Integrated Methods in Catchment Hydrology—Tracer, Remote Sensing and New Hydrometric Techniques
(Proceedings of IUGG 99 Symposium HS4, Birmingham, July 1999). IAHS Publ. no. 258, 1999.

Preliminary analysis of boron isotope ratios in leachate-contaminated groundwater

EDUARD HOEHN
Swiss Federal Institute of Water Science and Technology (EAWAG), CH-8600 Dübendorf, Switzerland
e-mail: hoehn@eawag.ch

Abstract Boron isotope ratios of municipal solid waste leachate and groundwater yielded values between –7.0 and 16.6‰. We feel that these ratios have the potential to be used as a tracer for the assessment of mixing of leachate-contaminated groundwater. The values were interpreted as a mixture of waters of a different origin. This interpretation is corroborated by independent findings from a hydrogeological site assessment.

INTRODUCTION

Boron (B) is found in natural groundwater in concentrations in the range of 10–1000 μg l^{-1} (Matthess, 1973). The use of B isotopes for the characterization of geochemical systems has become of interest in the last decade, and reviews of the variations of B isotope ratios in aquatic and solid environments were given by Bassett (1990) and Barth (1993). The ability of B isotope ratios to act as a tracer for the mixing of groundwaters with contaminated waters, even at low total B concentrations, was shown by Davidson & Bassett (1993), Vengosh *et al.* (1994), and Bassett *et al.* (1995). Total B concentrations in landfill leachate can be many times higher than the background, and B has become a valuable tracer for the identification of the sources of groundwaters contaminated with leachate from old municipal solid waste landfills (e.g. Kerndorff *et al.*, 1985; Uhlmann, 1991). The present paper reports about a first data set of B isotope ratios at a waste disposal site and leachate-contaminated groundwater from various compartments of old unlined landfills. The objective of this study was to find out whether B isotope ratios could be used as a tracer for the assessment of mixing rates of these groundwaters.

THEORETICAL BACKGROUND AND METHOD

A major source of anthropogenic B is in the form of sodium perborate-monohydrate [$Na_2B_4O_7{\cdot}10H_2O$], an oxidation-bleaching agent in domestic and industrial cleaning detergents. Sodium perborate is formed when sodium-borate minerals are treated with hydrogen peroxide. B is present in aqueous solutions with two dominant species near neutral pH, as boric acid (pK = 9.2). B is known to be retarded to some degree in groundwater environments with a high clay content, but in high-transmissivity aquifers B can be considered to behave as a conservative tracer (Davidson & Bassett, 1993). Two stable isotopes exist in natural B compounds, ^{11}B and ^{10}B. The isotopically lighter borate anion is preferentially sorbed onto solid phases and dissolved B becomes enriched in ^{11}B (Vengosh *et al.*, 1994).

A standard (NIST SRM-951) is given in a conventional δ notation such that $\delta^{11}B$ is the per mille (‰) deviation from this standard (Davidson & Bassett, 1993; Vengosh *et al.*, 1994):

$$[‰] = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \cdot 10^3$$

where $R = {}^{11}B/{}^{10}B$. Non-marine evaporite borate minerals have the lowest reported $\delta^{11}B$ values of about −30‰, while present-day sea water has a fairly constant value of about +40‰ (Barth, 1993). The main sources of sodium perborate are natural sodium borate minerals of non-marine origin from the USA (California) and Turkey, which account for almost 90% of world production. Non-marine sodium borates from these sources are characterized by specific $\delta^{11}B$ values in the range of −0.9 to +10.2‰ (Swihart *et al.*, 1986; Oi *et al.*, 1989). The end use of detergents enriched in bleaching agents results in the discharge of B with well-constrained isotopic signatures to a contaminated groundwater environment. Another source of B with possibly different isotope signatures could be in the weathering of various borosilicate glasses.

SITE DESCRIPTION

The study site, Riet, is located near Winterthur, northern Switzerland, an industrialized city of about 88 000 inhabitants. The subsurface of the city consists of a well permeable alluvial gravel-and-sand aquifer which fills a flat glacial trough valley. The ample groundwater resources in this aquifer are used for industrial and drinking-water purposes. The Riet site has been used during the last 70 years for the disposal of municipal solid wastes, partly mixed with industrial wastes (e.g. foundry sands from casting iron). A number of old unlined landfill compartments at the Riet site were successively filled, starting in 1918 (Fig. 1). The site is located at the edge of the valley which is filled from the bottom to the top with glacial till and coarse-grained alluvium of a thickness of 5–10 m. Towards the valley sides, the alluvium peters out to sandy material. The youngest surficial sediments above the alluvium consist of lacustrine silts and clays, and locally 2–3 m of peat (Simmler, 1993). The shallow subsurface at the Riet site was originally quite boggy with peat layers up to 3 m thick. The peat was utilized at the end of the last century, and the open pits were refilled with untreated wastes in Compartments I–III (Fig. 1). Compartment IV started to be constructed around 1960 and is the most recent of the unlined compartments. After the construction of an incineration plant around 1970, municipal solid waste incinerator bottom ashes became the predominant waste stream into Compartment IV until about 1990, when a new lined compartment came into use (Hoehn *et al.*, 1999). The groundwater flow direction is generally from well RS65 to well RS69 (NNE to SSW; Fig. 1), however, mainly at high groundwater levels, the flow direction points to some mixing with groundwater from Compartment II (i.e. WNW to ESE). This is known from head measurements, a groundwater flow model (Peter, 1997), a geophysical survey (EM31; Huggenberger *et al.*, in preparation), and water chemistry data (Hoehn *et al.*, in preparation).

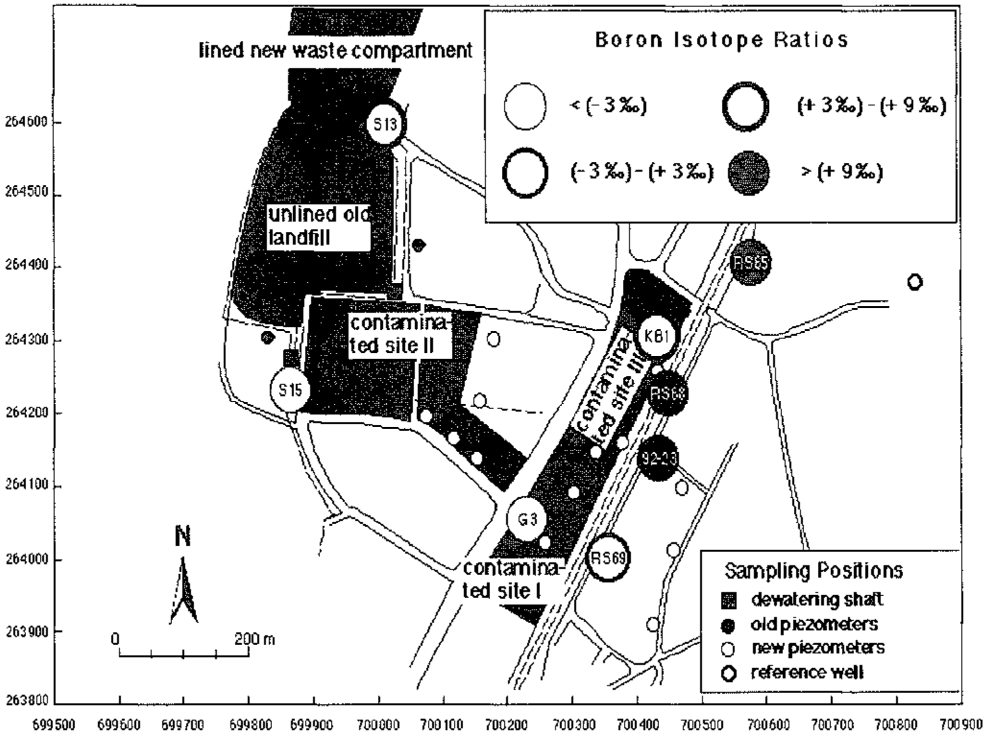

Fig. 1 Plan view of the Riet, landfill site, Winterthur, with various contaminated compartments. Age of contaminated compartments: I, 1918–1924; II, 1925–1935; III, 1950–1960; unlined old landfill, 1960–1992. Numbers in circles, sampling locations for data on boron isotope ratios.

RESULTS AND DISCUSSION

Table 1 shows the results of the first B isotope measurements at this site. The considerable variation in the isotope ratios between –7.0 and 16.6‰ allowed the clustering of samples to leachate from different waste compartments and the groundwater (see Fig. 1 and Hofer *et al.*, 1997): Shaft S15 yields leachate from Compartment II, and the observation well G3 yields groundwater downgradient from this compartment. These two sampling points revealed B isotope ratios of less than –3. Shaft S13 yields leachate from landfill compartments younger than 1960, and wells KB1 and KB2 yield groundwater from Compartment III. These sampling stations revealed B isotope ratios between 3 and 9. Groundwaters from the wells RS65, RS68, and 92-23 are characterized by high δ^{11}B of +11.2 to +16.6‰. They appear to be influenced by a natural or anthropogenic B source, whose δ^{11}B value cannot be related to sodium perborate products because the values are higher than the ones reported by Swihart *et al.* (1986) and Oi *et al.* (1989). The B isotope ratio of well RS69 yields a value of about zero. We do not know yet the range of B isotope ratios in uncontaminated groundwaters.

We interpret the ^{11}B pattern as mixing of the waters from two or three sources, the leachate of Compartment II, maybe the leachate of one or more younger

Table 1 Boron isotopic compositions (^{11}B) and boron (B) concentrations, of leachate (S13, S15) and groundwaters (others). ^{11}B (means) relative to NIST SRM-951 standard (δ^{11}B = 4.00125). ^{11}B measured on an NBS design 6 inch of curvature 60° sector solid source mass spectrometer adopting a refined NTIMS technique (negative thermal ionization mass spectrometry; high analytical sensitivity, allowing the measurement of B samples in the ng l^{-1} range; 3–4 replicates analysed by direct loading procedure with an analytical uncertainty of ±0.4‰ ($2\sigma_{mean}$); Barth *et al.*, 1996; Hemming & Hanson, 1994). B analyses on ICP (inductively coupled plasma) analytical techniques made for comparison, with an analytical uncertainty of ±5%.

Sampling location	^{11}B (mean) (‰)	*n*	B (ppm)
S13	9.0	3	2.8
S15	–6.0	3	0.21
G3	–7.0	3	0.08
RS65	11.9	4	0.03
RS68	11.2	3	0.13
RS69	0.0	3	0.08
92-23	16.6	3	0.03
KB1	6.1	9	0.33

compartments, and the upstream groundwater. The results of well RS69, e.g. points to mixing between the S15/G3 leachate and other groundwaters. The values of the groundwater from Compartment III could partly originate from a plume of the compartment younger than 1960. The samples seem to be mixed in a way which partly correlates increasing ^{11}B values with either decreasing age of the respective solid waste compartments or with an increasing content of groundwater without bleach perborate. This interpretation of the results of the B isotope ratios supports the interpretations of the head measurements, the results of the flow model, the geophysical survey, and the results of the water chemistry.

CONCLUSIONS

From the above, we are convinced that B isotope ratios have the potential for an assessment of mixing rates of groundwaters contaminated by leachate from various compartments of old unlined landfills with predominantly domestic wastes. The next step is to carry out a systematic laboratory study on municipal solid waste materials. Furthermore, a survey on the natural background and possible seasonal variations of B isotope ratios in groundwaters is necessary.

Acknowledgement Thanks to Susanne Barth for the B isotope analyses, and to C. Annette Johnson, the leader of the project, for extensive discussions and a review of the paper.

REFERENCES

Barth, S. (1993) Boron isotope variations in nature: a synthesis. *Geol. Rdsch.* **82**, 640–651.

Barth, S., Hemming, N. G., Hanson, G. N., Hoehn, E. & Gercken, B. (1996) Boron isotope systematics in groundwater from a solid waste disposal site (Switzerland): a new tracer for anthropogenic contamination. V. M. Goldschmidt Conf., 31 March–4 April 1996. *J. Conf. Abstracts* **1**, p. 46.

Bassett, R. L. (1990) A critical evaluation of the available measurements for the stable isotopes of boron. *Appl. Geochem.* **5**, 541–554.

Bassett, R. L., Buszka, P. M., Davidson, G. R. & Chong-Diaz, D. (1995) Identification of groundwater solute sources using boron isotopic composition. *Environ. Sci. Technol.* **29**(12), 2915–2922.

Davidson, G. R. & Bassett, R. L. (1993) Application of boron isotopes for identifying contaminants such as fly ash leachate in groundwater. *Environ. Sci. Technol.* **27**(1), 172–176.

Hemming, N. G. & Hanson, G. N. (1994) A procedure for the isotopic analysis of boron by negative thermal ionization mass spectrometry. *Chem. Geol.* **114**, p. 147.

Hofer, M., Aeschbach-Hertig, W., Beyerle, U., Imboden, D. M., Kipfer, R., Johnson, A., Hoehn, E., Ulrich, A., Haderlein, S. B. & Hofstetter, T. (1997) Tracers as essential tools for the investigation of physical and chemical processes in environmental systems. *Chimia* **51**(12), 941–946.

Hoehn, E., Johnson, C. A., Huggenberger, P., Amirbahman, A. & Zweifel, H. R. (in preparation) Risk assessment and investigative strategies of old municipal solid waste landfills. For *Waste Manage. Res.*

Huggenberger P., de Iaco R. & Zweifel H.-R. (in preparation) Optimizing observation wells for process studies by combining geophysical and geochemical approaches. For *J. Contam. Hydrol.*

Kerndorff, H., Brill, V., Schleyer, R. & Friesel, P. (1985) Erfassung grundwassergefährdender Altablagerungen, Ergebnisse hydrogeochemischer Untersuchungen. *WaBoLu* **5**.

Matthess, G. (1973) *Die Beschaffenheit des Grundwassers, Lehrbuch der Hydrogeologie 2.* Gebr. Bornträger, Berlin.

Oi, T., Nomura, M., Musahi, M., Ossaka, T., Okamoto, M. & Kakihana, H. (1989) Boron isotopic compositions of some boron minerals. *Geochim. Cosmochim. Acta* **53**, 3189–3195.

Peter, A. (1997) Deponie Riet, Modellierung der stationären Grundwasserströmung mit ASM. Unpublished Manuscript, EAWAG, Dübendorf, Swizterland, and University of Freiburg im Breisgau, Germany.

Simmler, M. (1993) Deponie Riet: Betrachtungen zur Langzeitsicherheit. Diploma Thesis, ETH-Zürich, Switzerland.

Swihart, G. H., Moore, P. B. & Callis, E. L. (1986) Boron isotopic composition of marine and non-marine evaporite borates. *Geochim. Cosmochim. Acta* **50**, 1297–1301.

Uhlmann, K. (1991) The geochemistry of boron in a landfill monitoring program. *Groundwat. Monitoring and Remediation*, fall, p. 139.

Vengosh, A., Heumann, K. G., Juraske, S. & Kasher, R. (1994) Boron isotope application for tracing sources of contamination in groundwater. *Environ. Sci. Technol.* **28**(11), 1968–1974.