Degryse F., Smolders E., Oliver I. & Zhang H. (2003). Relating soil solution Zn concentration to Diffusive Gradients in Thin Films measurements in contaminated soils. *Env. Sci. Technol.* 37, 3958-3965.

Abstract, tables and figures

The full version is available through ACS publications

<http://pubs.acs.org/doi/abs/10.1021/es034075p>

Relating soil solution Zn concentration to DGT measurements in contaminated soils

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Abstract

The technique of diffusive gradients in thin-films (DGT) has been suggested to sample an available fraction of metals in soil. The objectives of this study were to compare DGT measurements with commonly measured fractions of Zn in soil, viz, the soil solution concentration and the total Zn concentration. The DGT technique was used to measure fluxes and interfacial concentrations of Zn in 3 series of field contaminated soils collected in transects towards galvanized electricity pylons, and in 15 soils amended with ZnCl_2 at six rates. The ratio of DGT-measured concentration to pore water concentration of Zn, R , varied between 0.02 and 1.52 (mean 0.29). This ratio decreased with decreasing distribution coefficient, K_d , of Zn in soil, which is in agreement with the predictions of the DIFS model (DGT-Induced Fluxes in Soils). The R values predicted with the DIFS model were generally larger than the observed values in the ZnCl_2 amended soils at the higher Zn rates. A modification of the DIFS model indicated that saturation of the resin gel was approached in these soils, despite the short deployment times used (2 hours). The saturation of the resin with Zn did not occur in the control soils (no Zn salt added) or the field contaminated soils. Pore water concentration of Zn in these soils was predicted from the DGT-measured concentration and the total Zn content. Predicted values and observations were generally in good agreement. The pore water concentration was more than 5 times underpredicted for the most acid soil (pH=3) and for six other soils, for which the underprediction was attributed to the presence of colloidal Zn in the soil solution.

Synopsis: DGT measurements provide good estimation of pore water concentration of Zn in unpolluted and field contaminated soils..

TABLE 1. Selected characteristics of the control soils (OC = organic carbon content; BS = base saturation; θ = moisture content by weight; Zn_{BG} = background Zn) and range of Zn additions (Zn_{add}).

nr	Location	pH	OC	CaCO ₃	CEC	BS	θ		Zn _{BG}	Zn _{add}
		(CaCl ₂)	(%)	(%)	(cmol _c kg ⁻¹)	(%)	pF=0	pF=1.9	(mg kg ⁻¹)	(mg kg ⁻¹)
1	Gudow (Germany)	3.0	5.1	0.0	5.8	7	0.46	0.25	7	15 - 720
2	Houthalen (Belgium)	3.5	1.9	0.0	1.9	7	0.35	0.20	8	15 - 720
3	Zegveld (The Netherlands)	4.7	23.3	0.0	35.3	92	1.38	1.22	191	200 - 6400
4	Rhytdalog (UK)	4.8	7.8	0.0	14.9	72	0.73	0.54	83	201 - 2018
5	Souli I (Greece)	4.8	0.4	0.0	11.2	70	0.41	0.26	37	75 - 3600
6	Kövlinge (Sweden)	5.1	2.3	0.0	4.7	77	0.39	0.28	26	25 - 1200
7	De Meern (The Netherlands)	5.2	10.2	0.0	29.6	71	1.17	0.79	155	85 - 2365
8	Aluminusa (Italy)	5.7	0.9	0.0	22.6	59	0.43	0.34	53	175 - 5600
9	Zeveren (Belgium)	5.7	3.5	0.0	18.9	68	0.61	0.48	76	394 - 3665
10	Woburn (UK)	6.4	4.4	0.0	23.4	73	0.65	0.43	99	40 - 1800
11	Ter Munck (Belgium)	6.8	1.0	0.0	8.9	77	0.42	0.33	54	75 - 3600
12	Rots (France)	7.4	3.0	14.9	20.0	88	0.42	0.36	51	150 - 4800
13	Souli II (Greece)	7.4	8.3	47.4	36.3	95	0.63	0.38	51	75 - 3600
14	Marknesse (The Netherlands)	7.5	2.5	10.0	20.1	92	0.43	0.36	80	125 - 6000
15	Guadalajara (Spain)	7.5	4.8	36.5	16.9	89	0.45	0.24	27	75 - 3600

TABLE 2. Range of soil characteristics and total Zn content of the field contaminated soils, sampled along a transect around galvanized pylons.

Location	<i>n</i>^a	pH (CaCl₂)	OC (%)	CEC (cmol_c kg⁻¹)	Zn_{tot} (mg kg⁻¹)
Rhydtalog (UK)	6	5.0 – 5.2	5.6 – 12.6	11.1 – 18.5	284 -2101
De Meern (The Netherlands)	6	5.4 – 6.7	6.6 – 11.2	27.0 – 38.9	240 – 2520
Zeveren (Belgium)	6	5.5 – 6.1	3.9 – 7.7	17.0 - 21.0	470 - 3741

^a number of contaminated soil samples collected along the transect

TABLE 3. Effect of Zn addition on soil pH (in 0.01 M CaCl₂), soil solution composition, and on DGT-measured concentration (Zn_{DGT}). The value of *R* is the ratio of Zn_{DGT} to the soil solution concentration. Deployment time was between 19 and 24 hours for treatments a to d and 2 hours for treatments e to g. Data are given for two soils only as illustration.

		Zn _{added}			Ca _{pw} ^a	Zn _{pw} ^b	K _d ^c	Zn _{DGT}	
treatment		(mg kg ⁻¹)	pH _{CaCl2}	pH _{pw}	(mM)	(mg l ⁻¹)	(l kg ⁻¹)	(mg l ⁻¹)	R
Soil 2	a	0	3.5	4.1	0.03	0.33	23.8	0.04	0.13
	b	15	3.5	3.6	0.13	3.8	5.8	0.51	0.13
	c	30	3.6	3.4	0.56	30	1.0	1.4	0.05
	d	60	3.5	3.3	0.65	67	0.8	2.4	0.04
	e	120	3.6	3.2	1.63	375	0.1	24.7	0.07
	f	240	3.5	3.1	1.42	561	0.2	67.3	0.12
	g	720	3.5	3.1	1.77	2058	0.1	162	0.08
Soil 8	a	0	5.7	6.2	0.5	0.01	4697	0.01	0.65
	b	175	5.6	5.0	6.7	5.2	43	1.9	0.36
	c	350	5.5	4.9	13	29	14	7.3	0.25
	d	700	5.5	4.9	24	151	4.7	13.9	0.09
	e	1400	5.2	4.7	45	755	1.7	121	0.16
	f	2800	5.2	4.4	76	2934	0.7	277	0.09
	g	5600	5.0	4.2	115	10481	0.3	583	0.06

^a Ca_{pw}, pore water concentration of Ca. ^b Zn_{pw}, pore water concentration of Zn. ^c K_d, calculated as ratio of total adsorbed Zn concentration to pore water concentration.

Figure 1 The relation between increase in pore water concentration of Ca, $[Ca]_{pw}$, and decrease in the distribution coefficient of Zn, K_d , upon addition of $ZnCl_2$, for all Zn salt amended soils.

Subscripts 0 and tr refer to control soil (no $ZnCl_2$ added) and treated soil respectively.

Figure 2 (a,b) Plot of the ratio of DGT measured Zn concentration to pore water concentration (R) against the in situ distribution coefficient of Zn (K_d) for soils depleted during (a) 19-24 hours or (b) 2 hours. The lines represent predictions of the DIFS model (not fitted to these data) for a deployment time of (a) 24 hours or (b) 2 hours, and either low porosity ($\phi_s = 0.50$) and long response time ($T_c = 1000$ s) (dotted line) or high porosity ($\phi_s = 0.81$) and short response time ($T_c = 100$ s) (solid line). (c) Plot of R against the mass of Zn accumulated on the resin gel (μg device⁻¹) for soil 5. Closed symbols represent lowest Zn doses, and open symbols the highest Zn doses. The lines are predictions of the DIFS model ($T_c = 100$ s, $\phi_s = 0.54$, K_d as measured).

Figure 3 Effect of the molar ratio of Ca concentration to Zn concentration in the pore water on the mass of Zn, M , that can be accumulated on the resin gel – as a fraction of the total capacity K – before the flux is 25% lower than the initial flux, or before the flux is reduced to zero. (Calculations for sustained case with eq 12)

Figure 4 Predicted solution concentrations of Zn throughout soil and DGT device at different deployment times, for soil 8d (Table 3). Predictions were made with the extended model taking into account saturation of the resin gel (Equations 13a to d). Input parameters and initial conditions are as given in the lower panel, where S is the amount of Zn on the solid phase (background Zn + added Zn).

Figure 5 Comparison between observed R (ratio of DGT measured concentration to pore water concentration) and the values predicted with the DIFS model or with the extended model taking into account saturation of the resin gel, for all Zn salt amended soils (predictions with experimental K_d and porosity, and $T_c = 300$ s). The inset shows only those soils with more than $150 \mu\text{g}$ Zn accumulated on the resin gel (i.e., more than half of the resin capacity). The line represents the 1:1 line.

Figure 6 Theoretical plot of R as a function of the ratio of total metal content to c_{DGT} for different soil porosities, as calculated with the DIFS model (deployment time of 24 hours; $T_c=300\text{s}$).

Figure 7 Comparison between observed and predicted pore water concentrations for all control soils ($n=15$), all field contaminated soils ($n=18$) and the Zn salt amended soils with less than 150 μg Zn accumulated on the resin ($n=71$). Predicted pore water concentrations were calculated as the ratio of c_{DGT} and the R value estimated using Figure 6 (or an analogue figure for a deployment time of 2 hours). The line represents the 1:1 line. Data labels are shown for the soils for which the pore water concentration was more than 5 times underpredicted (numbers in Table 1).