

ISOTOPE TRACING IN GROUNDWATER APPLICATIONS

by
Nina Kortelainen

Kortelainen, N. 2011. Isotope tracing in groundwater applications. *Geological Survey of Finland, Special Paper 49*, 279–284, 3 figures.

Isotope methods in hydrogeological studies of Finnish shallow glacial formations have been developed and applied at the Geological Survey of Finland (GTK) since the late 1990s. The Laboratory for Isotope Geology has analyzed oxygen and hydrogen isotopes in water samples on a routine basis since 1995, and the isotopic composition of inorganic carbon and strontium dissolved in water since 2000. The first detailed records on spatial and annual variability in the isotopic composition of precipitation and groundwaters in Finland were generated during 1995 to 2005. GTK has three active precipitation stations related to the Global Network of Isotopes in Precipitation (GNIP) programme operated by the IAEA. Isotope “fingerprinting”, based on the isotopic difference between interacting water reservoirs, has been useful in several applied studies related to water management, especially artificial recharge (AR). At Tuusula Waterworks in southern Finland, the isotope ratios of oxygen and hydrogen have been utilized to calculate the mixing ratios between local groundwater and infiltrated lake water, and the carbon isotope method to quantify the processes of organic matter removal in artificial groundwater recharge. To understand the response of the natural groundwater system to artificial recharge and the mixing of infiltrated water with local groundwater, knowledge of the geochemical baseline and isotopic characteristics of the aquifer is essential. In the Virttaankangas groundwater formation, SW Finland, isotopic applications in AR have had a significant role in the planning of infiltration and monitoring of the active water plant, as well as assisting in the calibration of groundwater flow model. New isotope approaches for hydrogeology are being tested using the facilities of the Finnish Isotope Geology Laboratory (SIGL). Separation method for cations such as lithium, magnesium, calcium, strontium, lead and uranium are currently under development. The automated separation methods would significantly reduce the throughput time of samples. In contrast to oxygen and hydrogen, the isotopic differences in dissolved components in water are inherited from organic and inorganic atmospheric, industrial and anthropogenic sources, together with weathering processes during the interaction between minerals, soil and water.

Keywords (GeoRef Thesaurus, AGI): hydrogeology, isotopes, ground water, artificial recharge, surface water, infiltration, Finland

Geological Survey of Finland, P.O. Box 96, FI-02151 Espoo, Finland

E-mail: nina.kortelainen@gtk.fi

BACKGROUND

The Geological Survey of Finland (GTK) has been the first research organisation in Finland to introduce isotope methods in hydrogeological studies, especially for shallow glacial formations. The driving force behind these activities has been the need to develop and apply isotope methods particularly to water management and artificial groundwater recharge. Stable isotope methods have been known among hydrogeological studies since the beginning of the 1960s. Natural elements and compounds are composed of different isotopes of certain elements. Isotope ratios of oxygen, hydrogen, carbon and strontium are widely used in hydrological studies to track, for example, different water sources, groundwater recharge processes, subsurface processes, geochemical reactions and reaction rates (e.g. Clark & Fritz 1997, Kendall & McDonnell 1998, Kendall & Doctor 2003).

Precipitation has a geographically specific isotopic fingerprint, which is inherited by the local groundwater. In isolated surface water reservoirs, the water mass is exposed to evaporation, which leads to isotopic enrichment compared to groundwater (Gonfiantini 1986). In practice, significant differences are often recorded between local groundwater and surface water reservoirs, as illustrated in Figure 1 of the Virttaankangas groundwater formation, SW Finland. The isotopic composition of the stable nuclides of oxygen and hydrogen, for instance, are measured as isotope ratios, which are reported using δ notation as the per mil (‰) difference relative to the international standard for oxygen ($\delta^{18}\text{O}$) and hydrogen (δD). In shallow aquifers, the isotopic compositions of oxygen and hydrogen are conservative parameters, which can generally only be changed by mixing with isotopically different water masses (Clark & Fritz 1997). Separating sources of mixed natural waters without isotope data is practically impossible, and isotope tracers are therefore a significant addition to the selection of more traditional hydrogeological methods.

The Laboratory for Isotope Geology has analyzed oxygen and hydrogen isotopes in water samples on a routine basis since 1995, and the isotopic composition of inorganic carbon and strontium dissolved in water since 2000. The initial focus of the study was to generate a background data set on the isotopic composition of surficial waters, here containing mostly precipitation and modern groundwater. During 1995 to 2005, the first detailed records on spatial and annual variability in the isotopic composition of precipitation and groundwaters in Finland were generated (Backman et al. 1999, Tarvainen et al. 2001, Kortelainen & Karhu 2004, Kortelainen & Karhu 2006, Kortelainen 2007, Kortelainen & Karhu 2009, Kortelainen 2009). The systematic acquisition of oxygen and hydrogen isotopes in precipitation provided a framework for better understanding aquifer recharge processes, the dimensions of hydrological systems and the responses of recharge to temporal and seasonal climatic variations and water-mineral interactions. The active regional network of isotopes in Finnish precipitation has gradually been established since 1999 at three monitoring stations in Espoo (southern Finland), Kuopio (central eastern Finland) and Rovaniemi (northern Finland). This continuous research activity is related to the Global Network of Isotopes in Precipitation (GNIP) programme conducted by the International Atomic Energy Agency (IAEA) in coordination with the World Meteorological Organization (WMO). The GNIP programme has gathered isotope data on stable oxygen and hydrogen as well as the radioisotope of hydrogen, i.e. tritium, from hundreds of precipitation stations around the world since 1961 (IAEA/WMO 2006). Finnish isotope records can also be downloaded from the GNIP database. Monitoring of this kind is critical in creating the basic isotope tools for hydrogeological studies (Clark & Fritz 1997).

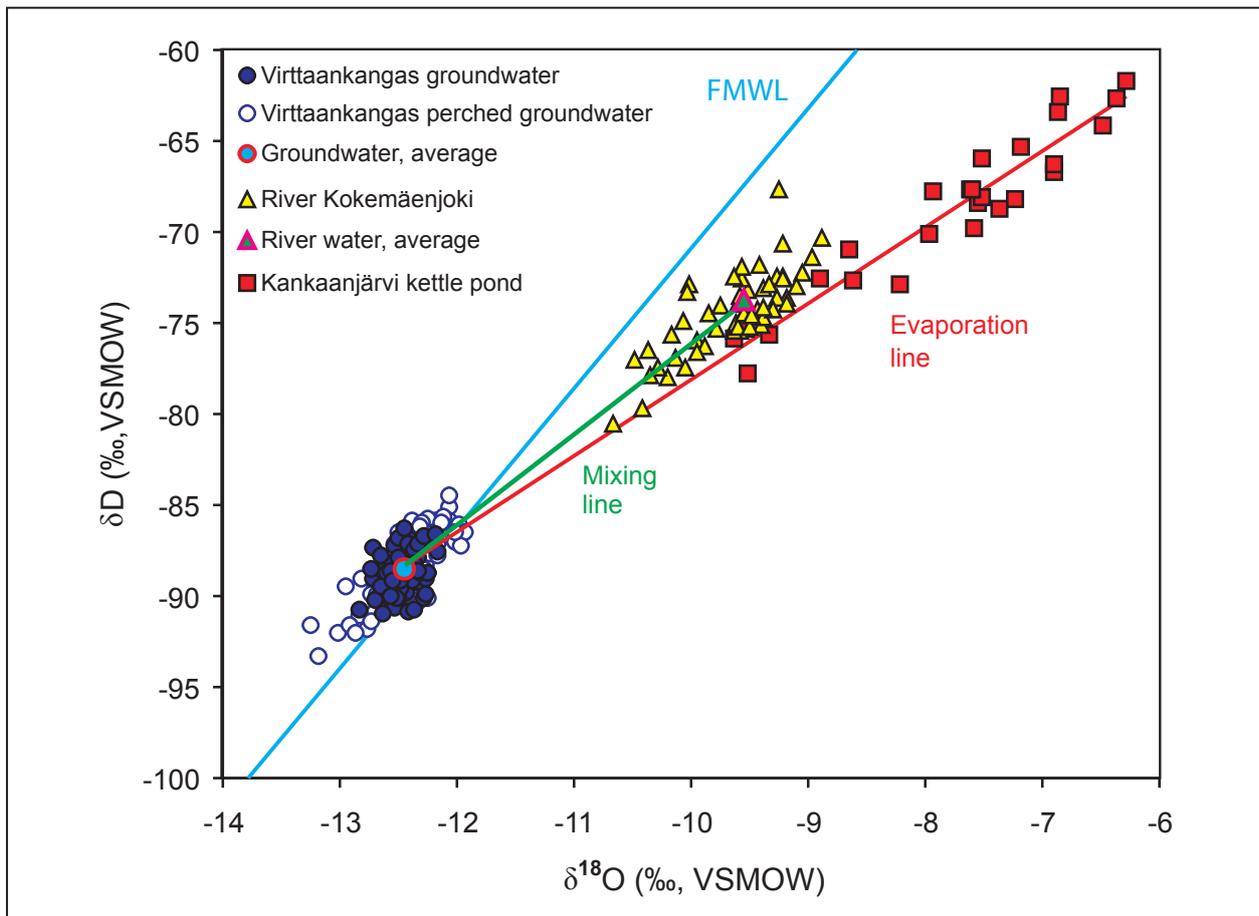


Figure 1. Isotopic composition of oxygen and hydrogen in Virttaankangas groundwater, Lake Kankaanjärvi and in Kokemäenjoki River. The groundwater is located on the Finnish meteoric water line (FMWL; blue line; Kortelainen 2007). The FMWL illustrates the linear correlation between the $\delta^{18}\text{O}$ and δD values recorded from the precipitation in Finland. The river water (yellow triangles) and the lake water (red squares) are dislocated from the FMWL. The lake water follows the local evaporation line (red line), which crosses the FMWL exactly at the mean isotopic composition of the Virttaankangas groundwater. This indicates that the Kankaanjärvi lake water originates completely from the Virttaankangas groundwater. The isotopic composition of Virttaankangas groundwater differs significantly from those of the illustrated surface waters, and mixing of them with groundwater would be easily detected from their isotope ratios. The green line is a mixing line between the long-term mean isotope values of groundwater and river water. Mixing of these two waters would settle the isotope values of the mixed water along the green line.

ISOTOPES APPLIED TO AR

Isotope “fingerprinting”, based on the isotopic difference between interacting water reservoirs, has been useful in several applied studies related to water management, and especially to artificial recharge (AR). In a boreal environment such as Finland, AR is generally carried out by infiltrating water from lakes or rivers into glacial aquifers in order to produce naturally purified drinking water. In most studies, the traditional water isotopes, meaning oxygen and hydrogen, have been analyzed. At Tuusula Waterworks in southern Finland, for example, the isotope ratios of oxygen and hydrogen have been successfully applied to calculate mixing ratios between local groundwater and infiltrated lake water (Kortelainen & Karhu 2006). Besides the two main constituents of water (O, H), minor elements dissolved in the water such as carbon have an isotopi-

cally distinct composition in groundwater and infiltration water. Therefore, carbon can be used as an additional isotopic tracer. In boreal regions, reducing the total organic carbon (TOC) content of the infiltration water is one of the main challenges in the process of artificial recharge. In Finland, the recommended maximum level of TOC in potable water is 2 mg/L (Ministry of Social Affairs and Health 1994). Determination of the isotope ratios of dissolved inorganic carbon (DIC) and the content of inorganic and organic carbon in water has provided new information on the removal of organic matter from infiltrated water (Kortelainen & Karhu 2006, Kolehmainen et al. 2009, Kolehmainen et al. 2010). At Tuusula Waterworks, isotope methods were used for the first time to quantify the processes of organic matter removal in artificial recharge (Kortelainen

& Karhu 2006). In an optimal situation, the use of isotope methods would already be initiated in the planning stage as a basic part of an AR scheme. In order to understand the response of a natural groundwater system to artificial recharge and the mixing of infiltrated water with local groundwater, the geochemical baseline and isotopic characteristics of the aquifer should be monitored over a sufficiently long time period so that all normal variation in isotopes and the geochemistry of the groundwater are known. For example, in the Virt-

taankangas area, operated by Turku Region Water Ltd., the isotopic composition of groundwater has been monitored since 2000 (Kortelainen & Gustavsson 2004, Kortelainen & Karhu 2009). Isotopic applications in AR have had an essential role in the planning of infiltration and monitoring of the active water plant by predicting water pathways and mixing and the responses of aquifer geochemistry to recharge, as well as assisting in the calibration of groundwater flow model (Artimo et al. 2007, Artimo et al. 2008).

PRESENT AND FUTURE

New isotope approaches for hydrogeology are about to be tested at the facilities of the Finnish Isotope Geology Laboratory (SIGL). High performance ion chromatography (HPIC) techniques consisting of an automated sampler, an ion chromatograph and a fraction collector will enable the automatic separation of several selected chemical elements for isotopic analysis from liquid samples. Separation methods for cations such as lithium, magnesium, calcium and strontium are currently under development (Figure 2). Ion fractions will be analysed using the SIGL MC-ICP-MS instrument. Besides the aforementioned elements, the isotope ratios of lead and uranium, for example, can be measured from water samples with little or no sample preparation. Most importantly, the automated separation methods will significantly reduce the throughput time of samples. In contrast to oxygen and hydrogen isotopes, representing water itself, the isotopic differences of these dissolved components in water may be inherited from organic and inorganic atmospheric, industrial and anthropogenic sources, together

with weathering processes during the interaction between minerals, soil and water (e.g. Clark & Fritz 1997, Kendall & McDonnell 1998, Kendall & Doctor 2003, Blum & Erel 2003). Isotopic differences may even exist within an aquifer, as illustrated in Figure 3 by the spread in the Sr isotopic composition, and these methods can therefore be used to reconstruct the hydrogeochemistry of a groundwater formation. Traditional isotope techniques such as those based on isotopes of oxygen, hydrogen and carbon will always play an essential role in water management studies, as they can be used to assess water pathways and provide a hydrogeochemical picture of a water reservoir. However, a revolution is also taking place in analysis using these traditional environmental isotopes. A completely new technique based on cavity ring-down spectroscopy (CRDS) will at least partially replace traditional mass spectrometric techniques (e.g. Brand et al. 2009, Newman et al. 2009), and most importantly, these new methods will significantly reduce the investment costs and thereby lower analytical costs.

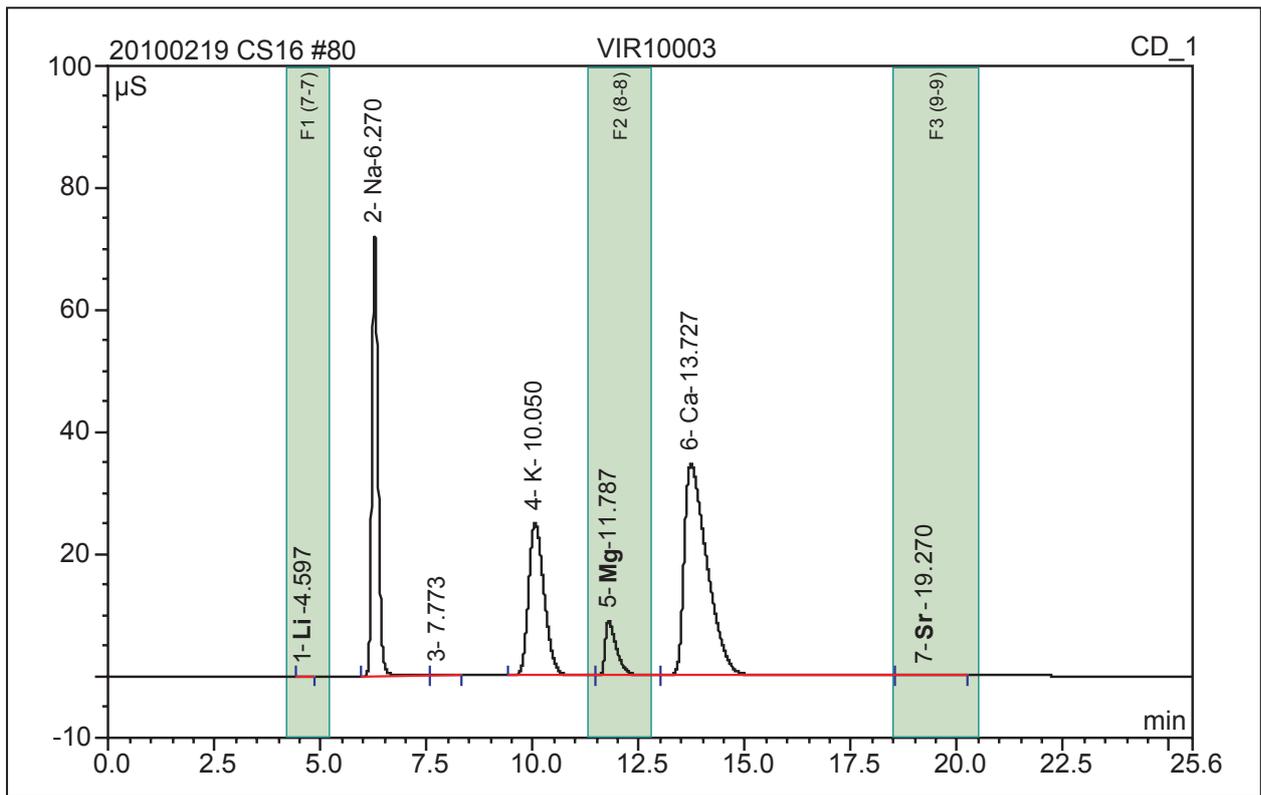


Figure 2. A cation chromatogram of Kokemäenjoki river water determined using GTK's ion chromatograph (Dionex, IC-3000). The collected ion fractions, including Li, Mg and Sr, are lined with green rectangles. The duration of the run was 25 minutes (horizontal axis) and the intensity of the detected ions was measured as electrical conductivity (μS ; vertical axis). The total area of the peaks defines the concentration of the ions illustrated in the graph.

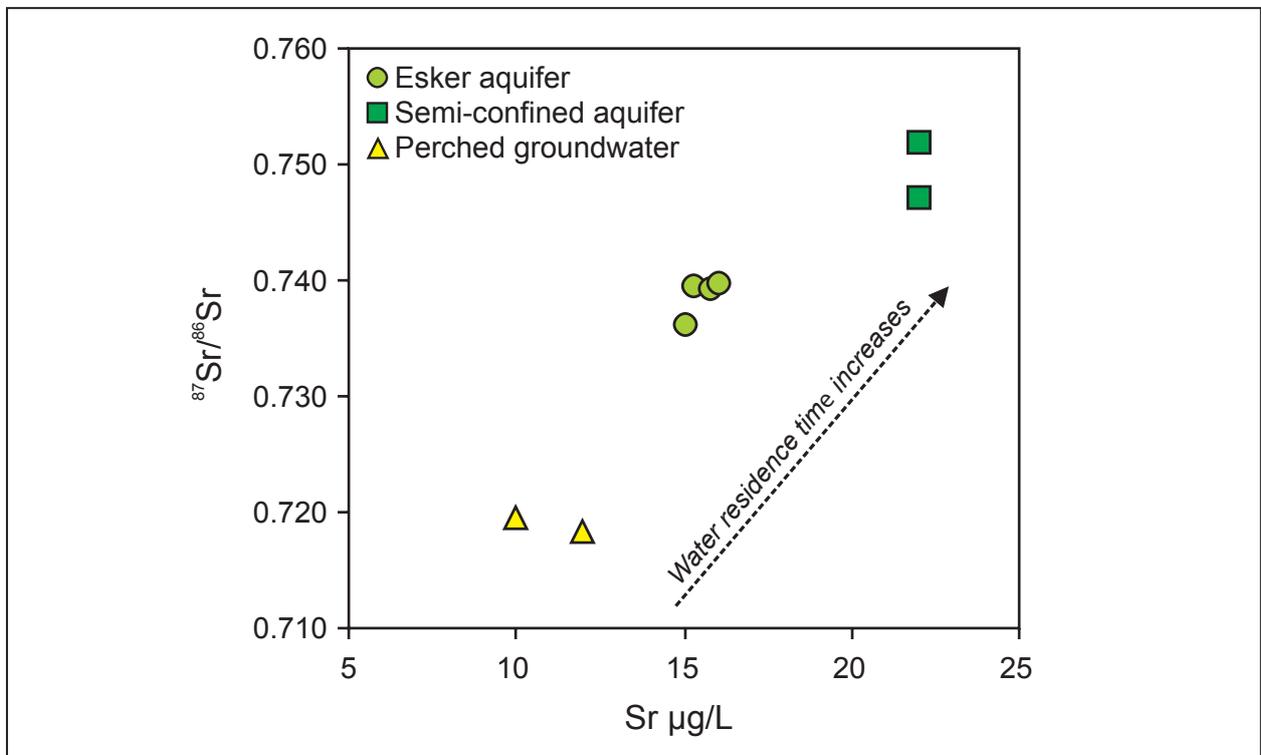


Figure 3. Variation in the strontium isotopic ratios and Sr concentrations in the Virttaankangas groundwater formation. The esker aquifer is the main productive aquifer, which is clearly differentiated from the perched groundwater and semi-confined aquifer by its Sr composition. Modified from Kortelainen & Karhu 2009.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to my colleagues, Hugh O'Brien and Yann Lahaye, and the official reviewer, Jarkko Okkonen, for their constructive and useful comments.

REFERENCES

- Artimo, A., Saraperä, S. & Ylander, I. 2007.** Methods for integrating an extensive geodatabase with 3D modelling and data management tools for the Virttaankangas artificial recharge project, southwestern Finland. *Water Resources Management* 22, 1723–1739.
- Artimo, A., Puurunen, O., Saraperä, S. & Ylander, I. 2008.** Geologinen informaatio tekopohjavesihankkeen toteuttamisessa: Pohjavesitutkimukset Virttaankankaalla. Lieto: Turun Seudun Vesi Oy:n julkaisu. (in Finnish)
- Backman, B., Lahermo, P., Väisänen, U., Paukola, T., Juntunen, R., Karhu, J., Pullinen, A., Rainio, H. & Taniskanen, H. 1999.** Geologian ja ihmisen toiminnan vaikutus pohjaveteen. Seurantatutkimuksen tulokset vuosilta 1969–1996. Summary: The effect of geological environment and human activities on groundwater in Finland. Results of monitoring in 1969–1996. Geological Survey of Finland, Report of Investigations 147. 261 p.
- Blum, J. D. & Erel, Y. 2003.** Radiogenic isotopes in weathering and hydrology. In: Drever, J. I. (ed.) *Surface and Ground Water, Weathering and Soils, Treatise on Geochemistry Vol 5*. New York: Elsevier, 365–392.
- Brand, W. A., Geilmann, H., Crosson, E. R. & Rella, C. W. 2009.** Cavity ring-down spectroscopy versus high-temperature conversion isotope ratio mass spectrometry; a case study on $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of pure water samples and alcohol/water mixtures. *Rapid Communications in Mass Spectrometry*, 23, 1879–1884.
- Clark, I. & Fritz, P. 1997.** *Environmental Isotopes in Hydrogeology*. Boca Raton: Lewis Publishers. 328 p.
- Gonfiantini, R. 1986.** Environmental isotopes in lake studies. In: Fritz, P. & Fontes, J. Ch. (eds.) *Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment, B, Vol. 2*. Amsterdam: Elsevier, 113–168.
- IAEA/WMO 2006.** Global Network of Isotopes in Precipitation. The GNIP Database. Available at: <http://isohis.iaea.org>.
- Kendall, C. & McDonnell, J. J. (eds.) 1998.** *Isotope tracers in catchment hydrology*. The Netherlands: Elsevier. 839 p.
- Kendall, C. & Doctor, D. H. 2003.** Stable isotope applications in hydrologic studies. In: Drever, J. I. (ed.) *Surface and Ground Water, Weathering and Soils, Treatise on Geochemistry Vol. 5*. New York: Elsevier, 319–364.
- Kolehmainen, R. E., Kortelainen, N. M., Langwaldt, J. H. & Puhakka, J. A. 2009.** Biodegradation of natural organic matter in long-term, continuous-flow experiments simulating artificial ground water recharge for drinking water production. *Journal of Environmental Quality* 38(1), 44–52.
- Kolehmainen, R. E., Crochet, L. M., Kortelainen, N. M., Langwaldt, J. H. & Puhakka, J. A. 2010.** Biodegradation of Aqueous Organic Matter over Seasonal Changes: Bioreactor Experiments with Indigenous Lake Water Bacteria. *Journal of Environmental Engineering* 136(6), 607–615.
- Kortelainen, N. 2007.** Isotopic fingerprints in surficial waters: stable isotope methods applied in hydrogeological studies. Geological Survey of Finland. (Academic dissertation)
- Kortelainen, N. 2009.** Isotopic composition of atmospheric precipitation and shallow groundwater in Olkiluoto: O-18, H-2 and H-3. Posiva, Working Report 2009-06. Olkiluoto: Posiva. 23 p. (Electronic publication)
- Kortelainen, N. & Gustavsson, N. 2004.** Virttaankangan pohjaveden ja Kokemäenjoen jokiveden hapen ja vedyn isotooppikoostumusseuranta: seossuhteiden virhetarkastelu simuloinneilla. Summary: The oxygen and hydrogen isotope ratio in Virttaankangas groundwater and Kokemäenjoki river water monitoring program. Turun Seudun Vesi Oy:n julkaisu 1/2004. 30 p.
- Kortelainen, N. M. & Karhu, J. A. 2004.** Regional and seasonal trends in the oxygen and hydrogen isotope ratios of Finnish groundwaters: a key for mean annual precipitation. *Journal of Hydrology* 285, 143–157.
- Kortelainen, N. M. & Karhu, J. A. 2006.** Tracing the decomposition of dissolved organic carbon in artificial groundwater recharge using carbon isotope ratios. *Applied Geochemistry*, 21 (4), 547–562.
- Kortelainen, N. M. & Karhu, J. A. 2009.** Geochemical and isotopic evolution of high-pH groundwater in a carbonate-bearing glacial aquifer, SW Finland. *Hydrology Research* 40.1, 19–31.
- Ministry of Social Affairs and Health 1994.** Decision to the Ministry of Social Affairs and Health relating to the quality and monitoring of water intended for human consumption, Statutes of Finland 1994, No. 74.
- Newman, B., Kurttas, T., Tanweer, A. & Aggarwal, P. 2009.** New IAEA resources for stable isotope analysis of liquid water samples using laser ablation spectroscopy. Vienna: IAEA, Water & Environment News, Newsletter of the Isotope Hydrology Section 25, 5–6.
- Tarvainen, T., Lahermo, P., Hatakka, T., Huikuri, P., Ilmasti, M., Juntunen, R., Karhu, J., Kortelainen, N., Nikkarinen, M. & Väisänen, U. 2001.** Chemical composition of well water in Finland – main results of the “one thousand wells” project. In: Autio, S. (ed.) *Geological Survey of Finland, Current Research 1999–2000*. Geological Survey of Finland, Special Paper 31, 57–76.