# Geogenic groundwater contamination – definition, occurrence and relevance for drinking water production

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**Abstract:** The present study provides an overview of geogenic contamination, its occurrence, impacts and possible treatment options for drinking water production. Natural background and anthropogenic contamination can be differentiated using an algorithm based on the frequency distribution of measured substance concentrations. Case studies for geogenic contaminants such as ammonium, fluoride, chloride, sulfate and uranium are discussed based on the origin, occurrence, controlling factors and treatment options. It is suggested that, in case of occurrence of geogenic contaminants, water must be treated or alternative sources need to be found, e.g., managed aquifer recharge, prior to the distribution as drinking water.

**Keywords:** groundwater; geogenic contamination; water treatment; drinking water

## Introduction

The chemical composition of groundwater is a combined result of the composition of water that enters the subsurface and kinetically controlled reactions with the aquifer matrix. Thus, long residence times in the aquifer may, for example, also increase the ion concentrations in the groundwater (Appelo & Postma 2005). Apart from natural processes, groundwater chemistry can also be modified by anthropogenic impacts, e.g. nitrate leaching due to extensive use of fertilizers or infiltration of industrial pollutants due to spills.

If a physical, chemical and/or microbiological water quality parameter exceeds certain a threshold we speak of groundwater contamination. This threshold can be e.g. a predefined natural background level or drinking water guideline values. While the natural background concentrations can be derived from the statistical analysis of large amounts of water quality samples (e.g. Wagner et al. 2011) drinking water guideline values are recommended based on the potential human health impacts (WHO, 2011). A contamination can originate from natural (geogenic) or anthropogenic sources. The most widespread forms of geogenic contamination with human health impacts are elevated concentrations of arsenic and fluoride (Johnson et al. 2008). Geogenic contamination may also be the cause for elevated concentrations of uranium (Smedley et al. 2006; Stalder et al. 2012), chloride (Panno et al. 2006) or sulfate (Toran 1987).

Anthropogenic groundwater contamination can be classified into **direct** and **indirect** impacts. Direct anthropogenic contamination is due to the direct input of substances from agricultural ($NO_3$, $PO_4$, salinity etc), industrial (salinity, heavy metals etc.) or urban (sewage, improper waste disposal etc.) activities as well as from accidents (e.g. oil spills). However, there are certain anthropogenic activities that are capable of changing the geochemical conditions in the subsurface thus potentially mobilizing hazardous geogenic substances. For example, the dewatering of former open pit lignite mines in Lusatia (Germany) lead to aeration of aquifers and subsequent pyrite oxidation, a process which increases Fe and $SO_4$ concentrations whilst reducing pH (Kohfahl 2004) – also known as acid mine drainage. Another example is arsenic, which may be mobilized by variations in redox conditions (e.g. increase in concentration under reducing conditions) due to groundwater abstraction for drinking water production, irrigation, geothermal power plants or mining activities (WHO, 1997). In case coastal aquifers are overexploited, this may lead to the saline intrusion, which increases Na and Cl concentrations in the coastal aquifers (Wen et al. 2011). All these cases can be classified as examples of indirect anthropogenic contamination.

## Algorithm to distinguish geogenic and anthropogenic contamination

Natural groundwater quality may be defined as status in which "the concentrations of the major cations and anions originate from not significantly anthropogenically influenced soils and the rocks of a watershed, including groundwater from areas under agricultural use or from areas where landcover changes has occurred over the last centuries" (Schenk 2001). This definition is taken as basis for differentiating between geogenic and anthropogenic impacts on groundwater quality. In general, groundwater samples collected from a shallow aquifer are affected by both, natural and anthropogenic processes. Thus, the observed concentration distribution ($f_{obs}$) may be described by the sum of two statistical distribution functions, representing the natural ($f_{nat}$) and the influenced ($f_{infl}$) component (after Wendland et al. 2003):

$$f_{obs}(c) = f_{nat}(c) + f_{infl}(c) \tag{1}$$

From the hydrochemical data analysis it is known that the natural component is lognormally distributed, (assumption: the only process impacting groundwater
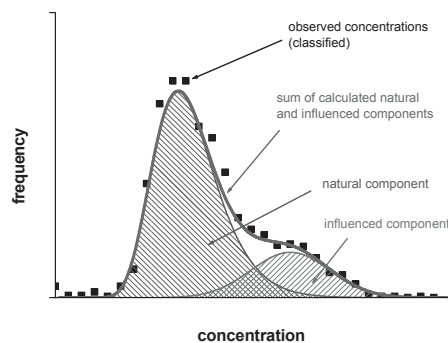


**Fig. 1.** Basic approach of separating the natural and influenced component from an observed groundwater concentration pattern (Wendland et al. 2003).

**Table 1.** Case studies for geogenic contaminants in groundwater.

| Contaminant | Geogenic sources | Influencing factors | Health effects &guideline values | Examples | Treatment options |
|---|---|---|---|---|---|
| **Fluoride** | Fluorite, micas, apatite, amphiboles etc. in granitic rocks | F minerals, pH, temperature, anion exchange capacity of aquifer materials (OH⁻ for F⁻), residence time, porosity, soil structure, depth, groundwater age and bicarbonates | Dental and skeletal fluorosis *Drinking water:* – 1.5 *mg/L* (WHO 2011), – 1.2 *mg/L* (BIS 1992) | – 57% of the Indian states: F>1.5 mg/L(Kumar 2012, Reddy et al. 2010) | Lime softening, coagulation and precipitation, activated alumina (Crittenden et al. 2005) |
| **Uranium** | Granitic rocks (*2.2–15 mg/kg*), clays, shales, Fe-rich rocks (Bernhard 2005) | pH, ionic strength, redox potential, availability of organic and inorganic ligands, formation of colloids, solubility product of limiting minerals etc. | Nephritis (Hursh & Spoor 1973) *Drinking water:* – *30µg/L* (WHO 2011) – *10µg/L* (BMG, 2011) | – Switzerland: 0.05–92.02 µg/L(Stalder et al. 2012) – Nalgonda (IN):0.2 to 68 µg/L(Brindha et al. 2011) | Natural: bioremediation (Abdelouas et al. 2000); technical: permeable reactive barriers (Barton et al. 2004) and ion exchange (URANEX ®) |
| **Chloride** | Natural weathering of bed rocks, volcanic activity, natural brines, saline intrusions and atmospheric deposition (Panno et al. 2006; Mullaney et al. 2009) | Availability of Cl sources, evapotranspiration, atmospheric precipitation, geographic locations, i.e. coastal/inland areas (Guan et al. 2009) | No health based guideline value is suggested by WHO (2011). Cl>250 mg/L may lead to a detectable taste (WHO 2011) | – West France: ≤ 1200mg/L (Grimaldi et al. 2009) – Belgam city (IN): ≤ 333 mg/L (Sameer et al. 2011) – Brandenburg (D)>250 mg/L (Hannappel 2009) | Reverse osmosis, distillation, ion exchange, and treatment using hydrotalcite (Hua & Lu 2006) |
| **Sulfate** | Sulfur-bearing minerals (e.g. gypsum, anhydrite and pyrite) | Availability of sulfate rich minerals in the aquifer, redox conditions | SO₄ > 1000 mg/L can cause laxative effects (WHO 2011) *Drinking water:* – Germany: 250 mg/L (TrinkWV 2011) | – Sachsen-Anhalt (D): >240 mg/L (Hannappel 2009) – Vaniyambadi (IN): up to 576 mg/L (Kumar et al. 2013) | Natural: anaerobic reduction in constructed wetlands (Košutić et al. 2004; Rustler et al. 2012) Technical: RO, NF, ion exchange (e.g. CARIX®) |
| **Ammonium** | Degradation of natural organic matter | Presence of organic matter, nitrogen mineralization, time and redox conditions; anthropogenic impact through waste water | No health based guideline value suggested (WHO 2011). A consumption of 33.7 mg/kg of body weight per day may cause metabolic disorders | – Malaysia: 3.7 mg/L (Hasan et al. 2011) – Brandenburg, Germany: >1 mg/L (Hannappel 1996) | Natural: bioremediation, zeolite Technical: ion exchange (Thornton et al. 2007, Li et al. 2011) |

quality is the reactive interaction of groundwater with the aquifer matrix) whereas the anthropogenic component follows a normal distribution (assumption: groundwater quality is only due to the variability of the different anthropogenic sources). Thus the shape of the distribution is the key factor in differentiating natural and anthropogenic sources (Fig. 1). The explicit shape of both distribution functions is determined by three independent parameters each (amplitude, median and variance), which have to be fitted to the observed frequency distribution using standard algorithms. As a result, the observed distribution pattern is represented by two distribution functions of known shape, which can be assigned to the natural and anthropogenic component.

A transparent measure for natural groundwater concentrations is the concentration range defined by the 10th and the 90th percentiles of the concentration distribution of the natural component (Wendland et al. 2003).

## Cases of geogenic groundwater contamination

Relevant geogenic contaminants that may be encountered in water supply schemes can be listed as ammonium, fluoride, chloride, sulfate and uranium. Case studies for each of these parameters are presented in Table 1.

## Countermeasures to avoid geogenic contamination of drinking water

In regions where groundwater generally shows geogenic concentrations of one or more substances above the drinking water guidelines, other resources (e.g. managed aquifer recharge, surface water reservoirs etc.) or water treatment should be taken into account. As water treatment technologies a broad selection of technologies is available (see Table 1). In recent years new developments can be observed in the field of ion exchange and membrane filtration. One example is the URANEX® system, an ion exchange process implemented by Krüger-WABAG for example in Trollmühle, Germany in 2011 for the safe removal of uranium which occurs at concentrations of up to 13 µg/L in the local groundwater. In combination with CARIX® for softening the resulting drinking water does not only comply with the guidelines for drinking water but also leads to i) less corrosion in the network, ii) lower consumption of household detergents and iii) reduction in scaling processes leading to higher energy efficiency.

## Summary and conclusions

Geogenic contamination is defined as the overstepping of certain thresholds (e.g. drinking water guidelines) in the aquifer without direct or indirect anthropogenic influence. Often it is the result of long residence times combined with favorable geologic conditions and mineralogy of the aquifer. An algorithm using the frequency distribution of measured concentrations can be used for differentiating natural background and anthropogenic sources of groundwater contamination. Uranium, arsenic and fluoride were found to be the most hazardous geogenic contaminants in terms of human health impacts. In many cases the levels of these ions in groundwater are exceedingly higher than the permissible limit and treatment is therefore necessary to reduce the concentrations to meet drinking water guideline values. Apart from shifting to alternative resources (e.g. MAR)

treatment methods are available, ranging from natural (e.g. bioremediation) to more advanced methods (e.g. reverse osmosis or ion exchange).

## References

Abdelouasa, A. U., Lutze, W., Gong, W., Nuttall, E. H., Strietelmeier, B. A. & Travis, B. J. (2000): Biological reduction of uranium in groundwater and subsurface soil. –Sci. Total Environ. **250**: 21–35.

Apambire, W. B., Boyle, D. R. & Michel, F. A. (1997): Geochemistry, genesis and health implications of fluoriferous ground waters in the upper regions of Ghana. – Environ. Geol. **33**:13–24.

Appelo, C. A. J. & Postma, D. (2005): Geochemistry, Groundwater and Pollution, second ed. Balkema, Rotterdam, pp. 241–309.

Barton, C. S., Stewart, D. I., Morris, K. & Bryant, D. E. (2004): Performance of three resin-based materials for treating uranium-contaminated groundwater within a PRB. – J. Hazardous Materials **B116**: 191–204.

Bernhard, G. (2005): Speciation of uranium in environmental relevant compartments. – LandbauforschungVolkenrode **55**:139–148.

BIS (1992): Indian standard specifications for drinking water. – BIS:10500.

Brindha, K., Rajesh, R., Murugan, R. & Elango, L. (2011): Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. – Environ. Monit. Assess. **172**: 481–492. DOI 10.1007/s10661-010-1348-0

Bundesministerium für Gesundheit (2011): Erste Verordnung zur Änderung der Trinkwasserverordnung, Bundesgesetzblatt Teil I, p. 748.

Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. & Tchobanoglous, G. ( 2005): Water Treatment: Principles and Design. MWH publications.

Guan, H., Love, A. J., Simmons, C. T., Makhnin, O. & Kayaalp, A. S. (2010): Factors influencing chloride deposition in a coastal hilly area and application to chloride deposition mapping. – Hydrol. Earth Syst. Sci. **14**: 801–813.

Grimaldi, C., Thomas, Z., Fossey, M., Fauvel, Y. & Merot, P. (2009): High chloride concentrations in the soil and groundwater under an oak hedge in the West of France: an indicator of evapotranspiration and water movement. – Hydrol. Process. **23**:1865–1873.

Hannappel, S. (1996): Die Beschaffenheit des Grundwassers in den hydrogeologischen Strukturen der neuen Bundesländer. – Dissertation Freie Universität Berlin, Berliner Geowiss. Abh., Reihe A, Bd. 182, Berlin.

Hannappel, S. (2009): Flächenhafte Ermittlung der Konzentrationen diffus eingetragener Nährstoffe in das oberflächennahe Grundwasser Nordostdeutschlands. – Wasser und Abfall **6**: 47–54.

Hua, J. & Lu, L. (2006): Chloride removal from wastewater by thermally treated hydrotalcite. – Chinese J. Geochem. **25**: 255–256.

Hursh, J. B. & Spoor, N. L. (1973): Data on man. – In: Hodge, H. C. et al. (eds), Handbook of experimental pharmacology, vol. **36**. Uranium, plutonium, transplutonic elements, pp. 197–240, Springer Berlin.

Johnson et al. (2008): Geogenic contaminants. – Eawag News 65e/December 2008.

Kohfahl, C. (2004): The Influence of Water Table Oscillations on Pyrite Weathering and Acidification in Open Pit Lignite Mines; Column Studies and Modelling

of Hydrogeochemical and Hydraulic Processes in the LOHSA Storage System, Germany; Ph.D Thesis. dissertation.de, Berlin, 111 pp; ISBN 3-89825-774-6.

Košutic, K., Novak, I., Sipos, L. & Kunst, B. (2004): Removal of sulfates and other inorganics from potable water by nanofiltration membranes of characterized porosity. – Separation and Purification Technol. **37**: 177–185.

Laura, T. (1987): Sulfate contamination in groundwater from a carbonate-hosted mine. – J. Contam. Hydrol. **2**:1–29.

Li, M., Zhu, X., Zhu, F., Ren, G., Cao, G. & Song, L. (2011): Application of modified zeolite for ammonium removal from drinking water. – Desalination **271**: 295–300.

Mullaney, J. R., Lorenz, D. L. & Arntson, A. D. (2009): Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, northern United States: U.S. Geol. Surv. Sci. Investigations Rep. 2009-5086, 41 p.

Panno, S. V., Hackley, K. C., Hwang, H. H., Greenberg, S. E., Krapac, I. G., Landsberger, S. & O'Kelly, D. J. (2006): Characterization and Identification of Na-Cl Sources in Ground Water. – Ground Water **44**:176–187.

Reddy, D. V., Nagabhushanam, P., Sukhija, B. S., Reddy, A. G. S. & Smedley, P. L. (2010): Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda District, India. – Chem. Geol. **269**: 278–289.

Rustler, M., Scharffetter, D. & Lompa, A. (2012): Decision Support for managing substance flows within the Berlin water cycle under climate change conditions – Synthesis Report. PREPARED Project. D. 5.1.2.b

Sajil Kumar, P. J. (2012): Assessment of Fluoride Contamination in Groundwater as Precursor for Electrocoagulation. – Bull. Environ. Contam. Toxicol. **89**:172–175.

Sajil Kumar, P. J., Delson, P. D., Vernon, J. G. & James, E. J. (2013): A linear regression model (LRM) for groundwater chemistry in and around the Vaniyambadi industrial area, Tamil Nadu, India. – Chin. J. Geochem. **32**: 019–026.

Sameer, V. Yamakanamardi, Hampannavar, U. S. & Purandara, B. K. (2011): Assessment of chloride concentration in groundwater: A case study for Belgaum City. – Internat. J. Environ. Sci. **2**: 271–280.

Schenk, V. (2001): Natürliche Grundwasserbeschaffenheit. Stellungnahme des PK Natürliche Grundwasserbeschaffenheit" an den DVGW, Bergheim.

Stalder et al. (2012): Occurrence of uranium in Swiss drinking water. – Chemosphere **86**: 672–679.

Smedley et al. (2006): Uranium Occurrence and Behaviour in British Groundwater. CR/06/050N. British Geol. Survey.

Thornton, A., Pearce, P. & Parsons, S. A. (2007): Ammonium removal from digested sludge liquors using ion exchange. – Water Res. **41**: 433–439.

TrinkWV (2011): Verordnung über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung-TrinkWV 2001).

Wagner, B., Beer, A., Brose, D., Budziak, D., Clos, P., Dreher, T., Frische, H.-G., Hübschmann, M., Marczinek, S., Peters, A., Poeser, H., Schuster, H., Steinel, A., Wagner, F. ,Walter, T., Wirsing, G. & Wolter, R. (2011): Erläuterung zum Web Map Service (WMS) „Hintergrundwerte Grundwasser". Hof: 22 p., http://www.bgr.bund.de/DE/Themen/Wasser/Projekte/abgeschlossen/Beratung/Hintergrundwerte/wagner2011_pdf.pdf?__blob=publicationFile&v=8

Wen, X., Diao, M., Wang, D. & Gao, M. (2011): Hydrochemical characteristics and salinization processes of groundwater in the shallow aquifer of Eastern Laizhou Bay, China. – Hydrol. Process. **26**: 2322–2332.

Wendland et al. (2003): A procedure to define natural groundwater conditions of groundwater bodies in Germany. – Diffuse Pollution Conference Dublin.

WHO (1997): Guidelines for Drinking-water Quality, third edition, World Health Organization, Geneva, Switzerland.

WHO (2011): Guidelines for Drinking-water Quality, fourth edition, World Health Organization, Geneva, Switzerland.