mm were prepared. The diffusive gels were washed in nanopure water and stored in 0.01 M NaNO₃ at room temperature. The resin gel was stored in water at 4°C. In order to prepare the resin gel, 0.12 g of dried Chelex 100 (Na⁺, 200–400 mesh, Fluka) was added to 2 mL of gel solution. The resin gel and the diffusive gel were placed on a modified Sartorius filtration unit (for 25-mm filters) with a cellulose acetate filter (0.45 μm, Sartorius) on top to protect the diffusive gel. The 0.7-mm diffusive gels were assembled with 0.7-mm resin gels (named 0.7-mm DGT devices). In the same way 0.4-mm diffusive and resin gels were configured (named 0.4-mm DGT devices). The cap of the filter unit was cut off to expose an area of 3.8 cm² of the filter. The inlet into the filtration unit was sealed. Four DGT devices were placed for 24 h in pots (one device per pot) containing 1 kg of the aforementioned mine tailings in a climate chamber with humidity (50–90%) and controlled temperature conditions (night 16°C and day 23°C). Pots were irrigated with deionized water to field capacity, and then two different experiments were performed (a) allowing free drainage and (b) maintaining the water saturation. Metals were eluted from the chelating resin with 1 M HNO₃. Eluted Zn, Cd, Pb, and Cu from the chelating resin were measured using ICP–OES (Vista-MPX Varian).

Because it is known that at pH below 5 the chelating resin decreases its binding properties (INAP 2002), we quantified the reduction factor by testing DGT devices in solutions at pH3 with similar properties to the soil solution measured in the acid tailing (Table 1): (a) 2,000 mg L⁻¹ ZnSO₄, (b) 2,000 mg L⁻¹ ZnSO₄ and 30,000 mg L⁻¹ Na₂SO₄, (c) 2,000 mg L⁻¹ ZnSO₄, 100 mg L⁻¹ of CaSO₄, and 3,000 mg L⁻¹ of MgSO₄. The following reagents were used: ZnSO₄ · 7H₂O (Fluka), Na₂SO₄ (Merck), MgSO₄ · 7H₂O (Merck), and CaSO₄ · 2H₂O (Merck). The 0.4- and

0.7-mm DGT devices were immersed for different times in those solutions. Eluted Zn was measured using ICP–OES (Vista-MPX Varian).

The accumulated mass in the chelating resin (*M*, μg) was calculated as follows:

$$M = FC(V_n + V_{rg})/f_c \tag{1}$$

- F* (dilution factor) 10
- C* in mg L⁻¹; measured from the aqueous extract obtained from the chelating resin
- V_n* 1 ml=0.001 L (it is the volume of 1 M HNO₃ where the chelating resin is eluted)
- V_{rg}* volume of chelating resin
- f_c* 0.8 (*f_c* correction factor that compensates for the fraction of metals that cannot be released from the chelating resin (Zhang and Davison 1995)).

From the accumulated mass of metal (*M*) the concentration *C*_{DGT} (μg L⁻¹) was calculated as follows:

$$C_{DGT} = (M \Delta g / ADT) \tag{2}$$

- M* in μg; accumulated mass
- Δg in cm; diffusion layer thickness (diffusion gel+filter)
- A* in cm²; exposed gel area
- D* in cm²s⁻¹; diffusion coefficient of each metal in the diffusive gel (Zhang and Davison 1999)
- T* in s (Zhang and Davison 2001)

*C*_{DGT} is the time-averaged concentration at the DGT interface. We can then calculate the ratio *R* of the mean

concentration at the DGT surface and the bulk soil solution concentration (C_{SS}).

$$R = C_{DGT}/C_{SS} \tag{3}$$

R is a measure of resupply from the solid phase. $R > 0.8$ means rapid and sustained supply from the solid phase, $R < 0.1$ virtually no resupply from solid phase, and $0.1 < R < 0.8$ is an intermediate case.

All statistical analyses were carried out using log transformed data applying ANOVA and LSD test. Systat 10.2 was using as statistical software (Systat 2002). Differences at $P < 0.05$ level were considered significant.

3 Results

3.1 DGT deployment in mine tailings

The metal concentrations taken up by the DGT devices were affected by the different pH values of the tailings. The highest metal concentrations measured with DGT (C_{DGT} ; Table 2) were obtained in the pH3 treatments (both saturated and free drainage). In the limed pH5.5 tailing and the pH7.2 tailing, all the metals except Zn showed concentrations under the detection limit ($< 0.01 \text{ mg L}^{-1}$). The highest quantities of metals were accumulated in the DGT devices in the pH3–water saturation treatment ($M = 600\text{--}620 \mu\text{g Zn}$). For the rest of metals the quantities accumulated were below $25 \mu\text{g}$.

Significant differences for C_{DGT} were observed between water-saturated and free drainage treatments in the acid pH 3 tailing. When limed pH5.5 tailing and neutral pH7 tailing were considered, these differences were lower and not significant.

The C_{DGT} for the 0.4- and 0.7-mm DGT devices were not significantly different for most metals and conditions. However, for some metals such as Pb at pH3 (both, saturated and free drainage), Cd and Zn at pH3 with water saturation, or Zn in the neutral tailing with free drainage, the DGT device thickness had a significant influence on the value of C_{DGT} .

Table 3 shows the ratios $C_{DGT}/C_{\text{soil solution}}$ calculated with the data from Tables 1 and 2. The ratio increased with increasing pH from values below 0.014 at pH3 to 0.045–0.391 at pH5 and 0.139–0.936 at pH7 for Zn. For the other metals the ratios could only be determined at pH3 where it was in the same range as that for Zn (between 0.001 and 0.056).

3.2 Accumulation of Zn by DGT in pH3 solution

Figure 1 shows the accumulated Zn in the chelating resins for the two types of DGT devices after immersion in

Table 2 C_{DGT} measured for the three mine tailings after 24-h contact time under free drainage and water saturation for two DGT devices thicknesses (in mg L^{-1})

Tailing	pH and water conditions	Zn		Cu		Pb		Cd	
		0.4-mm DGT	0.7-mm DGT	0.4-mm DGT	0.7-mm DGT	0.4-mm DGT	0.7-mm DGT	0.4-mm DGT	0.7-mm DGT
Acid	pH3 free drainage	5.49 (0.98) a	6.4 (0.1) a	0.17 (0.01) a	0.21 (0.02) a	0.18 (0.05) a	0.33 (0.05) c	0.02 (0.05) a	0.03 (0.01) a
	pH3 water saturation	24.9 (1.4) b	43 (5.7) c	0.88 (0.18) b	0.89 (0.13) b	0.06 (< 0.01) b	0.19 (0.03) a	0.11 (< 0.01) b	0.18 (0.03) c
Acid limed	pH5.5 free drainage	0.05 (0.04) a	0.21 (0.24) a, b	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	pH5.5 water saturation	0.41 (0.06) b	0.43 (0.22) b	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Neutral	pH7 free drainage	0.28 (0.12) a	0.15 (0.02) c	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	pH7 water saturation	0.32 (0.04) a, b	0.44 (0.10) b	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Values between parentheses are standard deviations. Significant differences were calculated for each metal, both thicknesses and the same pH at $P < 0.05$ level after carrying out ANOVA with LSD test. Different letters mean significant differences. $N = 4$
 0.4-mm DGT DGT devices assembled by a 0.4-mm resin gel and a 0.4-mm diffusive gel, 0.7-mm DGT DGT devices assembled by a 0.7-mm resin gel and a 0.7-mm diffusive gel

Table 3 Ratios C_{DGT}/C_{SS} for the three mine tailings measured for the three mine tailings after 24-h contact time under free drainage and water saturation for two DGT devices thicknesses

Tailing	pH and water conditions	Zn		Cu		Pb		Cd	
		0.4-mm DGT	0.7-mm DGT	0.4-mm DGT	0.7-mm DGT	0.4-mm DGT	0.7-mm DGT	0.4-mm DGT	0.7-mm DGT
Acid	pH3 free drainage	0.002	0.002	0.011	0.013	0.04	0.073	0.001	0.002
	pH3 water saturation	0.008	0.014	0.055	0.056	0.013	0.042	0.006	0.011
Acid limed	pH5.5 free drainage	0.045	0.191	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	pH5.5 water saturation	0.373	0.391	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Neutral	pH7 free drainage	0.596	0.319	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	pH7 water saturation	0.681	0.936	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

0.4-mm DGT DGT devices assembled by a 0.4-mm resin gel and a 0.4-mm diffusive gel, 0.7-mm DGT DGT devices assembled by a 0.7-mm resin gel and a 0.7-mm diffusive gel, n.a. not available (soil solution concentration below detection limit)

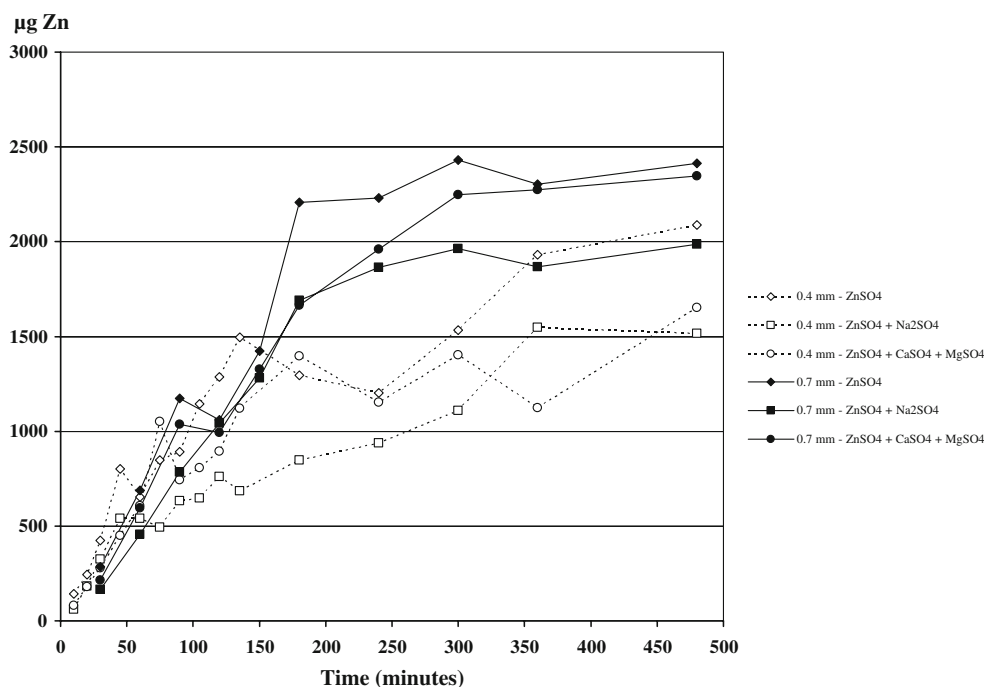
different solutions at pH3. A typical saturation-type behavior is observed: a first section with linear characteristics, a second one where the slope changes, and a third one that indicates the saturation of the resin. As expected, 0.4-mm DGT devices reached saturation before the 0.7 mm ones. Also the quantities accumulated in the chelating resin varied as a function of the thickness of the DGT devices. For the $ZnSO_4$ treatment the saturation for the 0.4-mm DGT devices was reached after 150 min (at 500–1,500 μg), whereas for the 0.7-mm DGT ones, this occurred after 180 min (at 1,800–2,200 μg). Resin gel layers of 0.7-mm DGT devices accumulated on average 380–450 μg more Zn than the ones of 0.4-mm DGT devices in all three solutions.

The 0.7-mm-thick resin gel contains 1.75 times the amount of resin of a 0.4-mm-thick resin gel.

More Zn was accumulated in the resin gel in the $ZnSO_4$ treatment compared to the solutions with Na_2SO_4 and $CaSO_4$, indicating an effect of Na and Ca on the Zn binding. This magnitude of the Zn binding followed the order $ZnSO_4 > ZnSO_4 + CaSO_4 + MgSO_4 > ZnSO_4 + Na_2SO_4$.

In order to calculate the reduction in binding metals by DGT devices, we used R' as the ratio $C_{DGT}/C_{solution}$, with $C_{solution}$ being the Zn concentration (2,000 $mg L^{-1}$) in the “mimicking” solutions. The average ratios $C_{DGT}/C_{solution}$ for the non-saturated state (≤ 150 min immersed for 0.4-mm DGT devices; ≤ 180 min for 0.7-mm DGT devices) enabled

Fig. 1 Micrograms of Zn accumulated in the resin gel for two DGT device thicknesses (0.4 and 0.7 mm) and three solution compositions: $ZnSO_4$ (2,000 $mg L^{-1}$ $ZnSO_4$), $ZnSO_4 + Na_2SO_4$ (2,000 $mg L^{-1}$ $ZnSO_4$ and 30,000 $mg L^{-1}$ Na_2SO_4), $ZnSO_4 + CaSO_4 + MgSO_4$ (2,000 $mg L^{-1}$ $ZnSO_4$, 100 $mg L^{-1}$ $CaSO_4$, and 3,000 $mg L^{-1}$ $MgSO_4$)



the calculation of a correction factor that relates the Zn concentration in the DGT to the Zn in solution (Table 4). These ratios were more dependent on the two thicknesses of the DGT devices employed than on the different competing ions: For 0.4-mm DGT devices, the ratios were 0.50 for the ZnSO₄ treatment, 0.38 for ZnSO₄+Na₂SO₄ treatment, and 0.43 for ZnSO₄+CaSO₄+MgSO₄, and significant differences only occurred between ZnSO₄ and ZnSO₄+Na₂SO₄ treatments. For the 0.7-mm DGT devices, lower ratios were obtained: 0.36 for the ZnSO₄ treatment, 0.23 for the ZnSO₄+Na₂SO₄ treatment, and 0.27 for the ZnSO₄+CaSO₄+MgSO₄. If we compare the same reagents and different thicknesses, statistical differences were obtained in all the cases.

4 Discussion

The use of DGT in mine tailings with pH>5 did not show good correlations with soil solution results: The Zn concentration in the soil solution at pH5.5 was two-fold higher than at pH7, while the C_{DGT} values were in the same range (except for 0.4-mm DGT devices at free drainage). In solutions with pH3 mimicking the soil solution composition of the tailings, a loss of the binding capacity of the chelating resin of 50–60% and 60–80% for Zn using 0.7- and 0.4-mm DGT devices, respectively, was observed (Table 4). As a consequence 0.7-mm DGT devices had better reliability to carry out in situ determinations in solutions with high metal concentrations and low pH. Sondergaard (2007) obtained a reduction coefficient for Mn around 40–50% at pH3 after immersing DGT devices in acid mine drainage and used this correction factor to

calculate C_{DGT} . However, taking the correction factor for Zn into account does not yield a very big increase in the ratio and still values below 0.05 are obtained.

The 0.4-mm DGT devices in the mine tailing under water saturation were already saturated with respect to Zn (>500 μg), and the results from the DGT devices cannot be used under these conditions. The ratios shown in Table 3 at pH3 for 0.4-mm DGT devices under water saturation are thus minimal values; the true values are definitely higher. However, 0.7-mm DGT devices reached saturation at around 1,800 μg accumulated Zn, and thus, the results in this case were not supposed to be affected.

According to Gimpel et al. (2001) Zn can be measured by DGT down to pH3.5; at lower pHs Zn showed low affinity for Chelex resin. However, other metals such as Cu could be still measured by DGT at pH2.0. In other cases, as for example for Cd, there is a reduction of the binding capability at pH<5. In general, the optimum pH range for DGT measurements is in the range between 5 and 10 (Zhang and Davison 1995; Gimpel et al. 2001). Therefore, the limits of the application of DGT measurements are strongly pH dependent (Garmo et al. 2003). This is especially relevant for studies conducted in extremely acid environments as it is the case of mine wastes or acid mine drainage waters.

The ratios C_{DGT}/C_{SS} indicate the magnitude of the metal resupply from the solid phase to the soil solution. Small ratios (<0.1) imply that resupply is low and that there is limited mobilization of metals from the solid phase after depletion of the soil solution. Values near one indicate a continuous resupply from the solid to the aqueous phase. At higher pH values the resupply from mine tailings was more effective than at pH3, although the soil solution concentration of Zn was extremely high at low pH. As the pH increased the buffering capacity of the soil also increased.

The low ratios C_{DGT}/C_{SS} at pH3 imply that the resupply from solid phase is low. At acid pH most of the soluble metals are in the solution, and the pool of metals in the soil phase is very low. With a water content at 30% (field capacity) in the acidic tailing, 17% of the total Zn is present in soil solution. Conesa et al. (2008) performed sequential extraction of these acid tailings and found that the most mobile fraction Zn was 25.6% of the total content.

DGT has been proposed as a good tool to assess Cu uptake in plants (Zhang et al. 2001). Conesa et al. (2007a) performed plant uptake experiments under the same conditions as used in this work (field capacity, light, and temperature) using the three aforementioned tailings and the grass *Lygeum spartum*. Zn uptake into *L. spartum* shoots and roots growing in pH7 tailings was in the same range or even higher (250 and 700 mg kg⁻¹, respectively) than in the pH5.5 tailings (226 and 500 mg kg⁻¹). C_{DGT} (of the 0.7-mm DGT devices) was thus able to predict plant

Table 4 Average of ratios $C_{DGT}/C_{solution}$ for DGT devices immersed in pH3 solutions working under non-saturated state: ≤150 min immersed for 0.4-mm DGT devices ($N=11$); ≤180 min 0.4-mm DGT devices ($N=6$)

DGT devices thickness	Reagents	Ratios $C_{DGT}/C_{solution}$
0.4-mm DGT	ZnSO ₄	0.50 (0.08) a
	ZnSO ₄ +Na ₂ SO ₄	0.38 (0.06) b, d
	ZnSO ₄ +CaSO ₄ +MgSO ₄	0.43 (0.07) a, b
0.7-mm DGT	ZnSO ₄	0.36 (0.07) d
	ZnSO ₄ +Na ₂ SO ₄	0.23 (0.06) c
	ZnSO ₄ +CaSO ₄ +MgSO ₄	0.27 (0.05) c

Values in parentheses are standard deviations. Different letters mean statistical differences ($P<0.05$)

0.4-mm DGT DGT devices assembled by a 0.4-mm resin gel and a 0.4-mm diffusive gel, 0.7-mm DGT DGT devices assembled by a 0.7-mm resin gel and a 0.7-mm diffusive gel

metal uptake much better than soil solution results (C_{SS}), which showed lower values at higher pH.

Plant responses to metal phytotoxicity are strongly influenced by soil water content. This aspect is especially important at low pH, where metals are easily mobilized from the solid phase. In the cases of saturated water treatments the ratios C_{DGT}/C_{SS} were higher and therefore the metal resupply was also more effective. Conesa et al. (2007a) observed a different behavior of *L. spartum* growing in tailings under semiarid field conditions, where no phytotoxicity was observed, and of specimens of the same plant species growing in the laboratory under water field capacity conditions, where most of the plants died. Conesa et al. (2007a) explained this fact by the higher reactive surface of the soils and the constantly high moisture content in the pot experiments. The C_{DGT}/C_{SS} ratios at pH3 showed seven-fold differences between free drainage (0.002) and water saturation conditions (0.014). However, these differences are lower in the case of pH5.5 and pH7 tailings (only two to three times). This has two implications: Water saturation under acidic conditions is able to mobilize more metals into soil solution, and second, phytotoxic effects in plants (and higher uptake) may occur under higher moisture content. In this case, C_{DGT}/C_{SS} ratios seem to be suitable to predict phytotoxicity. Nevertheless, C_{DGT} may miss aspects related to biochemical processes in the rhizosphere, spatial heterogeneity in metal concentrations, and preferential growth of roots, which have been shown as mechanisms of metal tolerance in plants (Moradi et al. 2009) and that may explain low Zn uptake and non-phytotoxicity in plant which grow in field conditions.

5 Conclusions

The use of DGT in mining soils can be a promising tool to study bioavailable metals concentrations in mine tailings but it has to be used carefully under acidic pH. Competition with other cations present at very high concentrations may hinder the accumulation of metals by the chelating resins, which should be tested under the conditions of the particular mine tailing. Additionally, it may be possible to change the deployment time of DGT devices for a shorter time in tailings with high metals in soil solution. Thicker diffusive gels could also be employed to prevent saturation of DGT and therefore meaningless results.

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