Testing a Geochemical Tool to Enhance Our Ability to Ensure Water Quality

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ABSTRACT

Chemicals transported in water can be used to our advantage. Natural and anthropogenically produced chemicals can be targeted to understand the way water behaves, this study targets boron. Water samples, from eleven locations, were collected from a small area of land adjacent to the Tarawera River in the North Island of New Zealand. Leachate from this area, a pulp and paper solid waste site, travels towards the river contaminating the water for downstream users. The results of the first phase of a temporal study analyzing boron isotope composition values (-5 - 14.4 %) used to characterise the water collected from different locations around the waste site are presented in this paper. They assist with understanding the potential relationships between water samples separating natural and anthropogenic contaminants in the area. This allows water quality authorities to be targetted in their approach to water quality management, through the use of this geochmical tool, and aids in ensuring water security in the region.

Keywords: water security, water quality, boron isotopes, tools

1 INTRODUCTION

The focus of this paper is to identify boron isotope composition (δ^{11} B) signatures for water collected at different locations within a pulp and paper solid waste site. It is the first phase of a temporal study. The ability to acquire signatures for each sample collected at different sampling locations within the small area (0.75 m²), which has different natural (geothermal) and anthropogenic (pulp and paper leachate) contaminants, provides the means of differentiating between contaminant sources. This information can be used manage to water quality more effectively by way of identifying the source of contamination and targetting specific activites to prevent the contamination of or, where necessary, remediate contaminated waterways.

Boron is a naturally occurring element that is found in freshwaters and contaminated water. Boron is used widely in household (e.g. detergents, pesticides, etc.) and commercial (e.g. borosilicate glass, fire retardents, fertilisers etc.) products. Once these products have been used or during the process of using them they are often combined with municipal water supplies and introduced into waste water which eventually enters natural waterways post-treatment. The treatment processes currently in use by municipal waste water treatment facilities are not equiped to remove boron.

During any journey boron takes through a hydrologic system it will be exposed to a range of chemical and physical conditions. The isotope ratio (¹¹B/¹⁰B) given by the natural isotopes of boron, ¹¹B and ¹⁰B, will change during this journey and this change provides the distinct chemical signatures that assists in differentiating between contaminant sources in water sampled from the different sampling locations.

Boron isotopes have been studied over 20 years in connection with water quality.[1-8] During this time sample preparation techniques have improved and scientific advances have lead to the enhancement of analytical instruments which has made it possible to obtain reliable and reproducible data.[9-11]

The utilisation of boron isotopes in studies for tracking water movements in groundwater systems is on the rise due to the continued success of employing this element as a natural tracer.[8] However, to the best of our knowledge, transitioning from the realm of research to the creation of a usable tool for water quality authorities in order to help manage water quality in their regions is underdeveloped.

The next phase in the research is to test a geochemical tool, the use of $\delta^{11}B$ signatures, to enhance our ability to ensure water security. The research discussed in this paper is work carried out in the first phase of creating such a tool in a New Zealand context.

This paper details: 1) the pulp and paper solid waste site water sampling locations; 2) δ^{11} B values obtained for water samples collected from eleven separate locations on the waste site; 3) the ability to assign δ^{11} B signatures and the effectiveness of using them to separate natural and anthropogenic contaminants in the waste site; and 4) how the resulting information fits into a plan to create a tool for water quality authorities to use to ensuring water security in a New Zealand context.

2 DISCUSSION

2.1 Pulp and Paper Solid Waste Site History

The pulp and paper waste site is in Kawerau which is situated within the Taupo Volcanic Zone (TVZ), a volcanically active region in the North Island of New Zealand, and the home of many geothermal resources currently being utilitised for power generation, thermal baths and as tourist attractions. The TVZ starts at the centre of the North Island and travels northeast across the land continuing offshore to White Island. Due to the geologic history most sediments found in the region are highly permeable pumiceous solids. The natural geology in the area of the pulp and paper solid waste site is characterised by a thin layer (0.5 - 1.5 m) of lacustrine clay topped with pumice.

The solid waste site was originally a lake, Rotoitipaku, which had geothermal outlets surrounding the southern end of this body of water, on top of which primary solid waste and general pulp and paper mill waste was deposited, commencing in 1972 and continues to this day. The pulp and paper solid waste site now hosts a large volume (in excess of 600,000 m³) of solid waste.[12]¹²

Due to the nature of the pulp and paper solid waste, the potential contaminants range from elevated concentrations of heavy metals to persistent organic pollutants. There are legitimate concerns that leachate from the site has been moving towards the Tarawera River on the eastern boundary of the waste site. The release of leachate from the site to the river could potentially contaminate the water for downstream users thus compromising this water resource and endangering the water security for the region.

The added complication with regard to contaminants enter fresh water bodies in the area of the solid waste site is the natural active geothermal activity present in the area and notably runs underneath the southern boundary of the waste site. Geothermal fluids carry naturally high concentrations of a selection of chemicals (*e.g.* boron, mercury, arsenic, *etc.*). Thus in an area with a complex system of contaminants ascertaining the source of chemical contaminants, either natural or anthropogenic, allows water quality authorities to manage the activities that impact the water resources in their region more effectively.

2.2 Water Sampling Locations

Eleven sampling locations were selected based on their position around and proximity to the pulp and paper waste site (see Image 1). A selection of surface water and groundwater features were included in the study as a means to determine if leachate was influencing fresh groundwater in shallow and deep bores found in close proximity to the site.

Table 1 explains the type of water sample collected at each location. L1-L3 are all in close proximity (~ 5 m) to the western boundary (WB) of the solid waste site. Although the major lateral water flow is away from the these three sites, travelling to the Tarawera River, the leachate from the waste site could potentially flow towards these water features therefore influencing the $\delta^{11}B$ values obtained. The leachate collected at L4 (see Image 1) is known to be a mixture of rainwater, as it is collected from an open air toedrain, and water pooling at the base of an embankment solid waste, approximately 10 m high. L5 is a pond filled with water overflowing from L1, however it has the added complication of being: 1) in closer proximity to the waste site (~ 2 m) than L1; and 2) it is level with the solid waste and has experienced overflow from the waste site uring periods of flooding.



Image 1: Picture of the pulp and paper waste site and sampling locations L1-L11.

Code	Sampling Locations	δ ⁿ B (‰)
L1	Surface Water Pond	14.4
L2	Groundwater Shallow Aquifer	4.6
L3	Groundwater Deep Aquifer	8.5
L4	Leachate	5.0
L5	Surface Water Pond	10.1
L6	Groundwater Deep Aquifer	-5.0
L7	Groundwater Shallow Aquifer	-1.1
L8	Groundwater Deep Aquifer	-4.6
L9	Surface Water River	-1.9
L10	Surface Water Aeration Pond	-1.5
L11	Surface Water River	4.0

Table 1: Codes for each water sampling locations, type of water sampled and $\delta^{11}B$ values for each sample.

Groundwater collected between the waste site and the river on the eastern side (L6-L8), both from shallow and deep aquifers, provides a snapshot of the water directly before it enters the river. The first river water sample (L9) collected was adjacent to a natural geothermal vent on the bank of the Tarawera River. L10 was a sample of the aeration pond water immediately prior to the being discharged. The second river sample (L11) was collected after the aeration pond water discharge point to the Tarawera River.

2.3 Boron Isotope Composition (δ¹¹B) Values

The boron isotope composition values for the water samples collected were distinctly different with $\delta^{11}B$ values ranging from -5.0 – 14.4 ‰ (see Graph 1). Therefore, within the 0.75 m² pulp and paper waste site area the range of $\delta^{11}B$ values was 19.4 ‰.



Graph 1: Range of δ^{11} B values for water samples L1-L11 per mil (‰).

By breaking down the values by sampling location and based on what is known about each location an interpretation of the connectivity between the water bodies sampled can be made. More importantly following on from the establishment of these connections boron signature values can be assigned to the water collected at each location at the end of winter in August 2010.

There is a clear difference between the positive values provided by the surface water samples (L1 and L5) along with the deep groundwater bore L3. Even given that L5 is predominantly feed by L1 there was a dramatic shift (-5 ‰) in the δ^{11} B value (see Graph 1) over a relatively short distance (~ 120 m). The δ^{11} B value for the leachate water sample (L4) was approximately the same as the L2 groundwater sample which suggests potential connectivity between the solid waste leachate and the shallow aquifer from which the L2 sample was taken.

The four sampling locations closest to the river (L6-L9) share negative δ^{11} B values however they can still be separated into two separate groups based on these values. The two deep groundwater samples taken from L6 and L8 had almost identical δ^{11} B values of -4.6 ‰ and -5.0 ‰. A similar trend was observed for the shallow groundwater sample L7 and the river water sample L9 suggesting connectivity between L7 and L9, and conversely a separation between the shallow aquifer and the deep aquifer in this area.

Samples L10 and L11, associated with the pulp and paper liquid aeration ponds, were further away from the actual solid waste site however the sludge collected from these ponds is periodically removed and distributed on top of the solid waste site as secondary waste. Any water associated with the ponds contributes to the chemical makeup of the solid waste and therefore the aeration pond water provides information about the chemistry of the water located in the waste site. L10 has a similar δ^{11} B value as both L7 and L9 whereas the δ^{11} B value for L11 increases to a level that more closely resembles the leachate water sample L4.

With the exception of water samples L10 and L11, italicised in Table 2, the water sampled can be roughly divided into four groups based on δ^{11} B values (see Table 2).

These groupings are coincidently aligned with their location on the waste site and have been separated under four geographical location on the waste site.

Groups	δ ¹¹ B Range (‰)
Western Boundary (WB)	
Surface Water Pond (L1 and L5)	10.1 - 14.4
Groundwater Deep (WB) (L3)	8
Solid Waste	
Leachate (L4)	5.0
Groundwater Shallow (WB) (L2)	4.6
Surface Water River (L11)	4.0
Eastern Boundary (EB)	
Surface Water River (Geothermal) (L9)	-1.9
Surface Water Aeration Pond (L10)	-1.5
Groundwater Shallow (EB) (L7)	-1.1
EB Deep Aquifer	
Groundwater Deep (EB) (L6 and L8)	-5.04.6

Table 2: Water samples divided into four groups based on the δ^{11} B values obtained for each sample.

The western boundary of the solid waste site is predominantly influenced by natural spring water. The solid waste site receives meteoric water and groundwater moving laterally from the west. Geothermal activity along the southern boundary potentially contributes to the chemistry of the water collected within the waste site. The groundwater along the waste site's eastern boundary (EB) is influenced by geothermal activity, leachate from the the solid waste site and potentially river water.

3 CONCLUSION & FUTURE WORK

Phase one results of the temporal study detailed in this paper provide a quick look at the ability to obtain distinct $\delta^{11}B$ values for water samples collected from different locations within a small area. The $\delta^{11}B$ values allow $\delta^{11}B$ signature ranges to be assigned to the different sources of contamination.

Assessing the consistency of $\delta^{11}B$ values over time to establish: 1) the reliability $\delta^{11}B$ signatures to identify sources of contamination; and 2) boron as a target chemical in water quality management programmes, is necessary in order to continue the process of creating a useful tool for water quality authorities to use.

The next phase is to carry out a temporal study using specific set of sampling locations and assess how consistent the δ^{11} B values are at each location over a six month period. In addition, incorporate more chemical data (*e.g.* major cations and anions) and physical parameters (*e.g.* pH, temperature, conductivity) into the discussion in order to provide water quality authorities with a comprehensive user-friendly tool by packaging the δ^{11} B values together with information they are already familiar using.

4 METHODS

Water sampling programme was carried out at the end of winter, August 2010. All relevant methodology is detailed in Sections 4.1 and 4.2.

4.1 Sample Collection and Preservation

Every water sample was collected in a clean HDPE containers (1 L) or a clean HDPE bailer (1 L) rinsed three times with the source water. Each rinse was disposed of downstream or away from the sampling location. The fourth volume of water taken from the source was retained as the water sample for that location. Each water sample was filtered through 0.45 μ m Millipore filter into a 125 mL HDPE bottles.

4.2 Analytical Procedures and Instruments

Sample preparation for boron isotope analysis: The volume of each sample required for boron isotope ratio analysis was calculated using boron concentrations. Samples were passed through cation exchange resin columns and an aliquot of the eluent was used for isotope analysis on a thermal ionisation mass spectrometer on negative mode (N-TIMS).

Instruments: Boron isotope ratios $({}^{11}B/{}^{10}B)$ were analysed using N-TIMS. The boron isotope composition values were calculated using Equation 1. (NIST SRM – 951 Standard was the boron standard reference material used.)

 $\delta^{11}B (\) = \{ [(^{11}B/^{10}B) \text{sample}/(^{11}B/^{10}B) \text{NIST SRM} - 951 \\ \text{Standard}] - 1 \} \times 1000$ (1)

Equation 1: Boron isotope composition calculation.

ACKNOWLEDGEMENTS

The Foundation for Research Science & Technology in New Zealand need to be acknowledged for providing the funding that made this research possible. I would also like to give a special thank you to Professor Avner Vengosh, Nathaniel Warner and their research group at the Earth and Ocean Science Division of the Nicholas School at Duke University, USA, for their unwavering and generous support.

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