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Figures

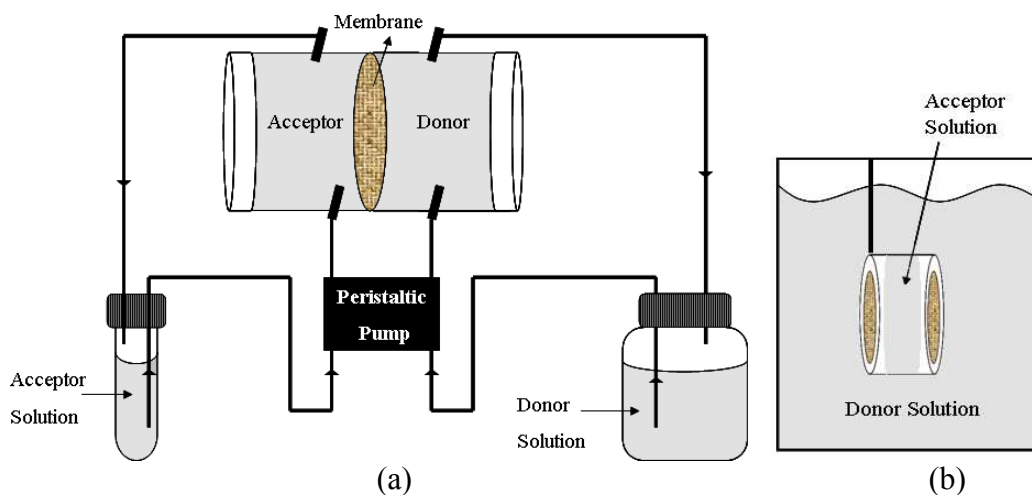


Figure 1. Schematic representation of the DMT cell. (a) Lab cell. (b) Field cell.

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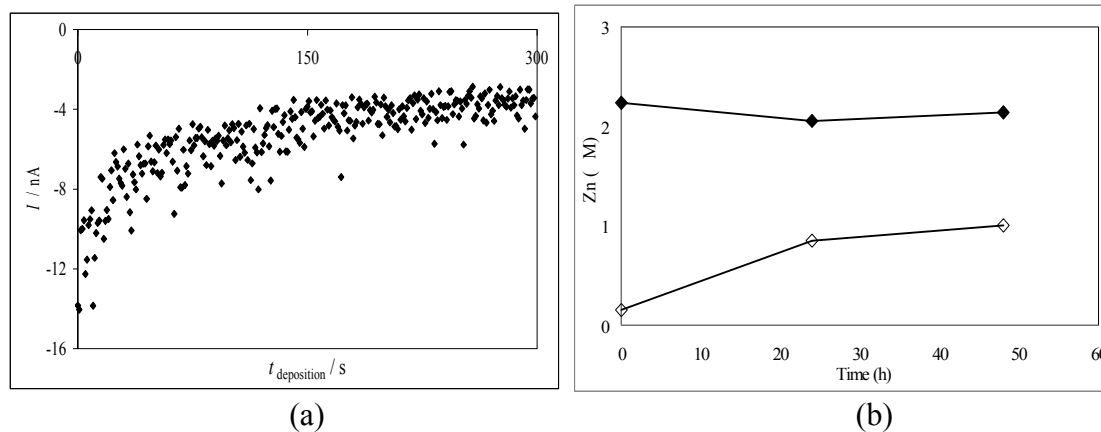
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593 Figure 2. Equilibrium situation achieved in AGNES and DMT procedures in a solution

594 containing $c_{T,Zn}=2.23 \mu M$, $c_{T,NTA}=2.00 \mu M$ and concentration of $CaCl_2=0.01 M$ (a) First

595 stage of AGNES one pulse: $Y=10$, $t_1=300 s$. (b) Evolution of total Zn concentration in

596 (♦) donor and (◇) acceptor solution during DMT analysis.

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600 **Tables**

601

602 Table 1. pH, cation exchange capacity (CEC), organic matter content, clay and
603 dissolved organic content (measured after the extraction and filtering process) of the 4
604 analysed soils.

Soil	pH	CEC (meq/100g)	Organic Matter (%)	Clay (%)	Initial DOC (mg / L)
Rivier clay	5.0	206	8.5	18	20.2
Cover sand	4.5	47	4.8	-	17.8
Loam	6.2	122	5.2	17	18.7
Reclaimed peat	5.2	126	8.3	-	21.4

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608 Table 2. AGNES parameters used to determine the free Zn concentration in synthetic
 609 and natural samples. $t_{1,b}$ in some cases was greater than the standard recommended time
 610 ($t_{1,b} = 3 \times t_{1,a}$ (Companys et al., 2005)) in order to be on the safe side.

Sample	$Y_{1,a}$	$t_{1,a} / s$	$Y_{1,b}$	$t_{1,b} / s$	t_w / s	Y_2	t_2 / s	
NTA-low Zn concentration	10^{10}	160	100	480	50	10^{-8}	50	
NTA-high Zn concentration	-	-	10	200				
				300				
Rhine River	10^{10}			450				
				500				
				1400				
				900				
				2700				
Rivier clay	10^{10}			50				
				150				
	-	-		20				300
								700
Cover sand	10^{10}			50				
				40				
				40				
				40				
				150				
				50				
Loam	10^{10}			50				
				50				
				150				
				800				
Reclaimed peat	-	-	40	1500				
				400				
	-	-	20	700				
				50				
	10^{10}			40				
				150				

612 Table 3. Total and free Zn^{2+} concentrations measured and predicted in Zn-NTA
 613 solutions with $c_{T,NTA}=2.00 \mu M$ and 10 mM concentration of $CaCl_2$. For each total
 614 concentration, replicates are distinguished as I and II (DMT), III and IV (AGNES).

$c_{T,Zn}$ / μM	DMT ($t=48h$)				AGNES			
	I		II		III		IV	
	pH	$[Zn^{2+}]/\mu M$	pH	$[Zn^{2+}]/\mu M$	pH	$[Zn^{2+}]/\mu M$	pH	$[Zn^{2+}]/\mu M$
0.71	5.33	0.27 (0.30)	5.11	0.30 (0.29)	5.35	0.29 (0.30)	5.38	0.28 (0.28)
2.23	6.43	0.95 (1.05)	6.20	0.93 (1.04)	6.37	1.09 (1.07)	6.20	1.11 (1.04)

615 Values in brackets correspond to the free Zn^{2+} concentration predicted by VMINTEQ speciation program.

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618 Table 4. Total Ca²⁺ concentrations measured with ICP-OES in donor and acceptor
 619 solutions at 48h of DMT experiments.

Sample	Replicate	Total Ca ²⁺ concentration (mM)	
		Donor	Acceptor
NTA-low Zn concentration	I	9.96	10.1
	II	10.0	10.1
NTA-high Zn concentration	I	9.66	9.51
	II	9.32	10.1
Rhine river	I	2.15	2.30
	II	2.15	2.35
River clay	I	16.70	16.8
	II	16.5	17.2
Cover sand	I	16.3	16.9
	II	16.6	17.2
Loam	I	16.5	17.1
	II	17.0	17.2
Reclaimed peat	I	16.7	16.7
	II	16.7	17.1

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623 Table 5. Correction of the concentrations of Zn^{2+} in Zn+NTA solutions (see Table 3)
 624 to a common pH value in order to facilitate the comparison between AGNES and DMT.
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Correction to pH	$c_{T,Zn}$ / μM	Corrected concentration/ μM				Average		% Difference (AGNES-DMT) /AGNES
		DMT		AGNES		DMT	AGNES	
		I	II	III	IV			
		5.29	0.71	0.27	0.31	0.29	0.30	
6.30	2.23	0.96	0.93	1.09	1.13	0.94	1.11	14.96

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629 Table 6. pH, temperature, electric conductivity (EC), ionic strength (*I*) and dissolved
630 organic carbon (DOC) in the Rhine river water. The measurements were performed *in*
631 *situ* at the day of sampling for AGNES (March 28th 2011), at the day that DMT was
632 placed *in situ* (April 13th 2011) and when collecting the device, i.e. 48 h after DMT
633 started.

Technique	pH	Temperature (°C)	EC ($\mu\text{S cm}^{-1}$)	<i>I</i> (mM)^a	DOC (ppm)
DMT <i>in situ</i> (<i>t</i> =0)	7.88	16.1	731	12.1	3.80
DMT <i>in situ</i> (<i>t</i> =48 h)	7.95	16.0	-	-	3.20
AGNES	7.94	12.8	720	11.5	4.80

634 ^a It was calculated by $I=1.6 \times 10^{-5} \text{ C} \times \text{EC}$ (see Table 2330 of Ref (APHA,1998)).

635 Table 7. pH, total Zn, and free Zn concentrations in Rhine river water. Free Zn²⁺ was
 636 measured with DMT (*t*=48h) *in situ* and AGNES purged with N₂/CO₂. pH in DMT
 637 measurement corresponds to the measurement performed in the river when collecting
 638 the device (i.e. 48 h); pH of AGNES is the pH of the sample during the analysis.

Technique	pH	<i>c</i> _{T,Zn} / μM	[Zn ²⁺] / μM	
			I	II
DMT <i>in situ</i>	7.95	0.14	0.097	0.094
AGNES (<i>n</i> =8)	7.91	0.17	0.084 (0.012) ^a	

639 ^a Number in brackets is the standard deviation between replicates (*n*=8)

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642 Table 8. pH, total Zn and free Zn²⁺ concentrations measured in 10 mM CaCl₂
 643 extractions made in duplicate with 4 soil samples collected from grassland in The
 644 Netherlands. Free Zn²⁺ concentration was determined with AGNES and DMT (*t*=48h)
 645 techniques and total Zn with ICP-MS. Free Zn predicted through NICA-Donnan model
 646 (see section 4.3) is derived from measured DOC values.

Soil	Replicate	<i>c</i> _{T,Zn} / μM	AGNES			DMT				% Difference (AGNES- DMT) /DMT	
			[Zn ²⁺] / μM	%Free Zn	pH	[Zn ²⁺] / μM	%Free Zn	pH	DOC 72 h predicted [Zn ²⁺] / μM		
Rivier clay	I	1.43	0.990	69.2	5.00	1.19	83.2	5.37	19.2	1.19	16.8
	II	1.48	0.961	64.9	5.00	1.10	74.3	5.40	19.7	1.18	12.6
Cover sand	I	3.19	2.38	74.6	4.93	2.23	69.9	5.04	15.3	2.76	6.73
	II	3.14	2.25	71.7	4.91	2.33	74.2	5.05	16.0	2.70	3.43
Loam	I	1.18	0.808	68.5	6.23	0.640	54.2	6.81	16.2	0.71	-26.3
	II	1.07	0.785	73.4	6.24	0.790	73.8	6.67	13.5	0.71	0.63
Reclaimed peat	I	2.67	1.91	71.5	5.40	1.93	72.3	6.09	14.7	2.14	1.04
	II	3.08	1.16	37.7	5.40	1.36	44.2	5.76	18.9	2.56	14.7

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