Accepted Manuscript

Title: Speciation of nickel in surface waters measured with the Donnan membrane technique

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PII: S0003-2670(06)01402-4
DOI: doi:10.1016/j.aca.2006.06.070
Reference: ACA 227693

To appear in: *Analytica Chimica Acta*

Received date: 29-3-2006
Revised date: 27-6-2006
Accepted date: 27-6-2006

Cite this article as: L. Van Laer, E. Smolders, F. Degryse, C. Janssen, K.A.C. De Schamphelaere, Speciation of nickel in surface waters measured with the Donnan membrane technique, *Analytica Chimica Acta* (2006), doi:10.1016/j.aca.2006.06.070

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Tables

Table 1

Selected characteristics of the six water samples.

Water sample	pH	DOC mg/l	IC mM	Ni	Cu	Zn	Fe	Al	Mn
				μM					
Ankeveen	7.13	23.6	0.75	0.072	0.022	0.094	2.50	1.061	0.012
Beneden Regge	7.85	12.6	2.60	0.063	0.016	0.086	0.93	<0.0005	0.010
Bihain	6.10	6.4	0.13	0.048	0.031	0.321	1.16	0.852	<0.0005
Brisy	7.48	3.1	0.33	0.044	0.026	0.101	1.77	0.876	0.047
Eau d'Eppe	7.71	5.0	1.50	0.075	0.007	0.033	1.96	0.748	0.090
Markermeer	8.06	7.6	1.86	0.065	0.015	0.049	0.10	0.100	<0.0005

Water sample	Na	Mg	K	Ca	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ^{- (a)}	CO ₃ ^{2-(a)}
	mM								μM
Ankeveen	0.75	0.29	0.19	1.03	0.82	<0.05	0.84	0.64	0.49
Beneden Regge	1.88	0.32	0.31	1.72	1.26	0.12	0.59	2.49	10.1
Bihain	0.18	0.04	0.02	0.11	0.25	0.06	0.07	0.05	0.01
Brisy	0.30	0.16	0.06	0.25	0.46	0.21	0.09	0.31	0.51
Eau d'Eppe	0.39	0.25	0.12	0.84	0.44	0.11	0.19	1.42	4.05
Markermeer	3.41	0.64	0.24	1.54	2.69	<0.05	1.15	1.80	12.1

^(a) based on measurements of inorganic carbon and speciation calculation

Table 2

Effect of equilibration time on measured free Ni^{2+} fractions in two waters. The solutions were spiked with 1.7×10^{-7} M, and Donnan dialysis was performed after various equilibration times (1 hour, 2 days, and 7 days). The pH refers to the solution after dialysis.

			1 h	2d	7d
Ankeveen	rep1	fraction Ni^{2+}	0.069	0.048	0.069
		pH	7.18	7.35	7.19
	rep2	fraction Ni^{2+}	0.067	0.049	0.068
		pH	7.18	7.32	7.18
Markermeer	rep1	fraction Ni^{2+}	0.21	0.22	0.20
		pH	8.17	8.09	8.21
	rep2	fraction Ni^{2+}	0.24	0.20	0.17
		pH	8.15	8.09	8.26

Table 3

Effect of Ni concentration on the measured free Ni^{2+} ion fraction (standard deviation of two replicates in brackets) for six surface waters. The pH refers to the solution after dialysis.

	pH	Ni concentration (μM)	fraction of Ni^{2+} (%)
Ankeveen	7.36	0.07	6.9 (± 0.0)
	7.36	0.66	13.8 (± 0.3)
	7.36	2.52	27.2 (± 1.4)
Beneden Regge	8.54	0.06	4.0 (± 0.7)
	8.58	0.12	7.7 (± 0.7)
	8.58	1.82	23.0 (± 0.3)
Bihain	6.17	0.05	45.3 (± 2.7)
	6.17	0.08	45.1 (± 0.0)
	6.17	0.25	55.3 (± 2.2)
Brisy	7.23	0.04	31.0 (± 1.0)
	7.23	0.06	39.0 (± 2.9)
	7.23	0.36	60.2 (± 2.5)
Eau d'Eppe	7.85	0.07	31.4 (± 2.0)
	8.04	0.10	26.9 (± 2.6)
	8.17	0.36	37.4 (± 3.3)
Markermeer	8.26	0.06	15.3 (± 0.7)
	8.26	0.10	20.6 (± 1.0)
	8.26	0.90	39.8 (± 0.1)

Table 4

Default stability constants in WHAM VI and adjusted values (used for the speciation calculations) for complexation of Ni with inorganic and organic ligands.

	Parameter	Default stability constant (pK) in WHAM VI	Adjusted stability constant (pK)	Reference
Inorganic complexation	$K = [\text{NiCO}_3] / \{[\text{Ni}^{2+}].[\text{CO}_3^{2-}]\}$	5.78	4.57	NIST ^a
	$K = [\text{NiHCO}_3^+] / \{[\text{Ni}^{2+}].[\text{H}^+].[\text{CO}_3^{2-}]\}$	13.41	12.42	NIST ^a
Organic complexation	$K_{\text{MA}(\text{Zn})}$	1.6	1.8	Cheng et al. [10]

^a National Institute of Standards and Technology

Table 5

Summary of the parameterization of model (WHAM VI) parameters, based on goodness-of-fit of the measured Ni speciation data. The optimized parameters are the Ni-fulvic acid binding constant ($\log K_{MA}$), the distribution parameter ΔLK_2 , and the fraction of active fulvic acid (%AFA). The goodness-of-fit was evaluated by the sum of squared errors of the log-transformed free Ni^{2+} fractions (SSE), by the slope of the linear regression line of predicted versus observed log free Ni^{2+} fraction, and by the median of the ratios of predicted and observed free Ni^{2+} fractions. The best-fit is shown in bold.

Model parameters			Model fit indices		
$\log K_{MA}$	ΔLK_2	%AFA	SSE	slope	median predicted/observed Ni^{2+}
Default values					
1.4	1.57	65	10.45	0.24	2.40
Increasing DOM capacity					
1.4	1.57	100	7.72	0.29	2.03
1.4	1.57	200	5.26	0.36	1.65
Increasing binding constant					
1.60	1.57	65	2.18	0.57	1.22
1.65	1.57	65	0.95	0.69	0.94
1.70	1.57	65	1.18	0.82	0.68
Increasing site heterogeneity					
1.4	2	65	4.44	0.49	1.75
1.4	2.35	65	0.63	0.87	1.03
1.65	1.57	65	0.95	0.69	1.22
1.75	1.57	40	0.69	0.84	0.86
1.80	1.57	30	0.75	0.9	0.89

**Speciation of nickel in surface waters measured with the
Donnan membrane technique**

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Abstract

The evaluation of the ecotoxicological risk of nickel (Ni) in surface water is hampered by a lack of speciation data. Six surface waters were sampled and speciation of Ni(II) was measured by the Donnan membrane technique (DMT) combined with radiochemical determination of ^{63}Ni . The free Ni^{2+} ion fraction in the dissolved ($<0.45\ \mu\text{m}$) phase was determined at background Ni concentration ($4\text{--}8 \times 10^{-8}\ \text{M}$) and at concentrations in the range of toxicity thresholds for the Ni sensitive species *Ceriodaphnia dubia* ($5 \times 10^{-8} - 2 \times 10^{-6}\ \text{M}$). The free ion fraction ranged from 4% to 45% at background Ni and increased with increasing Ni concentration and water hardness and with decreasing pH. The equilibration time after addition of Ni^{2+} (3 hours – 7 days) did not significantly change the measured free ion fraction. Predictions of the Humic-Ion Binding Model WHAM (Windermere Humic Aqueous Model) VI overestimated the observed free Ni^{2+} fraction (median > 2 -fold), even when assuming that all dissolved organic matter (DOM) was present as fulvic acid (FA). The impact of several model parameters affecting the prediction of Ni speciation were evaluated, including the solubility product of $\text{Fe}(\text{OH})_3$, which affects the Fe competition for complexation by DOM. The best fit ($R^2=0.88$) was obtained by increasing only the distribution term ΔLK_2 , which modifies the binding strength of multi-dentate sites, to accommodate the observed dependence of free ion fraction on Ni concentration.

Keywords: nickel speciation; surface water; WHAM (Windermere Humic Aqueous Model); Donnan Membrane Technique (DMT)

Introduction

Predictions of metal toxicity in freshwater require information on metal speciation, i.e. the fraction of metal that is present as the free ion. The accurate prediction of nickel (Ni) speciation in surface water is an essential step towards the development of the Ni Biotic Ligand Model (BLM). The BLM [1] combines a chemical model that describes equilibrium metal speciation with a toxicity model that relates accumulation of metal at the biotic ligand to toxic effect. The equilibrium speciation model often used in the BLM is the Windermere Humic Aqueous Model (WHAM) that describes metal complexation with dissolved organic matter (DOM). There are little data to calibrate the Ni complexation parameters in a speciation model such as WHAM, with most data based on model solutions and only a few studies reporting Ni speciation in natural waters. The default parameters in WHAM VI describing the interaction between Ni and fulvic acid are mainly based on Ni binding with fulvic acids isolated from groundwater at trace concentrations of Ni ($<4 \times 10^{-10}$ M) [2,3]. It is, however, unclear to what extent the DOM isolated from groundwater is a relevant model for DOM in surface water.

Speciation of Ni has also been measured in mixtures of synthetic solutions and groundwater affected by landfill leachates [4], and it was found that the free Ni^{2+} ion fraction ranged from 10 to 100% depending on pH and DOM concentration of the solution. The verification of the WHAM parameters with these data may not be useful for the Ni-BLM development because total Ni concentration ($>10^{-6}$ M), DOC (dissolved organic carbon) concentrations (>40 mg L^{-1}) and water hardness (>350 mg CaCO_3 L^{-1}) in these solutions were larger than in most surface waters. Similar free Ni^{2+} ion fractions (2–98%) were found in soil solutions with varying pH and DOM concentrations [5]. These data may also not be convenient for calibration, because the low pH of the soil solutions (3.7–6.1) is not representative for the pH

range mostly found in surface waters (6–8.5). Some studies [6-7] reported speciation of Ni in natural waters at background Ni, i.e. about 10^{-8} M. In the study of Xue *et al.* [6] the Competitive Ligand Exchange – Adsorptive Stripping Voltammetry (CLE-AdSV) technique applied highlighted slow exchange kinetics of Ni between the natural ligand and the competing ligand (DMG) with half lives for exchange of several hours to days. Equilibrium based values derived from this technique yielded surprisingly small free Ni^{2+} ion fractions (<0.1%). Recent data [7] obtained with the Donnan Membrane Technique (DMT) showed a free Ni^{2+} fraction between 2-4% in 3 freshwaters, one of which was sampled in the same Lake Greifen for which Xue *et al.* [6] reported a free Ni^{2+} fraction value that was almost 10^4 -fold smaller. Kinetic speciation methods, based on competing ligand techniques, have also been used to study Ni speciation. However, in these studies [8-10], no attempt was made to measure equilibrium speciation, but information on the lability of the Ni-DOM complexes in surface waters was derived from the rate of dissociation. Fractions of labile Ni in surface water were found to range from 20 to 80% [8], 40 to 100% [9] and 31 to 88% [10]. The labile fractions are assumed to include free Ni^{2+} ion, inorganic Ni complexes and small Ni-DOM complexes that dissociate within the operational conditions. Therefore, these labile fractions are an upper estimate of free ion fractions. Clearly, there is a contrasting range of fractions of free Ni^{2+} ion or labile Ni among studies.

The aim of this study is to calibrate the WHAM VI model to new equilibrium Ni speciation data that are relevant for surface water, in order to use that model for the incorporation into a BLM. Rather than deriving stability constants from Ni titration data on isolated DOM, we adjusted model parameters of WHAM VI to obtain a best fit between measured and predicted free metal ion fractions in freshwater samples covering a wide range of chemical properties. This approach has already been followed for zinc (Zn) [11] and copper (Cu) [12]. In addition, we determined the kinetics of Ni complexation so that an appropriate equilibration time could

80 be applied during further speciation experiments. In earlier studies slow dissociation kinetics
81 of natural Ni-DOM complexes have been demonstrated [6,10,13-16], however no data were
82 found on association kinetics. We used the Donnan speciation technique [17], a method which
83 minimizes the disturbance of the equilibrium composition in the test solution and which does
84 not rely on a priori knowledge of the conditional stability constant of a competing ligand.

85 **Materials and methods**

86 *Surface water samples*

87 Natural water samples, covering a wide range of water chemistry conditions, were collected at
88 six different sites. The surface waters were membrane filtered in the field (0.45 μm) and
89 collected in metal-free poly-ethylene containers. The samples were immediately transported
90 to the laboratory where they were stored at 4°C in the dark until analysis. For the
91 characterization of the six surface water samples, the parameters important for speciation
92 were determined (Table 1). Cation concentrations (Ca, Mg, Na, K, Fe, Al, Mn, Ni, Cu, Zn,
93 Pb, and Cd) were measured by inductively coupled plasma optical emission with axial plasma
94 (ICP-OES, Perkin Elmer Optima 3300 DV, Wellesley, MA, USA). The Ni detection limit in
95 water is 0.2 $\mu\text{g L}^{-1}$ or 3×10^{-9} M), anion concentrations (Cl, NO_3 , and SO_4) were measured by
96 ion chromatography (Dionex QIC analyzer, Sunnyvale, CA, USA). The dissolved organic
97 carbon (DOC) and inorganic carbon (IC) content were determined by a TOC-analyzer (TOC-
98 5000, Shimadzu, Duisburg, Germany). Solution composition was also measured after Donnan
99 speciation to account for small changes in chemistry during speciation measurements. The
100 composition after the speciation was used as input for all model calibrations. The major
101 change in composition was increased Na concentration from the pH buffer added (see below)
102 while changes, compared to initial values (Table 1), were smaller than 0.5 unit for the pH
103 (except for Beneden Regge) and smaller than 15% for the Ca and Mg concentration. The
104 chemical composition of the waters after Donnan dialysis can be obtained from the
105 corresponding author.

106 *Donnan dialysis*

107 The principle of Donnan Dialysis as speciation technique is the selective dialysis of very
108 small quantities of the free metal ion from a large volume of donor solution to a small volume

of acceptor solution. Free metal ions freely diffuse through the microporous membrane that carries a negative charge while anions and metal complexes with larger molecular weight are excluded based on charge or size. A full description of the method and its verification with model solution is given elsewhere [17,18]. The Donnan equilibrations were carried out on 100 mL-samples of the surface waters, using a custom-machined exchange cell made from Teflon and Kel-F plastics. The cell holds a strong-acid cation-exchange membrane (Nafion-117, E.I. Dupont de Nemours) which separates the sample solution (donor) from an initially pure solution of $\text{Sr}(\text{NO}_3)_2$ (acceptor). Nafion-117 is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ethers. During equilibration, the sample solution was continuously circulated past the bottom of the membrane by a Teflon pump at a rate of 200 mL min^{-1} . The acceptor solution (200 μL) rests on the top surface of the membrane and is held by an annular ring in the top part of the cell. We used two Donnan cells that were placed in parallel to the pump. The data reported below refer to the average of the two values obtained from each of the acceptor solutions.

In preparation for Donnan equilibration, the membranes were stored in a mixture of 10% methanol, 10% HNO_3 and 80% Milli-Q water to replace adsorbed cations with H^+ . Prior to use, the membranes were consecutively rinsed and soaked in Milli-Q water, in $\text{Ca}(\text{NO}_3)_2/\text{MgCl}_2$ solutions ($\pm 2.5 \text{ mM}$) with Ca/Mg molar ratio 2.75, and finally in a subsample of the spiked donor solution. The pre-equilibration of the membranes in the Ca/Mg solution rather than in a Sr solution deviates from the standard procedure of Helmke *et al.* [17]. This modification was made to avoid large changes in Ca/Mg during the equilibration with solutions of low ionic strength. The exchange capacity of one Nafion-117 membrane ($\pm 3.14 \text{ cm}^2$, 0.1 g) is 0.09 meq charge, while a 100 mL solution of the low ionic strength water Bihain (0.15 mM Ca + Mg) has only an equivalent charge of 0.03 meq. If the

membranes were only preloaded with Sr, exchanges between Ca^{2+} , Mg^{2+} and Sr^{2+} would occur which may modify solution composition and Ni speciation.

The pH of the freshwaters often increased by >0.5 pH units during Donnan dialysis due to the CO_2 degassing of the solutions. This shift is unwanted since speciation is largely pH dependent. Therefore, solutions were pH buffered in all final experiments. The buffer MOPS (3-Morpholinopropanesulfonic acid; pK_a 7.2) was added (3.6 mM) to the surface water samples (100 mL). The pH of the buffer was adjusted to the same pH as the water sample with NaOH 1 M prior to adding it to the solution. To test whether this buffer does not complex Ni, an experiment was set up using the surface water Markermeer (spiked with stable Ni to 1.7×10^{-7} M). The free Ni^{2+} ion fraction in the original, unbuffered solution, in which the pH changed from 8.15 initially to 8.30 finally, was 25.5%. The free Ni^{2+} ion fraction in the MOPS buffered solution, in which pH was maintained at 8.15, was 24.2%, indicating that adding buffer had negligible effect on the Ni speciation.

Prior to Donnan dialysis, the donor solution was spiked with a small volume (1 mL) of carrier-free $^{63}\text{NiCl}_2$ solution (50 kBq mL^{-1}). The acceptor solution (200 μL) was a $\text{Sr}(\text{NO}_3)_2$ solution with ionic strength identical to that of the sample solution, as estimated by a complete analysis of the sample solution by ICP-OES and calculation. In the surface water samples with low ionic strength (< 1 mM), it was found that the acceptor activities were not yet in equilibrium after the standard 2 hours dialysis and, based on preliminary experiments (1–8 hours dialysis), a 4 hours dialysis time was selected. Hereafter, aliquots (150 μL) of donor and acceptor solution were taken and mixed with 850 μL water and 4 mL scintillation cocktail, and radioactivity (cpm) of these samples was determined by a beta-counter (Packard 1600CA, Wellesley, MA, USA). The free Ni^{2+} ion fraction was calculated as the ratio of the radio-activity in the acceptor solution to that in the donor solution.

Subsamples of 5 mL were taken from the donor solution before and after the Donnan dialysis and analysed by ICP-OES. The composition of the solution after dialysis was used as input for WHAM.

Helmke *et al.* [18] validated the Donnan dialysis by comparing experimental and predicted results of free ion activities of Cu, Cd and Zn in systems with ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and citrate. They observed a good agreement between the measured activities and those calculated by the computer models MINTEQA2 [19] and GEOCHEM-PC [20]. Here, we validated the Donnan dialysis with nitrilotriacetate (NTA) and Ni. The test solution consisted of 5 mM $\text{Ca}(\text{NO}_3)_2$, 10^{-6} M NTA, 10^{-7} M Ni, 3.6 mM MOPS and an amount of NaOH to adjust the solutions at 3 different pH values (6, 7 and 8). The predicted free Ni^{2+} ion fractions (with GEOCHEM-PC; $K_{\text{NiNTA}^+} = 12.8$, $K_{\text{NiNTA}_2} = 17$) are 12.7, 12.1 and 12.1 % at these pH values while observations were (standard deviation in brackets) 11.5 (0.3), 10.9 (0.2) and 8.3 (-) %.

At high pH values (pH >8), carbonates start to play a significant role in complexation. Calculations with the computer model GEOCHEM-PC, which uses the NIST (National Institute of Standards and Technology) parameters for Ni-carbonate complexes (stability constants at infinite dilution: $\log K = 4.57$ for NiCO_3 and 12.42 for NiHCO_3), showed that at pH>8 up to 10% of Ni can be complexed with carbonates. In order to check for the presence of carbonates in the acceptor solution, either through CO_2 absorption from air or because of diffusion of carbonate-species in the donor solution through the membrane, the inorganic carbon concentration of the acceptor solution was measured (Skalar Formacs^{HT} TOC Analyser, Breda, The Netherlands) after 4h equilibrating with a donor solution with pH 8 and 2.6 mM inorganic carbon. Less than 0.08 mM inorganic carbon was detected and it was

concluded that no correction for carbonate complexation in the acceptor solution was required.

Kinetics of Ni complexation

Two surface waters (Ankeveen and Markermeer) were spiked with stable Ni to 1.7×10^{-7} M and radioactive tracer (^{63}Ni). The waters were equilibrated for 1 hour, 2 days or 7 days, before speciation of Ni was determined with Donnan dialysis. The equilibration time of the Donnan dialysis in these experiments was 2 hours, i.e. the first measurements refer to 3 hours reaction between added Ni and DOM.

Determination of Ni speciation in six surface waters and in two waters with adjusted pH and hardness

The free Ni^{2+} ion fraction was measured in all water samples at 3 Ni concentrations: background concentration and concentrations in the range of 10d-EC10 (concentration at which the reproduction of 10% of the population is inhibited after 10 days) and 48h-LC50 (lethal concentration for 50% of the population after 48h) values of *Ceriodaphnia dubia*. These toxicity thresholds were derived from toxicity tests run on the same freshwater samples (De Schamphelaere *et al.*; unpublished data). Solutions were spiked with carrier-free ^{63}Ni . After 16 hours of equilibration, the speciation at background concentration was determined with Donnan dialysis. An aliquot of Ni stock solution was subsequently added to the same donor solution to increase the concentration of stable Ni to about the 10d-EC10 level and the solution was equilibrated for 10 minutes prior to Donnan analysis. Finally, Ni was again added to the same donor solution up to the 48h-LC50 level and speciation was again determined by dialysis, after 10 minutes of equilibration. The experiment on complexation kinetics revealed that 1h was sufficient for equilibration (see results), however for practical

reasons only 10 minutes was used because the Donnan dialysis itself takes 4h during which equilibration will be complete.

In order to determine the effect of pH and hardness, Ni speciation was also measured at four pH values (range 6.2–8.1) and four hardness levels for two surface waters (Ankeveen and Bihain). For Ankeveen, the pH level was first increased by adding NaOH 1 M, and then three times decreased by adding HCl 0.5 M until the target value was reached. The pH of Bihain was increased by adding NaOH 1M. Water hardness was increased by adding an aliquot of a Ca/Mg stock solution (0.4 M $\text{Ca}(\text{NO}_3)_2$ + 0.2 M MgCl_2). After adjustment of pH or hardness, the solutions were equilibrated for 10 minutes before Donnan dialysis.

Speciation modelling

The Ni speciation measurements were used to calibrate the parameters in WHAM VI [2,21] which describe binding of Ni to fulvic acid (FA). The stability constant of Ni with fulvic acid ($\log K_{\text{MA}}$), the binding parameter ΔLK_2 which determines the range of the binding strength of the bi- and tridentate sites, and the active fulvic acid fraction (%AFA) were optimized to get the best agreement between predicted and experimental speciation data. Details of the optimization method are given below.

Results

Ni speciation data

There was no consistent decrease of the free Ni^{2+} ion fraction when increasing the equilibration time between added Ni and DOM solutions from 1 hour to 7 days before the 2 hours lasting Donnan dialysis (Table 2), suggesting that the association reactions are complete within 3 hours. There was a small difference in the free Ni^{2+} fraction in the Ankeveen water

after 2 days equilibration, compared with the other equilibration times, but this difference could be ascribed to small drifts in pH values. It was concluded that an equilibration time of 1h prior to Donnan dialysis was sufficient for all further experiments.

The free Ni^{2+} ion fractions at background ranged from 4% to 45% (Table 3). Increasing Ni concentration increased the free Ni^{2+} fraction. Varying the pH level of the Ankeveen water from pH 8.1 to 6.5 increased the free Ni^{2+} ion fraction from 4.0 to 8.2% and increasing the water hardness from 112 to 396 $\text{mg CaCO}_3 \text{ L}^{-1}$ almost doubled the free ion fraction, from 6.5 to 12.5% (at pH 7.3). The pH sensitivity was relatively larger in the soft Bihain water with low DOM concentration; a 4-fold decrease in the free ion fraction – from 45% to 10% – was found when increasing the pH from 6.2 to 8.0. When water hardness was increased 6-fold (to 94 $\text{mg CaCO}_3 \text{ L}^{-1}$), the free Ni^{2+} ion fraction in the Bihain water increased from 44 to 71%.

Calibration of the WHAM model VI

The speciation code WHAM (Windermere Humic Aqueous Model) VI is based on the Humic Ion Binding Model VI [2]. This is a discrete site/electrostatic model for equilibrium ion binding by humic substances. The model has four metal-specific parameters: $\log K_{\text{MA}}$, $\log K_{\text{MB}}$, ΔLK_1 and ΔLK_2 . The $\log K_{\text{MA}}$ and $\log K_{\text{MB}}$ are median values of the log-transformed equilibrium constants that express binding strength of a given metal to carboxyl sites and weaker-acid sites, respectively. The parameter ΔLK_1 defines the spreading of values around these median constants. The parameter ΔLK_2 is an empirical parameter that increases the complexation constant of multi-dentate sites to provide for a greater range of binding strengths. Tipping [2] found a correlation between $\log K_{\text{MA}}$ and $\log K_{\text{MB}}$, that is incorporated in WHAM VI. Moreover, a universal average value of ΔLK_1 was obtained. As a result, the speciation data are fitted by the adjustment of only 2 parameters: $\log K_{\text{MA}}$ and ΔLK_2 .

As input for the speciation calculation, dissolved cations and anions were expressed in total concentration, except for Fe (III) and Al. In natural waters, Fe(III) and Al may occur as colloidal Fe(OH)₃ and Al(OH)₃. Since these colloids can easily pass 0.45 µm filters, this may result in measured values of ‘dissolved’ Fe and Al that are higher than the true ‘dissolved’ Fe and Al that can interact with DOC and other ligands. This could lead to an overestimation of the free Ni²⁺ ion fraction. Therefore, free ion activities of Fe³⁺ and Al³⁺ were used as input, if dissolved Fe and Al were presumably controlled by a solid phase, an approach that has been used in several studies, e.g. [11-12]. The free ion activity of Fe³⁺ is estimated from the solubility constant of colloidal Fe(OH)₃:

$$(\text{Fe}^{3+}) = K_{\text{sol,Fe(OH)}_3} \cdot 10^{-3 \cdot \text{pH}} \quad (1)$$

Reported log *K* values vary from 2 to 5, but in accordance with [21] we used a value of 2.5 (at 25° C) throughout the present study. The measured Fe concentrations were always well above the predicted (when assuming equilibrium with Fe(OH)₃) concentrations of dissolved Fe (i.e. Fe³⁺, Fe-DOC complex and inorganic Fe(III)-complexes) suggesting that colloidal Fe(OH)₃ was present in all waters. The Al³⁺ activity is estimated in the same way as Fe³⁺ activity, with log *K*_{sol,Al(OH)₃} = 8.5 (at 25°C) [2]. If the dissolved Al concentration predicted with WHAM VI (with estimated Al³⁺ activity as input) is higher than the measured Al concentration, indicating that there is no Al(OH)₃ controlled Al³⁺ activity, measured concentrations are used as input instead. This latter situation was the case for all water samples investigated.

For the input of organic matter in WHAM VI, dissolved organic matter was assumed to consist of a certain fraction of active fulvic acid and a fraction inert for ion binding, in line with the approach reported elsewhere [11,12]. We assumed that the organic matter consisted of fulvic acid, and not of humic acid, since fulvic acid is the more common humic substance

in natural surface waters. A typical distribution is 80% fulvic acid and 20% humic acid [22]. To convert DOC (g L^{-1}) to FA (g L^{-1}), the DOC concentration was multiplied by 2, assuming 50% carbon content of DOM [23]. In accordance to Bryan *et al.* [12] and Cheng *et al.* [11] we used 65% AFA as a starting value for the modelling. The FA_{input} (g L^{-1}) for running the model was thus obtained by $\text{DOC} \times 2 \times \% \text{AFA} / 100$.

In order to calibrate WHAM model VI to the speciation data of all natural waters (including those with adjusted Ni, hardness and pH, i.e. 33 data points), the parameters were optimized by minimizing the residual sum of squares (SSE):

$$\sum_{i=1}^{33} \left[\log(\% \text{Ni}^{2+}_{\text{observed}}) - \log(\% \text{Ni}^{2+}_{\text{predicted}}) \right]^2 \quad (2)$$

The values were transformed to log values to remove skewness. Selected default parameters of WHAM VI were modified (Table 4). For the inorganic metal complexation, the default stability constants of Ni-carbonate complexes were adapted to those of NIST. The default stability constant for the organic complex of fulvic acid with Zn was adjusted, based on the results of Cheng *et al.* [11]. These parameters were used for all speciation calculations.

Predicted values of the free Ni ion fractions largely overestimated the observed values if the default stability constant ($\log K_{\text{MA}}(\text{Ni})=1.4$) and default binding parameter ($\Delta \text{LK}_2=1.57$) were used for the prediction (Fig. 1a), i.e. binding of Ni to DOM is underestimated with the default parameters. Even when the %AFA fraction was increased from the starting value (65%) to 100%, or even to 200%, Ni complexation was still underestimated (Table 5). Increasing the binding constant 1.8-fold from its default value in WHAM VI to $\log K_{\text{MA}}(\text{Ni})=1.65$ yielded small residuals, however, the slope of regression line (0.69) for predicted versus observed log-transformed Ni^{2+} fractions was smaller than 1, indicating a bias in the predictions, i.e. the

smaller free Ni^{2+} ion fractions were still overestimated, while the reverse was true for the largest free Ni^{2+} fractions. This result suggests that site heterogeneity is underestimated. Site heterogeneity can be accounted for by increasing the ΔLK_2 parameter or by increasing the binding constant in combination with a reduction of the capacity of the fulvic acid. The best fit for the latter approach was obtained for $\log K_{\text{MA}}=1.75$ and 40 %AFA, which resulted in a small SSE and predicted/observed slope near unity (0.84). Alternatively, increasing the ΔLK_2 parameter to 2.35, while maintaining the default value for the stability constant ($\log K_{\text{MA}}=1.4$) and the generally assumed starting value of 65% for the capacity of the fulvic acid, yielded the smallest SSE and the slope of the log % free Ni^{2+} ion fraction and the median of the predicted/observed Ni^{2+} closest near unity, resp. 0.87 and 1.03 (Fig. 1b). This value for the ΔLK_2 parameter is the same as used for copper (2.34) in WHAM VI.

The solubility constant of $\text{Fe}(\text{OH})_3$ was also varied to assess if a change in this parameter value affected the predicted Ni speciation. A larger solubility constant of $\text{Fe}(\text{OH})_3$ increases the Fe^{3+} activity and Fe(III)-DOM concentration, thus reducing the available Ni binding sites, an ion competition effect that becomes important at small DOM concentrations. However, neither the slope of the predicted/observed line nor the SSE were strongly affected by changing the solubility constant of $\text{Fe}(\text{OH})_3$ in the range $\log K_{\text{sol}} = 2$ to 5 and the best fit was still obtained with the same adjustable parameter values as when a value of 2.5 was used for $\log K_{\text{sol}}$.

A sensitivity analysis was performed for the waters Ankeveen and Brisy, to assess how much the predicted Ni speciation is affected by a change in parameters values (Fig. 2). The surface water Ankeveen has a relatively high DOC concentration (23.6 mg L^{-1}) and average water hardness ($112 \text{ mg CaCO}_3 \text{ L}^{-1}$). Brisy has a relatively low DOC concentration (3.06 mg L^{-1}) and a low hardness ($41 \text{ mg CaCO}_3 \text{ L}^{-1}$). The starting values of the parameters (relative change

= 1) are the values of the best fit ($\log K_{MA}(\text{Ni})=1.4$, $\%AFA=65$, $\Delta LK_2=2.35$). Varying the value of ΔLK_2 dramatically changes the predicted free Ni^{2+} fraction. A 2-fold increase or decrease in $\%AFA$ or in the stability constant for Ni complexation with fulvic acid strongly affects the predicted free Ni^{2+} fraction, although to a lesser degree than a change in ΔLK_2 . This effect is more pronounced for Brisby, the water with low DOC concentration and hardness.

Discussion

The free Ni^{2+} fraction, as measured by Donnan dialysis, varied > 10-fold depending on water characteristics, suggesting that Ni bioavailability largely varies among waters. These measured free ion fractions are assumed to represent the equilibrium speciation, since it is unlikely that dissociation kinetics controlled our speciation results, notwithstanding the relatively slow dissociation kinetics of Ni-DOM complexes [6]. This assumption can be taken because the volume of the acceptor solution is about 0.2% of that of the donor solution, and therefore, only ~0.2% of the free metal ion present in the donor solution is sampled during Donnan dialysis, thereby minimizing disturbance of the equilibrium composition.

All our data refer to speciation of Ni that is added to the water. One may argue that some Ni present in the water may have a stronger complexation than Ni added to the system and that the Ni already present in the system does not fully exchange with the ^{63}Ni added. The isotope exchangeability of Ni has been measured in filtered soil extracts by means of the DMT (Nolan and McLaughlin, personal communication). They found Ni to be fully isotopically exchangeable in 11 out of 13 soil extracts and for 86-90% exchangeable in the two other

extracts. These data suggest that our data obtained on speciation of added Ni is very close to that of Ni present in most natural systems.

It was found that WHAM VI largely underestimates Ni complexation by DOM when using the default parameters. A possible explanation is that the total binding capacity of DOM in the surface water is larger than the binding capacity in WHAM VI when 100% of the DOM is assumed to be fulvic acid. Cheng *et al.* [11] had to assume a fulvic acid capacity equivalent to 1.7 times the default value in order to fit measured Zn complexation data, when using the default stability constant for Zn-DOM binding. In this study, the free Ni^{2+} fractions were still overpredicted when assuming a capacity of 2 times the default value. The total binding capacity of DOM of standard humic acid, fulvic acid and natural organic matter samples, as estimated by pH titration (pH 3–11), varies from 8.5 to 17 $\text{meq g}^{-1} \text{C}$ [23]. The default capacity of fulvic acid in the WHAM model is 7.2 $\text{meq g}^{-1} \text{FA}$ (or 14.4 $\text{meq g}^{-1} \text{C}$). Therefore, a DOM site capacity that is more than 2 times the default value of FA is well beyond the range found by pH titration [23]. More likely, the Ni binding parameters in DOM underestimate Ni complexation in freshwaters. However, a bias in the predictions was obtained when merely increasing the Ni complexation constant (K_{MA}). The lowest free Ni^{2+} ion fractions are still overestimated, suggesting that site heterogeneity was not sufficiently accounted for. A better, less biased, fit was obtained when increasing K_{MA} to 1.75 and decreasing the AFA to 40% simultaneously, which resulted in an estimated capacity of 2.9 $\text{meq g}^{-1} \text{DOM}$ or 5.8 $\text{meq g}^{-1} \text{C}$ (40% AFA, 60% inert). This value is small compared with the range (8.5 to 17 $\text{meq g}^{-1} \text{C}$) reported for standard samples [23].

Another approach to increase the predicted Ni binding at small Ni concentrations only, is by using a larger value for ΔLK_2 , which is an empirical parameter that increases the binding strengths of a small number of (multi-dentate) sites. Eventually, maintaining the default value

of the binding constant K_{MA} and increasing the value of ΔLK_2 gave the best fit of all. Changing the value for ΔLK_2 is acceptable, since the default value in WHAM VI was not derived by applying WHAM VI on experimental data and optimizing ΔLK_2 . Instead, because of a lack of data, ΔLK_2 for Ni was derived from a linear regression equation that relates ΔLK_2 to the NH_3 complexation constant for six other metals not including Ni [2]. Revisiting this regression equation reveals the large uncertainty in the (default) ΔLK_2 value (1.57) for Ni, and the best-fit value obtained in this study ($\Delta LK_2 = 2.35$) is within the 95% confidence interval (0.28–2.86) of the regression. Moreover, the data of Higgs *et al.* [3] suggest an uncertainty in the value of $\log K_{MA}$ of about 0.1 log units, and using a value of 1.5 (rather than 1.4) for $\log K_{MA}$ yields a best-fit value of 2.2 for ΔLK_2 , i.e. a value that is closer to the default value in WHAM VI (details not shown).

We used our best fit parameters to fit measured free Ni^{2+} fractions reported in other studies [4-7]. We found an improved prediction, compared to the prediction based on the default parameters in WHAM VI for the data of Christensen and Christensen [4] (details not shown). However, complexation of Ni by DOM was still underestimated for the data of Weng *et al.*, who measured Ni speciation in soil solution of acid soils [5]. Values for the free Ni^{2+} fraction predicted by WHAM VI, using our best fit parameters, ranged from 90 to 100%, and were larger than the measured values (range 3–98%). Although our parameters gave a better prediction, there was still a large difference between the observed and predicted values for the samples with a low observed free Ni^{2+} ion fraction. Recent data of Ni speciation in freshwater obtained with a field DMT [7] are also better approximated with our best fit parameters than based on default parameters. Data of 3 freshwater ranged 3-4% free Ni^{2+} [7]. Model predictions with WHAM VI with the default values and 100% of DOC as fulvic acid overestimated these free Ni^{2+} ion fractions 12-18-fold [24]. A prediction with our best fit

parameters ($\log K_{MA}(Ni)=1.4$, $\%AFA=65$, $\Delta LK_2=2.35$) yielded 2-7.5% for two waters whereas we also overestimated the fraction free Ni^{2+} 9-fold for the third water which only contained 1.9 mg L^{-1} DOC.

The Ni speciation data obtained by a competing ligand method in freshwater samples by Xue *et al.* [6] yielded extremely low values free Ni^{2+} ion fraction ($<0.1\%$) that largely differ from the predictions with WHAM VI, using either the default or our best-fit parameters. As explained in the introduction of this paper, it appears that this discrepancy is related to the speciation methods since data obtained on the same water varied 10^4 -fold between methods. The data of free Ni^{2+} ion fraction obtained by the competing ligand method directly rely on the value of conditional stability constant of Ni with the competing ligand DMG. Based on ligand-exchange with Ni-EDTA, the authors calculated a stability constant ($\log K_{Ni(DMG)_2}$) of 22.9 and this value is 5 orders of magnitude above the value reported by Martell & Smith [25] ($\log K=17.8$). Their titration curves of the natural water samples with DMG showed that addition of $\sim 10^{-4} \text{ M}$ DMG was necessary for complete complexation of Ni by DMG. However, calculations of WHAM VI for the groundwater GW1 in Glattfelden (from the study of Xue *et al.* [6]) using the same stability constant for $Ni(DMG)_2$ ($\log K=22.9$), indicated that 10^{-6} M DMG should be sufficient to complex all Ni. Moreover, when using the stability constant reported by Martell and Smith [25] ($\log K = 17.8$), the predicted titration curve by our best fit model corresponded quite well with these reported by Xue *et al.* [6]. This reanalysis suggests that the conditional stability constant for $Ni(DMG)_2$ was overestimated by Xue *et al.* [6], which may explain the extremely small free Ni^{2+} ion fractions and the large stability constants for Ni complexation with natural ligands ($\log K_{NiL}=12.1-14.6$) that were derived in their study. Based on a different reasoning, van Leeuwen and Town [26] also concluded that complexation of Ni with natural ligands was likely overestimated in ref. [6] and other studies that used CLE-AdSV. They showed theoretically that the reported stability

426 constants for Ni complexation with natural ligands were likely overestimated because no
427 equilibrium was attained within the experimental time.

428

429 **Acknowledgement**

430 This work was funded by the Nickel Producers Environmental Research Association
431 (NiPERA). Karel De Schamphelaere is supported by a post-doctoral fellowship from the Fund
432 for Scientific Research – Flanders (FWO-Vlaanderen, Belgium).

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Figure captions

Figure 1

Comparison between predicted and observed free Ni^{2+} fractions. The predictions were made with the WHAM VI model using the default parameter values (a), or optimized parameter values (b) for the stability constant $\log K_{\text{MA}}$, the active fulvic acid fraction (AFA) and the binding parameter ΔLK_2 . The solid line represents the 1:1 line and the dotted line the regression line.

Figure 2

Sensitivity analysis of predicted Ni speciation for the surface waters Ankeveen and Brisy at their background Ni concentration. The parameter values were varied independently between 0.5 and 2.5 times the starting values. The starting values (Relative parameter change = 1) are the parameter values of the best fit shown in Fig. 1b.