

Al nanoclusters in coagulants and granulates: application in arsenic removal from water

Jasmin Mertens

Published online: 13 May 2011
© Springer Science+Business Media B.V. 2011

Abstract The contamination of drinking and irrigation water by arsenic is a severe health risk to millions of people, particularly in developing countries. Arsenic treatment methods therefore need to advance to more durable and cost-effective solutions. In recent years, the unique properties of nanomaterials have received much attention in water treatment research, and their properties (e.g., high number of reactive surface binding sites) may make them suitable for arsenic removal. The aluminum nanoclusters Al_{13} ($\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}\text{H}_2\text{O}_{12}^{7+}$) and Al_{30} ($\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}$) have high specific surface charge, deprotonate over a wide pH range and exhibit a high reactivity due to a great number of OH^- and H_2O groups. This contribution evaluates these chemical properties of aluminum nanoclusters and their efficiency for water treatment, particularly for arsenic removal. It assesses the advantages and constraints when applied in an industrially produced aluminum coagulant or in Al granulate during water treatment.

Keywords Arsenic · Water treatment · Al nanoclusters · Al_{13} · Al_{30}

1 Introduction

The abundance of the carcinogenic arsenic in drinking and irrigation water is a severe and widespread health threat to more than 100 million people worldwide, especially in South and Southeast Asia (Charlet and Polya 2006; Winkel et al. 2008). Arsenic enters groundwater either naturally by dissolution of arsenic-bearing minerals or by anthropogenic sources such as mining industry or metal processing plants. Arsenic in natural waters is mostly present in inorganic form as trivalent arsenide (As(III)) under reducing conditions or as pentavalent arsenate (As(V)) under oxidizing conditions (Smedley and Kinniburgh 2002).

For arsenic treatment technologies to become a realistic option for more people, new developments need to address the challenges of reducing both treatment costs and waste generation while simultaneously enhancing durability and efficiency. Recently, inorganic nanoparticles have received increasing interest as removal agents for arsenic from water due to their high surface area-to-mass ratio, chemical properties and high surface reactivity (Auffan et al. 2009). Nanoparticles are added to water as powder or are incorporated in conventional remediation methods to increase their efficiency, e.g. in membranes or polymers (Nilchi et al. 2011; Theron et al. 2008).

Polyaluminum chloride (PACl) is a coagulant widely used in water remediation. It generally consists of Al species such as $[\text{Al}_2(\text{OH})_2]^{4+}$, $[\text{Al}_3(\text{OH})_4]^{5+}$, $[\text{Al}_8(\text{OH})_{20}]^{4+}$ and $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}\text{H}_2\text{O}_{12}]^{7+}$ (Fan

J. Mertens (✉)
Institute of Biogeochemistry and Pollutant Dynamics
(IBP) ETH Zürich, Universitätsstrasse 16, 8092 Zürich,
Switzerland
e-mail: jasmin.mertens@env.ethz.ch

et al. 2003). Commercial polyaluminum coagulant forms large Al nanoclusters when produced with high total Al concentrations at high temperatures for a long time (Chen et al. 2006). A high content of nanosized aluminum clusters may increase the efficiency and reduce the costs of arsenic treatment.

Two main robust aluminum nanoclusters exist in aqueous PACl solutions: Al_{13} ($\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}\text{H}_2\text{O}_{12}^{7+}$) and Al_{30} ($\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}$) are the largest aqueous aluminum hydroxide complexes with 1 nm diameter and 1–2 nm length. Al_{13} is a cluster of four Al trimers placed around one tetrahedral coordinated aluminum atom. Al_{30} was characterized by ^{27}Al nuclear magnetic resonance (NMR) to be composed of two Al_{13} clusters connected to each other by four $\text{Al}(\text{O})_6$ octahedra (Allouche et al. 2000) (Fig. 1). These Al nano complexes stand out due to their high specific surface charge (+7 for Al_{13} and +18 for Al_{30}), deprotonation over a wide pH range (Furrer et al. 1992; Casey et al. 2005), and high specific surface area depending on pH and $[\text{OH}^-]/[\text{Al}]$ ratio (Bottero and Bersillon 1988). In addition, Al_{13} and Al_{30} exhibit a high reactivity due to a great number of hydroxide ions and water groups. The presence of Al_{30} in polyaluminum coagulants enhances turbidity due to strong floc formation (Chen et al. 2006). These characteristics make Al nanoclusters promising removal agents, but the extent to which Al_{13} and Al_{30} bind arsenic is poorly known. This

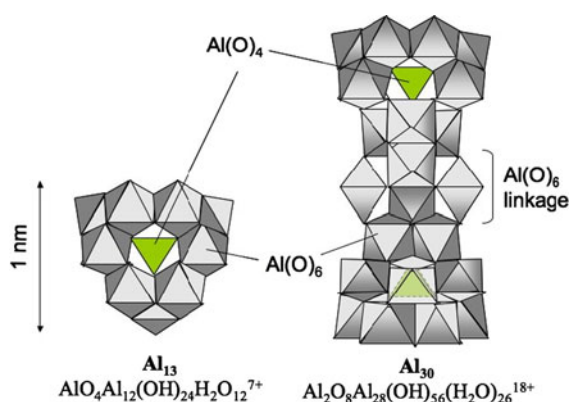


Fig. 1 Structure of Al_{13} ($\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}\text{H}_2\text{O}_{12}^{7+}$) and Al_{30} ($\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+}$): Al_{13} is composed of a tetrahedral coordinated aluminum ($\text{Al}(\text{O})_4$) surrounded by four trimers of octahedral Al. Al_{30} is composed by two Al_{13} Keggin, linked by a group of four octahedral coordinated Al (adapted after Casey et al. 2005)

Marie-Curie project aims to evaluate how the aqueous chemistry of Al nanoclusters affects the removal of the two inorganic arsenic species As(III) and As(V) from water when used as main constituents in polyaluminum chloride ($\text{PACl}_{\text{Al}_{130}}$) and $\text{PACl}_{\text{Al}_{130}}$ -based granulates.

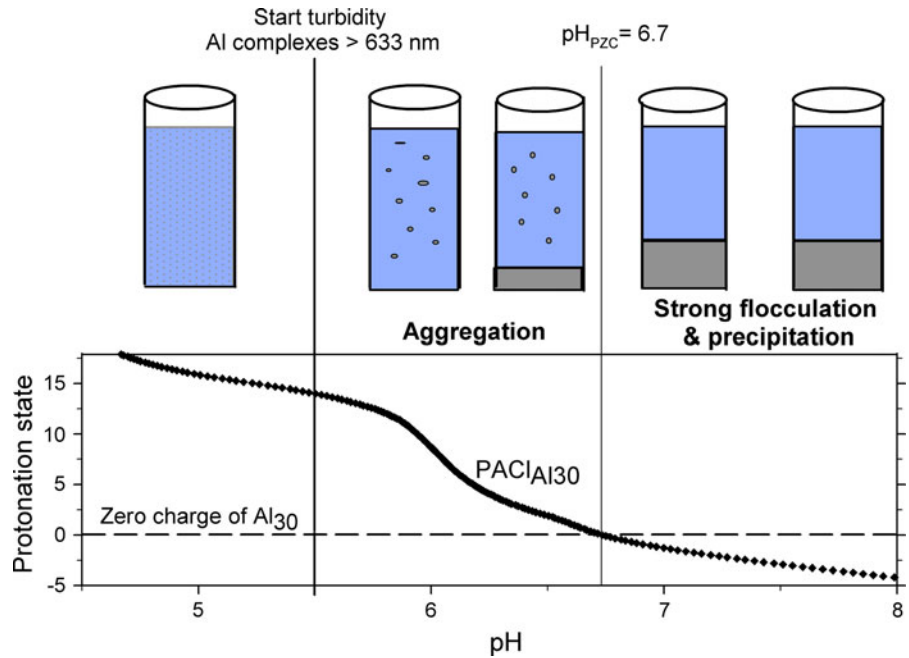
2 Working principles

After dissolution in water, industrially manufactured PACl with the formula $\text{AlCl}_{0.5}(\text{OH})_{2.5}$ produces an aluminum solution with a content of >70% Al nanoclusters. Depending on the pH of the solution, the Al clusters undergo coagulation, form aggregates, and precipitate resulting in the production of an amorphous solid. These processes are driven by the protonation state of dissolved Al nanoclusters—the more the Al clusters deprotonate, the more their surface charge and the electrostatic repulsion between single Al clusters decreases. Lower repulsion enhances the aggregation of Al nanoclusters. The structure of Al_{13} and Al_{30} contains a high number of OH^- and H_2O groups, and deprotonation proceeds over almost two pH units from pH 5 to 6.8 (Furrer et al. 1992; Casey et al. 2005). The state of protonation of the $\text{PACl}_{\text{Al}_{130}}$ solution is obtained from base titration data by taking into account the initial PACl solution volume, the total Al_{30} concentration, and the concentration and volume of the added base. Zero charge of the Al_{30} nanocluster is reached when all 18 positive charges are lost, and the state of protonation equals 0. The pH where the electrical charge density on the Al surface is zero (pH point of zero charge; pH_{PZC}) is determined by titration to be at 6.7 (Fig. 2).

By use of a laser with $\lambda = 633$ nm the formation of Al clusters >633 nm by aggregation in a $\text{PACl}_{\text{Al}_{130}}$ solution with 15 mM $\text{Al}(\text{tot})$ was observed after the pH reached a value of 5.5. Already at pH 6.5, where Al nanoclusters keep a charge of +2, a small amount of aggregates settles. However, the bulk of aluminum particles settle in big white flocs above a pH_{PZC} of 6.7, where most of the Al can be separated by sedimentation or centrifugation. A schematic view illustrates the Al removal processes in dependence of pH for PACl with high Al_{30} content (Fig. 2).

Arsenate adsorbs to Al_{30} and Al_{13} clusters during coagulation and aggregation by ligand-exchange reactions at the hydroxy and oxygen groups of the

Fig. 2 Deprotonation of a $\text{PACl}_{\text{Al}30}$ solution with $[\text{Al}_{\text{tot}}] = 15 \text{ mM}$ and Al removal processes with pH. Optimum Al removal takes place above pH_{PZC} at 6.7



aluminum, and together they form soluble complexes. Because the $\text{PACl}_{\text{Al}30}$ solution deprotonates from pH 5 to 7, As(V) adsorption can take place over a wide pH range. Removal of As(V) occurs with the precipitation of Al–As(V) complexes at a $\text{pH} > 6.5$. The highly charged Al nanoclusters are strong adsorbents for arsenate ions. However, the neutral arsenite H_3AsO_3 has a weak affinity for Al. Adsorption most likely occurs to low or uncharged Al clusters due to electrostatic interaction, Van-der-Waals forces and dipole–dipole interaction. As(III) coprecipitates with Al flocs above pH 7 where solid and liquid phase can be separated effectively.

In order to minimize the risk of aluminum contamination of treated water and to avoid a filtration step for small Al particles, granulates of 1–2 mm in size were generated from highly concentrated $\text{PACl}_{\text{Al}30}$ solutions after repetitive aggregation, precipitation, washing and consecutive drying. Dried material was grinded and compressed using a pill press operation.

The adsorption of arsenate occurs mainly on the surface of $\text{PACl}_{\text{Al}30}$ granulate as As(V) has a strong sorption affinity to the aluminum (Fig. 3a). Contrary, due to weak chemical interaction with the Al solid, As(III) diffuses into the grain pores, where it is adsorbed, and therefore it is evenly distributed over the entire grain (Fig. 3b).

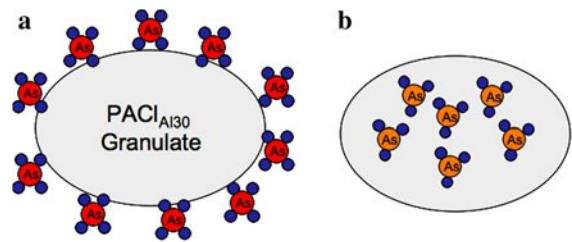


Fig. 3 a As(V) and b As(III) adsorption processes on Al granulate (not to scale)

3 Applications

Within the framework of the European project AquaTRAIN, polyaluminum chloride and Al granulate with a high content of Al nanoparticles were applied to groundwater from highly contaminated aquifers, but with different groundwater chemistry and usage at two field sites. The Pannonian Basin, a sedimentary basin stretching over the countries of Serbia, Hungary, Romania, Slovakia, and Croatia, is the largest area in Europe where groundwater is affected by geogenic arsenic contamination. Within this region, an estimated one million people are or have been exposed to water containing 5–30 times more arsenic than the World Health Organisation (WHO) and EU drinking water guide value of 10 ppb

Table 1 Comparison between $\text{PACl}_{\text{Al}_{30}}$ and $\text{PACl}_{\text{Al}_{30}}$ -based granulate in water treatment applications

	As removal mechanism	As removal	Advantages	Constraints	Application
$\text{PACl}_{\text{Al}_{30}}$	Coagulation/coprecipitation	As(V): 90–100% As(III): <40%	Easy applicable No pH adjustment necessary	Al remaining in treated water	Standing water bodies/specialized treatment facilities
$\text{PACl}_{\text{Al}_{30}}$ Granulate	Adsorption	As(V): 70–99% As(III): 33–57%	High As uptake capacity No Al in treated water	Inhibited by iron, phosphate	Flow-through systems

(EC 1998), mainly present as As(III) (Rowland et al. 2011; Gurzau and Gurzau 2001; Varsanyi and Kovacs 2006). This is a particular risk because many people in this area still rely on unfiltered water. For example, local artesian wells are the main source for drinking and household water in some villages in Western Romania.

In Northern Greece, groundwater in geothermal fields contains up to 3,000 ppb As. It is mostly used for irrigation in agriculture during dry summer months, and for this purpose stored in open water tanks, where As(III) undergoes oxidation in contact with air (Casentini et al. 2009).

Effective application of arsenic treatment systems in natural water needs to take into account the specifics of arsenic chemistry (e.g., As speciation) and the chemical properties of the bulk water that might influence the removal efficiency, such as total dissolved solids, organic substances, pH and other elements that might compete with As for sorption sites. Al nanoclusters as main constituents of an aluminum coagulant and granulate show advantages and limitations for As removal (Table 1). This work showed that $\text{PACl}_{\text{Al}_{30}}$ has the potential to remove As(V) to below the EU drinking water directive. As(III) removal, however, is less efficient, because the neutral As(III) species has a low affinity for Al. Therefore, oxidation of As(III) before removal is essential. The optimum pH for As removal with $\text{PACl}_{\text{Al}_{30}}$ is at or above pH 6.7 due to the deprotonation of Al_{30} . Conventional PACl achieved the highest arsenic removal at pH 5.5 (Fan et al. 2003). The typical groundwater pH ranges from 6.5 to 8.5, and therefore no pH adjustment is needed for groundwater treatment with Al_{30} . Although field applications showed that Al precipitation at this pH is effective with no remaining Al measured in the treated solution, some laboratory tests resulted in

aluminum concentrations slightly above the WHO drinking water guide value of 200 ppb (WHO 1998).

The use of solid granulates allows water to be treated in a flow-through system without the need for solid–liquid separation. Upward water flow through a column packed with adsorbent material increases the contact time with the granulates (Fig. 4). Polyaluminum granulate with a high content of Al nanoclusters removed 70–99% As(V) in a concentration range of 20 ppb–200 ppm. As(III) is removed from 57% at low concentrations (23 ppb) to 33% at high concentrations (200 ppm). Field tests showed furthermore that iron and phosphate compete for sorption sites vs. As(III) on polyaluminum granulate.

High contents of Al nanoclusters improved the coagulation and precipitation process while successfully reducing arsenate concentrations below the required limit. In water treatment facilities operating with coagulation/precipitation, the application of $\text{PACl}_{\text{Al}_{30}}$ might help reducing treatment steps -and therefore treatment costs- by removing the pH adjustment. Application of $\text{PACl}_{\text{Al}_{30}}$ in standing water bodies like open irrigation tanks in Greece is easy and convenient. For running water systems like

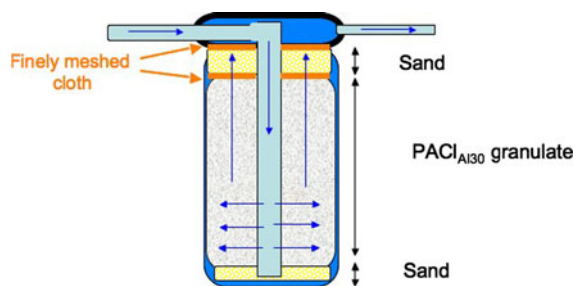


Fig. 4 Single-column set-up for the application of $\text{PACl}_{\text{Al}_{30}}$ -based granulate in a flow-through system for As-contaminated groundwater. Arrows in column indicate water flow

Table 2 AquaTRAIN partner institutions and their technical specialization in the project

AquaTRAIN Coordinator	Host institution of the project	Technical specialization	Location	Website
University of Manchester (UNIMAN)	Arsenic geochemistry and geomicrobiology	Manchester, UK	http://www.seaes.manchester.ac.uk/	
Dept. of Environmental Science, Swiss Federal Institute of Technology (ETH)	Al nanocluster and aquatic chemistry	Zurich, Switzerland	http://www.env.ethz.ch/	
Work package 3 “remediation” Leader	Inorganic water treatment	Chania, Greece	http://www.herslab.tuc.gr/	
Prof. Nikos Nikolaidis, Technical University of Crete (TUC)	Geology and field studies	Cluj-Napoca, Romania	http://www.ubbcluj.ro/	
Project collaborators	Nanoparticle research, aluminum characterization	Aix-en-Provence/Paris, France	http://www.cerege.fr/	
Prof. Calin Baciou, Babes-Bolyai University (UBB)	Water sampling and analysis	Dübendorf, Switzerland	http://www.eawag.ch/	
Dr. Jérôme Rose and Dr. Armand Masion, Centre National de la Recherche Scientifique (CEREGE/CNRS)	As speciation and cycling	Grenoble, France	http://www.ujf-grenoble.fr/	
Dr. Helen Rowland, Dr. Stephan Hug and Dr. Michael Berg, Swiss Federal Institute of Aquatic Science and Technology (EAWAG)	Reactive transport modeling	Utrecht, The Netherlands	http://www.geo.uu.nl/Research/Geochemistry/	
Other AquaTRAIN Partners	Selenium cycling	Girona, Spain	http://www.udg.edu/	
University Joseph Fourier-Grenoble 1 (UJF)	Science-Policy interactions	Budapest, Hungary	http://www.ceu.hu/	
University Utrecht (UU)	Geostatistics and thematic mapping	Ispra, Italy	http://euscoils.jrc.ec.europa.eu/	
University of Girona (UdG)	Isotope analysis	Orleans, France	http://www.brgm.fr/	
Central European University (CEU)	As biochemistry and uptake in humans	Leicester, UK	http://www.dmu.ac.uk/	
JRC-Institute for Environment and Sustainability (EC-DG, JRC)	Speciation techniques and analysis	Aberdeen, UK	http://www.abdn.ac.uk/	
Bureau de Recherches Géologiques et Minières (BRGM)	Biological remediation technologies	Mol, Belgium	http://www.vito.be/	
De Montfort University (DMU)				
The University Court of the University of Aberdeen (UNIABDN)				
Vlaamse instelling voor technologisch Onderzoek (VITO)				

water taps or artesian water wells in Romania, Al₃₀-rich granulate is a better alternative.

4 Training of young researchers

The Marie-Curie research training network (MCRTN) AquaTRAIN (www.aquatrain.eu) focused on the research of geogenic contamination and remediation of groundwater and soils within Europe and provided direct knowledge transfer to involved early-stage researchers (ESRs) and experienced researchers (ERs) by training and cross-disciplinary workshops (Polya 2010). It incorporated the expertise from 15 leading research institutes across 10 European countries structured in four work packages (Table 2) and was funded for 4 years under the 6th European Framework Programme.

Pursuing my PhD within AquaTRAIN gave me the opportunity for international scientific exchange and involvement in various research projects. In addition, participation in project management, interdisciplinary teamwork and the contact with political stakeholders was very valuable for personal skills development.

The encouragement of mobility made it possible to gain working experience in different research groups throughout Europe. A research visit of 6 months at the European Centre for research and education in Geosciences and Environment (CEREGE, France) gave me insights into X-Ray spectroscopic studies of As-Al interactions and the characterization of Al material by ²⁷Al NMR. During another 6 months period at the Faculty of Environmental Sciences of the University Babeş-Bolyai (Romania) the application and installation of a water treatment system at a village well was realized. These trainings widened my experience in the field of water treatment processes from the nano- to macroscale.

Acknowledgments The author would like to thank Prof. Gerhard Furrer, Prof. Bernhard Wehrli (ETH Zurich) and Dr. Jérôme Rose (CEREGE) for invaluable discussions throughout the entire period of this project. Prof. Calin Baciú (UBB) is gratefully acknowledged for field and administrative support in Romania, and Dr. Stephan Hug and Dr. Helen Rowland (EAWAG) for laboratory support and always helpful advices. This is a contribution of the AquaTRAIN Marie-Curie Research Training Network (Contract No. MRTN-CT-2006-035420) funded under the European Commission Sixth Framework Programme (2002–2006) Marie Curie Actions, Human Resources & Mobility Activity Area—Research

Training Networks. The views expressed in this contribution do not necessarily reflect those of the European Commission.

References

- Allouche L, Gérardin C, Loiseau T, Férey G, Taulelle F (2000) Al₃₀: a giant aluminum polycation. *Angew Chem Int Ed* 39(3):511–514
- Auffan M, Rose J, Bottero JY, Lowry GV, Jolivet JP, Wiesner MR (2009) Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nat Nanotechnol* 4:634–641
- Bottero JY, Bersillon JL (1988) Aluminum and iron(III) chemistry—some implications for organic substance removal. *Adv Chem* 219:425–442
- Casentini B, Nikolaidis NP, Hug SJ (2009) As mobilization and accumulation in topsoils (Chalkidiki, Greece). *Geochimica et Cosmochimica Acta* 73(Supplement 1):A 198
- Casey WH, Rustad JJ, Banerjee D, Furrer G (2005) Large molecules as models for small particles in aqueous geochemistry research. *J Nanopart Res* 7:377–387
- Charlet L, Polya DA (2006) Arsenic hazard in shallow reducing groundwaters in southern Asia. *Elements* 2:91–96
- Chen Z, Fan B, Peng X, Zhang Z, Fan J, Luan Z (2006) Evaluation of Al₃₀ polynuclear species in polyaluminum solutions as coagulant for water treatment. *Chemosphere* 64:912–918
- EC (1998) Council directive 98/83/EC. *Off J Eur Commun* L330/32
- Fan M, Brown RC, Sung SW, Huang C-P, Ong SK, van Leeuwen J (2003) Comparison of polymeric and conventional coagulants in arsenic(V) removal. *Water Environ Res* 75(4):308–313
- Furrer G, Ludwig C, Schindler PW (1992) On the chemistry of the Keggin Al₁₃ Polymer. I. Acid-Base properties. *J Colloid Interface Sci* 149(1):56–67
- Gurzau ES, Gurzau AE (2001) Groundwater in Transylvania, Romania: an overview. In: Chappell WR, Abernathy CO, Calderon RL (eds) *Arsenic exposure and health effects IV*. Elsevier, Amsterdam, pp 181–184
- Nilchi A, Rasouli Garmarodi S, Janitabar Darzi S (2011) Removal of arsenic from aqueous solutions by an adsorption process with titania-silica binary oxide nanoparticle loaded polyacrylonitrile polymer. *J Appl Polym Sci* 119(6):3495–3503
- Polya DA (2010) AquaTRAIN: Groundswell of Research, International Innovation (Research Media, UK), Environment, October 2010, 88–90
- Rowland HAL, Omeregie E, Millot R, Jimenez C, Mertens J, Baciú C, Hug SJ, Berg M (2011) Geochemistry and arsenic behaviour in groundwater resources of the Pannonian Basin (Hungary and Romania). *Appl Geochem* 26:1–17
- Smedley PL, Kinniburgh D (2002) Review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem* 17:517–568
- Theron J, Walker J, Cloete TE (2008) Nanotechnology and water treatment: application and emerging opportunities. *Crit Rev Microbiol* 34:43–69

- Varsanyi I, Kovacs LO (2006) Arsenic, iron and organic matter in sediments and groundwater in the Pannonian Basin. *Appl Geochem* 21:949–963
- WHO (1998) Aluminium in Drinking-water. Guidelines for drinking-water quality, 2nd edn. Addendum to vol 2. (Health criteria and other supporting information), p 14
- Winkel L, Berg M, Amini M, Hug SJ, Johnson A (2008) Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. *Nat Geosci* 1:536–542