Water in Celtic Countries: Quantity, Quality and Climate Variability (Proceedings of the Fourth InterCeltic Colloquium on Hydrology and Management of Water Resources, Guimarães, Portugal, July 2005).
IAHS Publ. 310, 2007.

113

Aluminium contents in drinking water from public water supplies of Galicia (northwest Spain)

DAVID A. RUBINOS[1], MANUEL ARIAS[2], CARLOS AYMERICH[3] & FRANCISCO DÍAZ-FIERROS[1]

1 *Dpto. Edafoloxía e Química Agrícola, Facultade de Farmacia, Universidade de Santiago de Compostela, ES-15785 Santiago de Compostela, Spain*
edrubi@usc.es

2 *Dpto. Bioloxía Vexetal e Ciencias do Solo, Facultade de Ciencias, Campus Ourense, Universidade de Vigo, Spain*

3 *Espina y Delfín, S. L. Polígono do Tambre, Santiago de Compostela, Spain*

Abstract Aluminium (Al) salts are used extensively as coagulants in drinking water treatment. Since several research works have linked Al levels in drinking water to elevated risks of Alzheimers disease, we have studied the Al content in drinking water from populations in Galicia (NW Spain). Drinking water from 35 cities and villages in Galicia were analysed for dissolved Al and other relevant parameters (pH, turbidity, sulphate, fluoride and DOM) for the period 1997–2003. The results obtained showed an average aluminium content of 126 $\mu g\ L^{-1}$, but the variability was high, with Al levels ranging from 8 to 650 $\mu g\ L^{-1}$. Of the waters studied, 19% and 34% contained Al above 0.2 and 0.1 mg L^{-1}, respectively. Speciation studies performed using the WHAM computer model showed that most dissolved Al was DOM-complexed, although some waters contained significant amounts of labile Al, mainly as hydroxo and fluoride complexes.

Key words aluminium; Alzheimer's disease; drinking water; speciation; WHAM

INTRODUCTION

Aluminium (Al) is the third-most-common element in the Earth's crust and is present in all natural waters. In addition, Al salts such as Al sulphate (alum) or polyaluminium chloride (PACl) are used extensively as coagulants in drinking water treatment to enhance the removal of particulate, colloidal and dissolved substances. Al-based coagulants have come under scrutiny in recent years due to concerns about metal residuals in the public water supply. The presence of Al in drinking water has given rise to discussion on possible health effects, because of its suspected connection with Alzheimers disease or dialysis encephalopathy (Jekel, 1991). In response, various regulations have been promulgated by several agencies, including the European Union and World Health Organisation, who have established a threshold value of 200 $\mu g\ L^{-1}$ Al for drinking water.

Epidemiological studies have suggested a link between an increase in the incidence of Alzheimers disease in regions where the levels of Al in drinking water are high (Forbes & McLachlan, 1996; Rondeau *et al.*, 2000). It has been shown that other water parameters, especially water pH, turbidity and concentration of Ca, Si, fluoride and dissolved organic matter (DOM) affects the solubility behaviour and the absorption of Al in the gastrointestinal tract. A complete review about Al exposure and Alzheimer's disease can be found in Jansson (2001) and Suay & Ballester (2002).

In addition to health effects, water supply problems associated with increased Al concentration in treated water have been identified; these include increase of turbidity (Costello, 1984), interference with the disinfection process (Hoff, 1974) and deposition of Al hydrolysis products on pipe walls, which decreases carrying capacity (Costello, 1984).

The toxicity of Al is highly dependent on its speciation ("free" and complexed Al) and mobility (Masion *et al.*, 2000). Total Al is the sum of suspended, colloidal and monomeric forms of Al. Particulate Al is the sum of suspended and colloidal Al. Monomeric Al can be divided into two forms: non-labile, and labile. Non-labile Al is Al associated with dissolved organic carbon. Labile Al includes aqueous (Al^{3+}), and hydroxide, fluoride and sulphate complexes of Al (Srinivasan *et al.*, 1999). The soluble Al, as defined by filtration through 0.45 μm or 0.1 μm membrane filters, includes free Al^{+3} [$Al(H_2O)_6^{3+}$] ion, monomeric inorganic complexes (mainly with OH^- and F^-), fine colloidal mineral Al, and Al associated with the dissolved organic matter (DOM). The organic complexes of Al are less toxic than free Al^{3+} ion and the monomeric complexes (Weng *et al.*, 2002).

Galicia is a region located in the NW of Spain. Soils are usually acid and rich in Al and organic matter. Surface waters in Galicia present pH values ranging from 7.9 to 5.2 (average pH value 7.1 for coast-Galicia and 6.9 for inner-Galicia) (Antelo & Arce, 1996). Alzheimer's disease incidence in Galicia has been reported to be high. This paper reports data for Al concentration and other related parameters in treated potable waters in Galicia supplied by Espina y Delfín, S. L. The data reported were obtained from a drinking water quality monitoring programme carried out between 1997 and 2003 for several populations in Galicia. The main objective of this work was to study the Al levels in drinking waters from public water supplies, considering its geographical distribution, Al speciation, and complexation by inorganic and organic ligands.

MATERIALS AND METHODS

Drinking water from 35 cities and villages in Galicia were collected over a five-year period, between November 1997 and December 2002 (Fig. 1). A total of 68 waters were sampled and analysed for Al and other relevant parameters (pH, temperature, turbidity, calcium, silica, fluoride, sulphate, phosphate and DOM). Variations of analysed parameters for the period studied were monitored on selected populations, based on number of habitants criteria. The waters were sampled from domestic and public utilities using sterilized acid washed polypropylene sampling bottles and conserved in the dark at 4ºC before analysis. Water samples were filtered (Millipore 0.45 μm cellulose acetate filters). Samples were acidified at pH<1 using concentrated HNO_3 (Merck Suprapur™). Al analyses were performed using graphite furnace atomic absorption spectrometry (GFAAS), employing pyrolytically coated graphite tubes and background correction (Perkin-Elmer). Argon was employed as the purge gas. Al standards were prepared by dilution with MilliQ^PLUS water (exceeding 18 M resistivity) of a commercial Al solution (1000 mg L^{-1} Al).

The detection and quantification limits (Gundersen & Steinnes, 2003) calculated for these conditions were 5 μg L^{-1} and 15 μg L^{-1} Al, respectively. pH was measured *in*
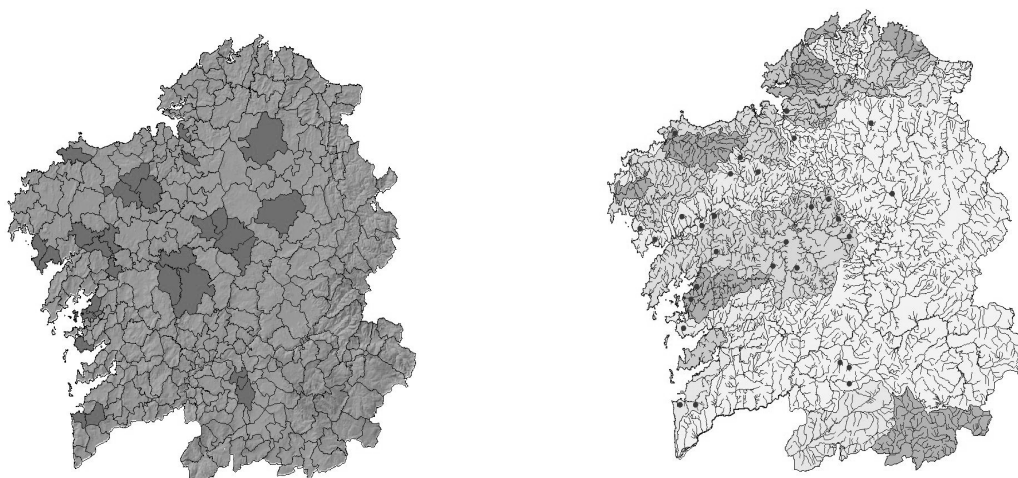
Fig. 1 Sampling points (Councils supplied by Espina y Delfín, S.L) and river basins in Galicia (NW Spain).

situ with a portable pH-meter. Dissolved organic carbon (DOC) content was measured with a fully automated TOC analyzer. Turbidity, in NTU, was measured in unfiltered samples using a turbidimeter. The concentrations of Ca and Si were measured by atomic absorption spectrometry (AAS). Fluoride concentrations were measured using a fluoride ion selective electrode. Sulphate was determined by the $AgNO_3$ method. It must be noted that Espina y Delfín, S.L uses polyAluminium chloride as the coagulant agent for treatment of drinking waters.

RESULTS AND DISCUSSION

All the waters analysed, except one, contained Al above the quantification limit. It represents a 98.5% frequency of detection of Al. This is not surprising, considering that soils in Galicia are Al-rich. Figure 2 shows the concentrations of Al for the populations studied, expressed as the ratio between determined Al concentration and MCL (0.2 mg L^{-1}). The results obtained showed an average Al content in treated waters of 126 µg L^{-1}, but the variability was high, with Al levels ranged from 8 to 650 µg L^{-1}.

The 19% of waters analysed contained Al concentrations above the maximum concentration level of 0.2 mg L^{-1}, whereas 34% of waters contained Al above 0.1 mg L^{-1}. The data presented in Table 1 are a summary of the results obtained for waters containing Al concentrations above 0.2 mg L^{-1}, also, as a comparison, the results for water containing the lowest Al concentration and for water containing an intermediate Al concentration are included.

When considering geographical distribution, following the criteria of Antelo & Arce (1996), we observed that, in general, the waters corresponding to Coast-Galicia basins contained more Al (mean = 0.154 mg L^{-1}, % waters with Al > 0.2 mg L^{-1} = 20.5%; $n = 44$) than the waters corresponding to Inner-Galicia basins (mean = 0.075 mg L^{-1}, % waters with Al > 0.2 mg L^{-1} = 8.3%; $n = 24$). Also, when excluding waters containing Al > 0.2 mg L^{-1}, an Al baseline average value for drinking waters of

66 µg L^{-1} can be established, which was near the mean Al concentration of 74 µg L^{-1} reported by Bodek *et al.* (1988) for US surface waters. It must be stated that in the present study all the waters containing Al concentrations above 0.2 mg L^{-1} were treated with Al-based coagulants.

When studying time dependency of Al concentrations for selected populations it was observed that Al concentrations increased for the period November 2000– November 2001. Various factors are capable of introducing a time dependency into the
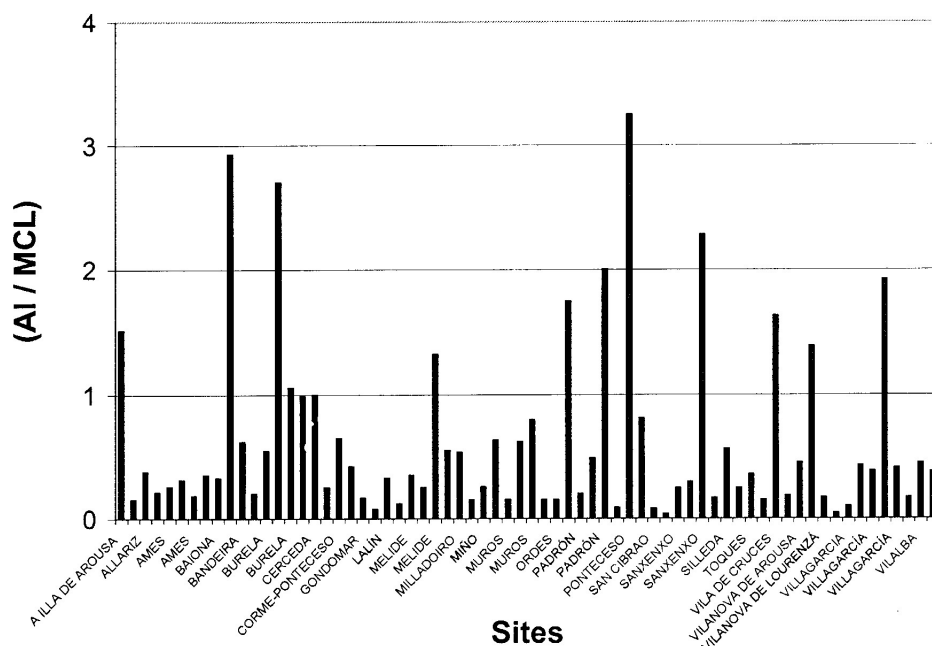
Fig. 2 Concentration of dissolved Aluminium, expressed as a ratio between Al and MCL (0.2 mg L^{-1}), for the studied drinking waters.

Table 1 pH, turbidity, temperature, dissolved Al, DOC, sulphate, calcium, fluoride and silica concentrations for selected drinking waters.

Site	pH	Turbidity (NTU)	T (ºC)	Al (mg L^{-1})	DOC (mg L^{-1})	Sulfate (mg L^{-1})	Calcium (mg L^{-1})	Fluoride (mg L^{-1})	Silica (mg L^{-1})
Burela	5.3	2.61	15	0.541	5.23	6.6	1.4	<0.05	4.5
Ponteceso	6.0	0.57	20	0.650	5.39	3.9	1.8	<0.05	4.7
Padrón	6.4	0.83	22	0.401	7.14	8.8	4.2	<0.05	8.1
Vilanova	6.8	0.68	23	0.278	6.71	3.2	2.8	<0.05	12.6
A Illa	6.7	0.67	24	0.303	7.13	5.2	3.4	<0.05	8.1
Ordes	6.5	1.31	18	0.350	6.27	5.5	4.5	<0.05	7.1
Melide	6.7	0.74	20	0.265	7.41	1.9	3.4	<0.05	9.6
Baiona	6.2	0.68	16	0.586	2.59	0.6	0.9	<0.05	6.1
Sanxenxo	6.5	0.60	15	0.456	2.18	1.5	3.0	<0.05	4.2
Vilagarcía	6.7	0.73	15	0.384	1.95	1.4	2.2	<0.05	6.0
Cerceda	6.3	0.58	19	0.200	1.99	45.9	11.6	<0.05	6.7
Cruces	5.6		12	0.327	1.30			<0.05	
Burela 2	6.0		12	0.211	1.70			<0.05	
San Cibrao	7.0	0.21	14	0.008	0.50	13.2	14.1	<0.05	2.4
Muros	7.4	1.00	17	0.124	4.60	4.0	3.1	<0.05	2.1

water quality parameters and may include some combination of climatic, land management and hydrological factors. The trends observed in this study can be explained considering that the addition of Al-based coagulants to waters, and the concentration employed, was intermittent, and it was mainly a function of turbidity of raw water, which in turn depended on rainfall amount. Since the total rainfall averaged for 2001 was higher, the use of Al-based coagulants to treat waters was more intense for that period, resulting in the higher Al residual concentrations detected. Reid *et al.* (2003) observed a relationship between total rainfall and failure rate for quality parameters of waters from Scotland. Measured dissolved Al concentrations in studied waters were not correlated with Al concentrations in soils.

Temperature, pH and turbidity of the water are important factors in determining Al solubility, and consequently residual Al (Srinivasan *et al.*, 1999). Al is soluble at acidic (pH < 6) and alkaline (pH > 6) conditions, but is insoluble at near neutral pH values (7.0 to 7.5). Figure 3 shows the dissolved Al concentrations *vs* measured pH. Although a low inverse relationship was observed, it can be seen that all the waters containing Al above 0.2 mg L^{-1} presented pH values below 7, and the waters with the highest Al content (above 0.5 mg L^{-1}) presented pH values below 6. When the comparison was made, including only the waters with Al concentrations above 0.1 mg L^{-1} or 0.2 mg L^{-1}, we observed an inverse relationship between dissolved Al concentration and pH ($R^2 = 0.398$ and $R^2 = 0.879$). This can be explained by the fact that some waters (presenting low pH) included in the first data analysis were not treated with Al-based coagulants. Jekel (1991) reported a correlation between residual Al and effluent turbidity, observing residual Al concentrations less than 0.1 mg L^{-1} when the effluent turbidity was less than 0.15 NTU. We did not obtain such a relationship for our data, but specifically, all waters containing >0.1 mg L^{-1} dissolved Al presented turbidity above 0.50 NTU, and all waters with turbidity below 0.5 NTU contained dissolved Al concentrations below 0.1 mg L^{-1}.

Speciation plays an important role in Aluminium toxicity, since the organic complexes of Al are less toxic than free Al^{+3} ion and the monomeric complexes. Researchers often rely on models to calculate speciation (Weng *et al.*, 2002). Tipping *et al.* (1995) used the WHAM chemical equilibrium model to calculate the solid-
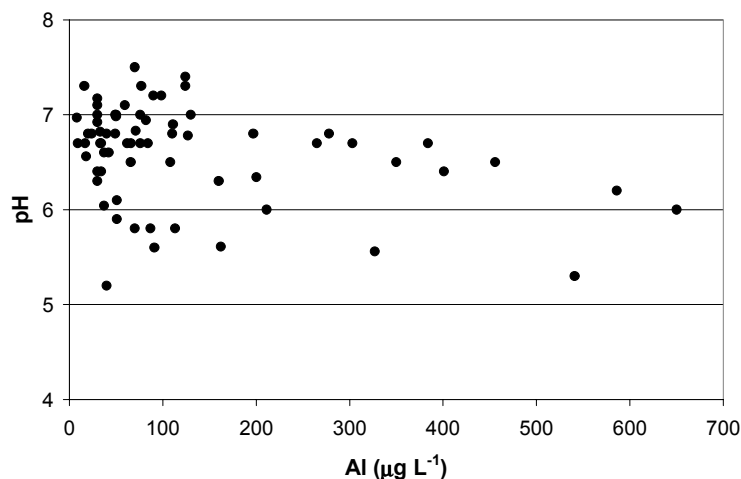

Fig. 3 Dissolved Al (μg L^{-1}) measured for drinking waters sampled *vs* measured pH.

Table 2 Aluminium complexed by dissolved organic matter (DOM) calculated using the WHAM model (Tipping, 1994) for selected drinking waters. Fractional distribution (% of labile Al) of inorganic Al species is also shown.

Site	Al-DOM	$Al(OH)_2^+$	$Al(OH)_4^-$	Al^{3+}	AlF^{2+}	AlF_2^+	AlF_3	$AlOH^{2+}$	$AlSO_4^+$
Burela	75.06	8.13	0.10	13.65	55.25	9.97	0.05	11.96	0.87
Ponteceso	98.04	43.74	23.22	1.54	15.16	6.83	0.09	9.36	0.06
Padrón	98.01	18.69	78.67	0.08	0.79	0.37	0.01	1.38	0.01
Vilanova	93.61	3.25	96.63	<0.01	0.02	0.01	<0.01	0.09	<0.01
A Illa	95.02	4.54	95.26	<0.01	0.04	0.02	<0.01	0.15	<0.01
Ordes	51.60	18.72	78.84	0.07	0.71	0.31	<0.01	1.35	0.01
Melide	96.82	6.95	92.61	0.01	0.10	0.04	<0.01	0.29	<0.01
Baiona	68.56	42.67	37.43	0.78	8.44	3.94	0.05	6.69	0.01
Sanxenxo	96.42	24.07	71.20	0.16	1.61	0.73	0.01	2.22	<0.01
Vilagarcía	94.29	11.72	87.11	0.03	0.31	0.14	<0.01	0.68	<0.01
Cerceda	94.54	28.50	64.52	0.27	2.44	1.03	0.01	3.13	0.09
Cruces	63.53	9.41	0.26	5.72	54.29	21.57	0.25	8.50	<0.01
Burela	93.14	32.30	6.66	3.29	32.00	13.70	0.18	11.65	0.21
San Cibrao	62.49	4.18	95.62	<0.01	0.04	0.02	<0.01	0.15	<0.01
Muros	81.67	0.42	99.57	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

solution distribution of Al. Christensen & Christensen (2000) successfully described the complexation of heavy metals by DOC in aqueous solutions at varying pH values and DOC concentrations using the WHAM model. The WHAM model (Tipping, 1994) is a combination of several sub-models. These include models for inorganic solution speciation and a humic metal ion binding model called Model V (Tipping & Hurley, 1992). Model V is a discrete-site adsorption model and includes electrostatic and competitive effects. In the present work it was assumed that 30% of DOM behaves as humic acid, 30% as fulvic acid, and 40% is inert in metal adsorption (Weng *et al.*, 2002). Table 2 shows the Al speciation calculated using the WHAM model. Most Al (between 51.6 and 98.05%) was associated with DOM (i.e. non-labile Al).

In general, the labile (inorganic) Al amounts were low, although for some waters significant amounts of labile Al were observed (ranging from 0.022 to 1.030 μmol L^{-1}). The main inorganic species were hydroxo-Al complexes, but for waters with acidic pH (pH < 6) Al was predominantly complexed with fluoride. It has been reported that at acidic pH (pH = 5.8) complexation reactions between Al and F are quite efficient (Roberson & Hem, 1969).

Since the waters studied present different pH values and they contain diverse concentrations of Al, DOM and other complexing ligands, the speciation calculated can not be explained by considering only one water factor. Multivariable correlation analysis showed that labile Al concentrations in the treated waters were related to pH, DOM and dissolved Al concentration ($R^2 = 0.703$).

REFERENCES

Antelo, J. M. & Arce, F. (1996) Características fisicoquímicas das augas superficiais. In: *As Augas de Galicia*, 351–423. Consello da Cultura Galega, A Coruña, Spain.

Bodek, I., Lyman, J. W. & Rosenblatt, D. H. (1988) *Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods.* Pergamon Press, Elmsford, NY, USA.

Christensen, J. B. & Christensen, T. H. (2000) The effect of pH on the complexation of Cd, Ni and Zn by dissolved organic carbon from leachate-polluted groundwater. *Water Res.* **34** (15), 3743–3754.

Costello, J. J. (1984) Post precipitation in distribution systems. *J. Am. Water Works Assoc.* **76**(11), 46–49.

Forbes, W. F. & McLachlan, D. R. C. (1996) Further thoughts on the Aluminium–Alzheimer's disease link. *J. Epidemiol. Commun. Health.* **50**, 401–403.

Gundersen, P. & Steinnes, E. (2003) Influence of pH and TOC concentration on Cu, Zn, Cd, and Al speciation in rivers. *Water Res.* **37**(2), 307–318.

Hoff, J. C. (1977) The relationship of turbidity to disinfection of potable water. In: *Conf. On the Evaluation of Microbiol. Standards for Drinking Water*. US Environmental Protection Agency, Office of Water Supply, Washington, DC, USA.

Jansson, E. T. (2001) Aluminium exposure and Alzheimer's disease. *J. Alzheimer's Disease* **3**, 541–549.

Jekel, M. (1991) Aluminium in water: How it can be removed? Use of Aluminium salts in treatment. *Proc. Int. Water Supply Assoc.* (25–31 May, Copenhagen, Denmark).

Masion, A., Vilgé-Ritter, A., Rose, J., Stone, W. E. E., Teppen, B. J., Rybacki, D. & Bottero, J. Y. (2000) Coagulation – Flocculation of natural organic matter with Al salts: speciation and structure of the aggregates. *Environ. Sci. Technol.* **34**, 3242–3246.

Reid, D. C., Edwards, A. C., Cooper, D., Wilson, E. & McGaw, B. (2003) The quality of drinking water from private water supplies in Aberdeenshire, UK. *Water Res.* **37**(2), 245–254.

Roberson, C. E. & Hem, J. D. (1969) Solubility of Aluminium in the presence of hydroxide, fluoride and sulfate. *US Geol. Survey Water Supply, Paper 1827-C*.

Rondeau, V., Commenges, D., Jacqmin-Gadda, H. & Dartigues, J. F. (2000) Relation between Aluminium concentrations in drinking water and Alzheimer's disease: a 1-year follow-up study. *Am. J. Epidemiol.* **152**(1), 59–66.

Srinivasan, P. T., Viraghavan, T. & Subramanian, K. S. (1999) Aluminium in drinking water: an overview. *Water SA.* **25**(1), 47–55.

Suay, L. & Ballester, F. (2002) Revisión de los estudios sobre exposición al aluminio y enfermedad de Alzheimer. *Rev. Espa. Salud Pública*. **76**, 645–658.

Tipping, E. & Hurley, M. A. (1992) A unifying model of cation binding by humic substances. *Geochim. et Cosmochim. Acta*. **56**, 3627–3641.

Tipping, E. (1994) WHAM—a chemical equilibrium model and computer code for waters, sediments and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Computers & Geosci.* **20**, 973–1023.

Tipping, E., Berggren, D., Mulder, J. & Woof, C. (1995) Modelling the solid-solution distribution of protons, aluminium, base cations and humic substances in acid soils. *Eur. J. Soil Sci.* **46**, 77–94.

Weng, L., Temminghoff, J. M. & Van Riemsdijk. (2002) Aluminium speciation in natural waters: measurement using Donnan membrane technique and modeling using NICA-Donnan. *Water Res.* **36**(17), 4215–4226.