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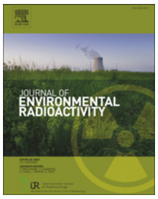

Environmental isotopes and major ions for tracing leachate contamination from a municipal landfill in Metro Manila, Philippines

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ABSTRACT

The surface water and groundwater sources in the vicinity of a major municipal landfill in Metro Manila, Philippines were investigated to determine contamination by landfill leachate. Tritium, stable isotopes of hydrogen and oxygen, and major ions in the leachate and freshwater within the landfill environment were determined. The leachate contained elevated tritium activities and high concentrations of sodium, chloride, potassium, and calcium. The concentrations of tritium and the leachate related ions in the affected surface water were significantly higher than the non-impacted water and correlated strongly with distance from the leachate source, following a negative exponential relationship, providing evidence of leachate transport along the affected surface water. Enrichment in deuterium was exhibited by leachate in the holding pond but not by the effluent leachate. The stable isotope signature of leachate is masked in the surface water due to dilution by stream water. Dilution similarly masked the effect of leachate in the shallow groundwater which was strongly influenced by precipitation. Evidence of leachate contamination in the deep groundwater was sporadic. In isolated cases, elevated tritium concentrations coincided with enrichment in deuterium. In the same case, leachate related ions, Na, Ca, Mg, and Cl, varied with rainfall but generally increased from 2003 to 2009. The effect on the groundwater of methane produced within the landfill was seen in the depletion in deuterium in groundwater in the drier months.

1. Introduction

One of the main environmental concerns related to the operation of solid waste disposal sites is the leaching and transport of contaminants into nearby surface water and groundwater. The Montalban Landfill, north of Metro Manila, commenced operation in 2002 and currently takes in the bulk of the generated solid waste of Metro Manila. While it is referred to as a sanitary landfill, the Montalban disposal facility does not have the appropriate containing structure and lining to prevent runoff and seepage of leachate outside of the landfill. A report on the interim evaluation of the site (National Institute of Geological Sciences, 2002; unpublished report) noted that the high density polyethylene (HDPE) liner, installed along the sides and at the base of the landfill was only 1.5 mm thick and already showed evidence of rips and seam parting. Leachate produced by the waste was being channeled through ordinary PVC pipes, not HDPE. These were buried in gravel material to facilitate the movement of the leachate from the waste to the temporary storage tanks which relied solely on gravity. The uncovered dumped wastes, unsegregated and uncompacted, has reached a considerable height that it could be seen even from the banks of the nearby river which was about 50 m below the facility. Moreover, a concern arises from the selection of the site, this being situated on a mountain ridge with a fractured volcanic geology, close to the Marikina Fault (Woodfields Consultants, Inc., 2002, unpublished report). Furthermore, surface water affected by the landfill comprises one of the headwaters of the Marikina River system which drains the main river systems of Metro Manila.

The assessment of environmental risks associated with leachate contamination of water resources requires the understanding of the transport of contaminants along the river networks and into the

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Abbreviations: IAEA, International Atomic Energy Agency; LMWL, local meteoric water line; NIGS, National Institute of Geological Sciences; PNRI, Philippine Nuclear Research Institute; PCHRD, Philippine Council for Health Research and Development; RCA, Regional Cooperation Agreement in the Asia Pacific Region; WMO, World Meteorological Organization; TU, Tritium units.

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aquifer. Conventional contaminants commonly measured in waste stream such as total dissolved solids (TDS), total suspended solids (TSS), hardness, alkalinity, chloride, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), and common inorganic ions, may not be effective in environments where the background levels of many of these chemical indicators are already high or when there are other sources of contamination that pre-date the landfill (Looser et al., 1999). The use of multivariate descriptive statistical analyses of several inorganic and organic parameters somewhat improves the recognition of leachate contamination in groundwater in fractured carbonate aquifer, still, the reliability of leachate impact identification is uncertain and cannot be expressed in terms of precise probabilities. (Barker et al., 1988). Measurements of pH and conductivity and other common leachate indicators may be similarly compromised by contributions from natural and other anthropogenic sources.

In the Philippines, the effect of an open dumpsite on the groundwater quality in selected communities in Metro Manila was investigated using pH, TSS, TDS, total coliform, conductivity, salinity, nitrate-nitrogen, sulfate, color, total chromium, total lead, and total cadmium as indicators (Sia Su, 2008). Measurements of these parameters in groundwater sources delineated to be “with dumpsite” and “without dumpsite” impact, showed significant differences only in the TDS, conductivity, salinity, and sulfate concentrations. Monitoring conducted during the early stage of operation of the Montalban landfill included the measurement of parameters covered by the effluent standards and drinking water standards set by the environmental regulatory agency in the Philippines. Data obtained for 2003 for the leachate effluent and surface water showed that none of the parameters exceeded the standard limits (Woodfields Consultants, Inc., 2002, unpublished report). However, xenobiotic organic pollutants (XOCs), such as aromatic hydrocarbons, halogenated hydrocarbons, pesticides, and phenols, are not monitored due to the labor and cost —intensive sampling and analysis needed.

This study investigates the utility of environmental isotopes in water, hydrogen and oxygen, in conjunction with major ions in verifying leachate contaminant migration and surface water—groundwater interaction in the water systems affected by the landfill. The results will be useful in improving the assessment of the effectiveness of leachate management in the facility and for other existing waste disposal facilities.

2. The study area

The municipality of Rodriguez, which hosts the landfill, is located northeast of Metro Manila, Philippines, in the province of Rizal, within latitudes 14° 46′ 50″ N to 14° 40′ 11″ N and longitudes 121° 06′ 30″ E to 121° 10′ 12″ E (Fig. 1). The landfill is located in the northernmost portion of the Marikina Valley, where elevation is from 50 to 260 m above sea level. The headwater of the Lukutan River is located in the immediate vicinity of the landfill. This river is a tributary stream of the Montalban River which is a part of the

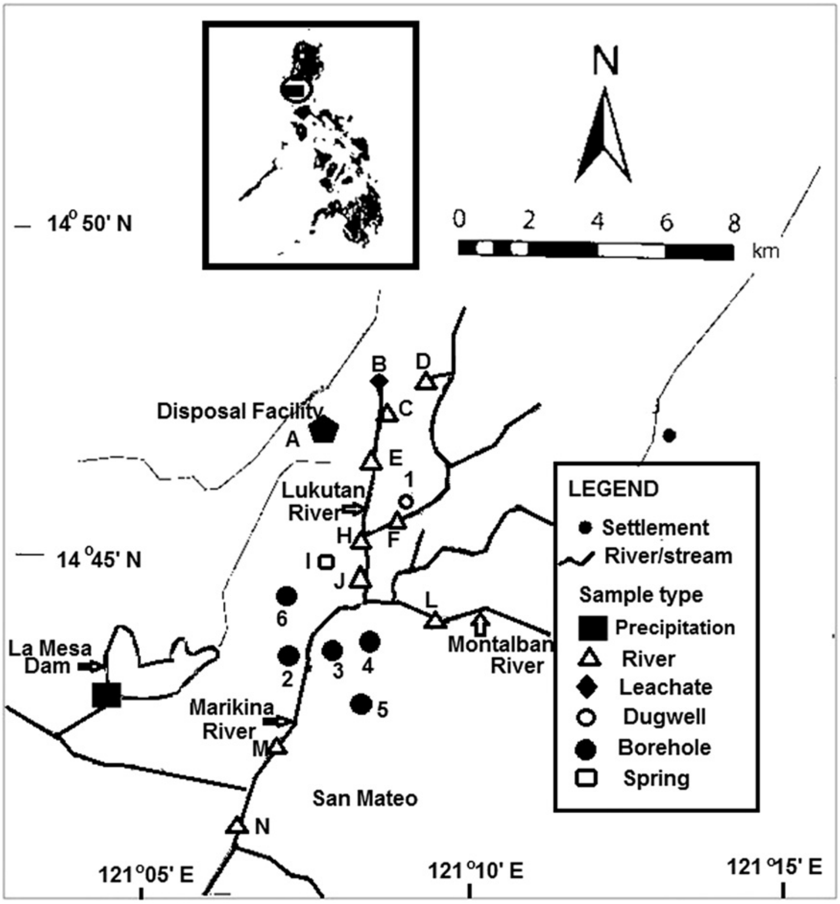

Fig. 1. The study area showing the sampling locations: A - landfill; B - Leachate from drainage pipes at the foot of the landfill; C - Lukutan River, leachate discharge point; D - small stream joining the Lukutan River; E - segment of Lukutan, landfill side; F - stream not affected by landfill; **1** - dugwell; H - confluence of landfill affected stream and F; I - spring; J, midstream of confluence; L - Montalban River, **2**, **3**, **4**, **5**, deep production wells; **6** - deep community well; M — Marikina River at San Mateo; N segment of Marikina River after Payatas stream.

northern tributary of the Marikina River system. The Marikina River system drains the whole Pasig and Marikina River watershed.

Two aquifer systems were identified in the Upper Marikina Valley, a shallow aquifer system consisting of permeable layers of alluvial deposits found at depths ranging from 10 to 30 m and a deep aquifer system that is dominated by permeable layers of the Guadalupe Formation, mainly consisting of layers of volcanic tuffs. Wells with depths of more than 200 m tap this aquifer. Separation of these two aquifer systems is not distinct as the two maybe vertically and horizontally connected through semi-permeable layers. The presence of an unconfined aquifer system was indicated by geophysical test conducted on a well in the vicinity of the landfill. (Woodfields Consultants, Inc., 2002). The results of the resistivity survey within the landfill area revealed that some sections of the property are locally faulted and that there are sufficient thickness of fractured volcanic and weathered portions of the same rock sequence make the materials potentially highly permeable. (Woodfields Consultants, Inc., 2002).

Climate in the study area is classified as Type 1 under the Modified Coronas Climate Classification. It is characterized by two pronounced seasons: dry, from December to April, and wet, from May to November with maximum rains generally occurring between July and September. The driest periods, with monthly average rainfall below 100 mm occur from January to April. The average annual rainfall recorded in the period 2003 to 2008 is 2100 mm with a maximum of 2700 mm in 2006.

3. Materials and methods

3.1. Sample collection

Field investigations were conducted from 2003 to 2008. Two sampling campaigns, before and after the rainy season, were undertaken each year, whenever possible. Sampling locations are indicated in Fig. 1. Four operational production wells (**2**, **3**, **4**, and **5**) with depths ranging from 190 m to 240 m, and a borehole (**6**) supplying a private subdivision, were sampled initially to get a general picture of water quality and isotopic characteristics of the water sources in the area. It should be noted that samples from these sources are mixtures of water originating from the multi-layered aquifers. Samples were collected from a shallow well along the Lukutan River bank (*1*). Another sample comes from a spring downstream of the landfill (*I*). Samples from the Lukutan River were collected downstream of the landfill at points *C*, *D*, *E*, *F*, *H* and *J*. The Montalban River which joins the Lukutan River towards Marikina River is sampled at point *L*. Leachate was collected from the holding pond (*A*) while effluent leachate which is discharged to the Lukutan River was collected at Point *B* from the discharge pipes. Points *D* and *F* represent streams not affected by leachate. Lastly, samples were also collected from the Marikina River at points *M* and *N*.

Groundwater samples were collected from the main faucet or valve of production wells and at the end of the discharge pipe of dug wells, initially, in a 10 L plastic bucket. Water was allowed to continuously flow into and out of this container while conductivity, pH, and temperature were measured and while samples for isotopic analysis were being collected. Surface water samples were obtained by submerging the sampling bottles into the water at areas where there is an active, but not turbulent flow. Water samples were filtered through 0.45 μm Millipore cellulose filters in the laboratory and analyzed as soon as possible for anions. Samples for cations were acidified to pH 2 after filtration and kept at 4–8 °C until ready for analysis.

Samples for isotopic analysis were collected in double capped PE bottles, with no headspace and immediately sealed tight to prevent exchange with the atmosphere. These were stored in the refrigerator until ready for analysis.

3.2. Tritium analysis

Tritium was determined in the Philippine Nuclear Research Institute (PNRI) as described in another paper (Mendoza et al., 2010). It involves initially performing electrolytic enrichment of tritium then measuring the tritium decay events via β-particle counting emission using a TRICARB 3170 TR/SL liquid scintillation counter. Prior to electrolytic tritium enrichment, water samples were purified by distillation to prevent corrosion of the cell anodes. Tritium activity was calibrated using a NIST SRM 4926E. Enrichment factors of around 25 were generally obtained. Tritium value is expressed as 'TU' (tritium unit), which represents the ratio of tritium to common hydrogen atoms. (1 TU = 10^{-18} [^{3}H]/[^{1}H] or 0.118 Bq/L or 3.19 pCi/L of water) (Mook, 2000). The method yielded a minimum detectable concentration of 0.3 TU at 95% confidence level.

3.3. Stable isotope analysis

Isotope ratio mass spectrometry of hydrogen and oxygen isotopes in water was performed at the Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan. Isotopic compositions are given as δ values, the relative deviations with respect to the standard value, the Vienna Standard Mean Ocean Water (VSMOW). Signifying R as the abundance ratio of the isotopic species, i.e. ^{2}H/^{1}H or ^{18}O/^{16}O, respectively, δ is defined by:

$$\delta = \left[R_{\text{sample}}/R_{\text{VSMOW}}\right] - 1, \tag{1}$$

Where δ is reported in ‰ (permil, equivalent to 10^{-3}). For deuterium-hydrogen, (^{2}H/^{1}H), δ^2H is used; for ^{18}O/^{16}O, the notation is δ^{18}O. The reported maximum uncertainty of each measurement is ±0.1‰ for δ^{18}O, and ±1‰ for δ^2H.

3.4. Major ion analysis

Major ions (Na, K, Ca, Mg, Cl, and SO_4), in water and in leachate were determined using a Shimadzu LC 20 AD liquid chromatographic system connected to a Shimadzu CDD 10 AVP conductivity detector. The mobile phase for cation analysis was a buffer solution of L-tartaric acid, dipicolinic acid and boric acid, while a buffer solution of phthalic acid and tris (hydroxymethyl) aminomethane was used for anion analysis. Concentrations were calibrated against a mixed ion standard traceable to NIST standard reference material.

4. Results and discussion

4.1. Tritium in leachate

The profile of tritium concentrations measured in the leachate and surface water in the study area is shown in the histogram in Fig. 2. The minimum and maximum values for each water group incorporate the lower and upper level uncertainties, respectively, of the measurements. Data represent results obtained within the period of 2003 and 2008, although most of the data are from samples collected in 2007–2008. Leachate data represent those from 2006 to 2008.

The levels of tritium in the leachate are two orders of magnitude higher than the tritium in precipitation in the last ten years, and even higher than the peak concentration reached in 1964 of around 120 TU in Manila that is attributed to the atmospheric H-

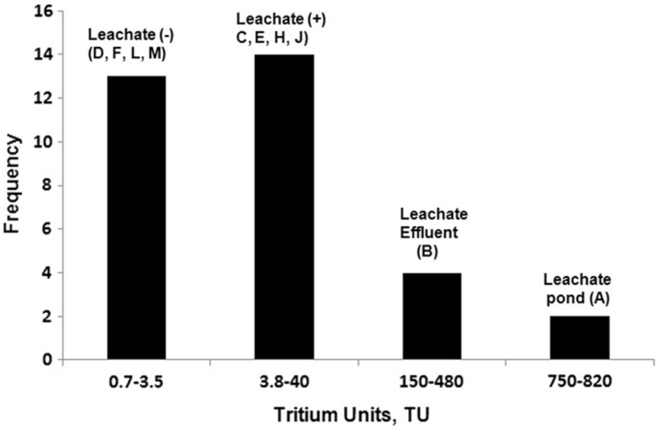

Fig. 2. Profile of tritium concentration in leachate and surface water. Results represent samples collected in the period 2003–2008, in TU (tritium unit). Leachate (+) indicates leachate impacted water. Leachate (−) indicates unaffected water. Letters in parentheses refer to the sampling points included. The minimum and maximum values for each water group incorporate the lower and upper level uncertainties, respectively, of the measurements.

Table 1
Concentration profile of major ions in leachate and surface water in 2007–2008. Leachate (+) indicates leachate impacted water. Leachate (−) indicates unaffected water. Mean values are in parentheses for ***n*** number of samples. Letters in parentheses refer to the sampling points included in the data set.

Element	Leachate effluent (*B*)	Surface water (*C*, *E*, *H*, *J*) leachate (+)	Surface water (*D*, *F*, *L*) leachate (−)	Marikina river (*M*, *N*)
n	2	8	5	6
Na	94–225 (159)	8–28 (16)	7–8 (8)	4–19 (10)
K	50–105 (78)	2–5 (3)	1–2 (1)	1–6 (3)
Ca	230–294 (262)	33–80 (45)	32–40 (35)	20–52 (38)
Mg	65–75 (70)	(9–26) (14)	4–18 (10)	4–9 (6)
Cl	462–575 (469)	8–204 (68)	1–5 (3)	3–38 (16)
SO4	10–12 (11)	10–34 (15)	6–48 (17)	5–18 (13)
HCO3	287–320 (304)	186–300 (249)	110–287 (206)	132–560 (258)

bomb tests between 1954 and 1963 (IAEA/WMO, 2010). Annual means of tritium concentrations in precipitation from 2003 to 2007 obtained from the GNIP station in Quezon City, the nearest station from the study area, ranged from 1.3 TU to 2.5 TU (IAEA/WMO, 2010).

Tritium has similarly been reported to occur in exceedingly high concentrations in leachate from municipal solid waste landfills in the US and in the UK, (Hackley et al., 1999; Kerfoot et al., 2003; Mutch et al., 2008), in Brazil (Bandeira et al., 2008), in Australia (Hughes et al., 2010), and in Korea (Park et al., 2005) well above those observed in global precipitation. The high levels of tritium make it potentially useful for tracing leachate contamination.

Anthropogenic sources of tritium, aside from nuclear weapon detonations and nuclear power plants, which are non-existent in the Philippines, are manufactured products that could be disposed as municipal waste such as gaseous tritium light devices (GTLDs), watches and clocks containing GTLSs, luminous paints, compasses, and electron tubes (Hughes et al., 2010; Mutch et al., 2008). Similar waste products in the Philippines may find their way into this municipal landfill considering that waste segregation has not been successfully implemented yet.

4.2. *Tritium in surface water*

Tritium in surface water is expected to reflect the concentration in precipitation that feeds it. The tritium concentrations in surface water presumed to be unaffected by leachate from points *D*, *F*, *L*, and *N* in 2007 and 2008 ranged from 0.7 to 3.1 TU. Tritium measured in precipitation within this period ranged from 1.5 TU to 2.7 TU. On the other hand, the leachate impacted waters yielded tritium values ranging from 3.8 TU to 46 TU, significantly higher than concentrations in precipitation and unaffected surface water. In the wet season, spring samples exhibited tritium similar to that of rainfall, 1.7 TU, then decreased, due to contribution of baseflow in the dry months to 0.8 TU.

4.3. *Major ions in leachate and surface water*

The concentrations of the major ions in effluent leachate, and surface water collected in 2007 and 2008 are presented in Table 1. Samples collected from the discharge pipes are believed to be more representative of the whole landfill since they average the leachate composition from different sections of the landfill. The concentrations of Na, K, Ca, Mg, Cl, and HCO_3 in leachate are significantly higher than those detected in the freshwater sources in the study area within the same period. The low sulfate concentration in the leachate is due to microbial reduction of SO_4^{2-} to S_2^2 and is indicative of the landfill being in the methanogenic phase (Christensen et al., 2001). Examination of the hydrochemical data shows the potential use of these major ions as indicators of leachate contamination. Ion concentrations of Ca and Mg are affected by pH and concentrations of other solutes such as dissolved organic matter. Furthermore, they are subject to sorption, complexation and precipitation (Christensen et al., 2001), which may lessen their utility as tracers. Na and Cl have been shown to be conservative, less affected by such processes, thus may be more useful as tracers.

In Table 1, surface water were classified to delineate the potentially landfill impacted waters from those that are not. The presumed unaffected surface waters, collected from *D*, *F*, and *L*, indicated as landfill (−), are low in Na, K, and Cl and show a narrow range of variability in the concentration of these ions. On the other hand, the concentrations of ions in the presumed landfill impacted surface waters, from points *C*, *E*, *H*, and *J*, indicated as landfill (+), are shown to be higher. The concentrations of Na, Cl, Ca, and Mg in these two groups of water were shown to be significantly different at 95% confidence level by the Kruskal–Wallis Test. The wider variability in the concentration of the leachate impacted waters pinpoints to a point source of contaminant that brings about variation with spatial distribution

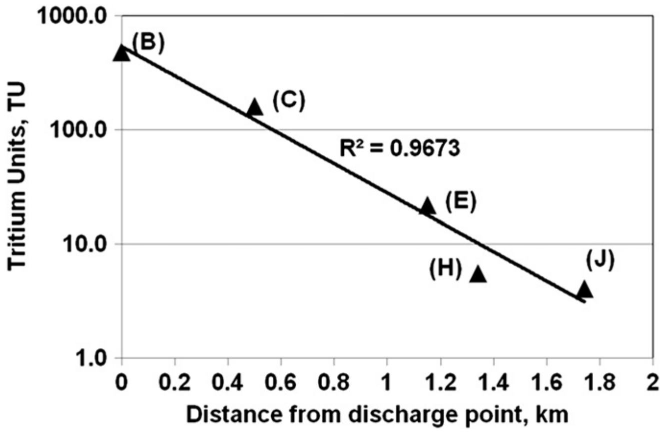

Fig. 3. Spatial distribution of tritium in leachate affected surface water. Log-linear plot of tritium concentration, in Tritium units (TU), against distance from leachate source in the Lukutan River in October 2007. Letters in parentheses refer to the sampling points.

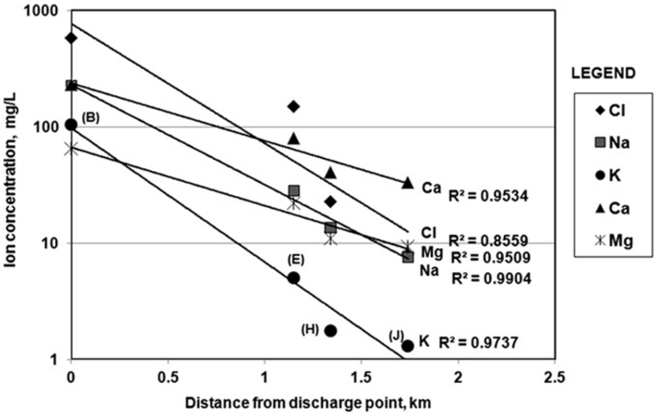

Fig. 4. Spatial distribution of major ions in leachate affected surface water. Log-linear plot of concentrations, in mg/L, against distance from leachate source of Na, K, Mg, Ca, and Cl in the Lukutan River. Samples were collected in October 2007. Letters in parentheses refer to the sampling points.

and season. The Marikina River, (points *M* and *N*) draining water from various sources, exhibit intermediate values of ion concentrations.

4.4. *Leachate transport in surface water*

The transport of the leachate contaminants along the Lukutan River in October, 2007 can be traced from the concentration gradient of tritium along the stream as seen in Fig. 3. The relationship of tritium concentrations with distance from the effluent source along the Lukutan River downstream of the landfill follows a negative exponential curve that fits a general hydrodynamic dispersion model for conservative toxicants in flowing streams (Chapra, 1997). The contaminant plume along the river reaches approximately 1.5 km from the source. Extrapolation of the line indicates that the tritium concentration approaches baseline levels at around 2 km from the discharge point. At sampling station *M*, along the Marikina River, about 10 km from the source, tritium was 2.5 ± 0.2 TU. This indicates complete dilution of the leachate at this point, its signature indistinguishable from uncontaminated surface water. During abnormal rain episodes, such as what occurred in 2003, where continuous rains have caused flooding in the Marikina Valley, the recorded tritium at point *J* of the Lukutan River was 38.4 ± 0.8 TU.

Similar behavior, as shown in Fig 4, was observed for the inorganic ions, Na, K, Ca, Mg, and Cl, which were found to be present in high concentrations in the effluent leachate than in natural waters. The dilution curves show better sensitivity with Na, K, and Cl as transport tracers than Ca and Mg. It appears from the graph that contaminant concentrations are attenuated to baseline levels at around 2 km from the source of contaminant.

4.5. *Tritium as an indicator of groundwater vulnerability to leachate contamination*

When water infiltrates the ground, it becomes isolated from the atmospheric tritium source, and its tritium concentration decreases over time due to radioactive decay. The tritium concentration of groundwater, therefore, reflects the time the water has been underground. Tritium is considered to be non-sorbing (conservative) during movement through porous media. This attribute, and the relatively low levels at which it can be reliably measured make tritium one of the most widely used tracers in groundwater studies. (Michel, 2005; Plummer, 2005).

The trends in the tritium concentrations in the groundwater in Rodriguez, the municipality immediately downstream of the landfill are shown in Fig. 5 for the period 2003 to 2008. The tritium concentrations in the shallow groundwater (Well **1**) indicate the immediate effect of rainfall. In the rainy season, infiltration from the river and/or directly of precipitation with modern tritium causes the tritium level in the well to rise. It subsequently decreases in the dry season as surface water contribution decreases. The tritium concentrations are not sufficiently high to indicate the effect of leachate. Although an increase in leachate load may be happening in the rainy season, at the same time, dilution masks this effect. Moreover, transformation reactions for both natural and anthropogenic constituents in riparian zones can be highly variable temporally and spatially with changes in hydrologic conditions in shallow environments (Lorah et al., 2009).

The deep groundwater, expected to contain low or no tritium, shows a wide variability in its tritium concentration. Wells **5** and **6** reflect background tritium throughout the period (0–0.4 TU). Tritium in wells **2** and **4** now reflect background levels but in September 2003, these wells showed elevated tritium concentrations. Well **4** registered 5.8 ± 0.4 TU of tritium, much higher than the mean value of 1.9 TU registered by precipitation in 2003. (IAEA/WMO, 2010). Well **6**, situated farther northwest of the production well field, registered a background tritium concentration of 0.4 TU in this period. This episode coincides with

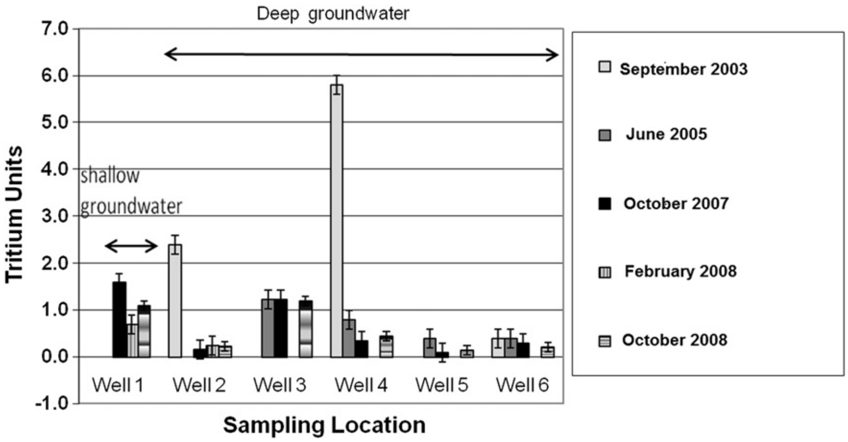

Fig. 5. Trends in the tritium concentrations, in Tritium units (TU), in shallow and deep groundwater in Rodriguez, the municipality immediately downstream of the landfill. Error bars represent the propagated uncertainties in the measurement.

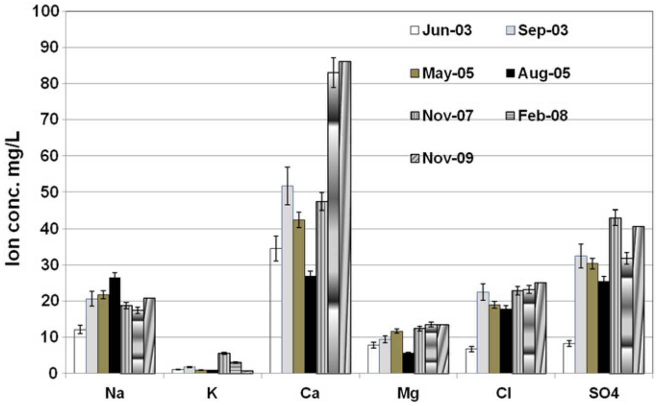

Fig. 6. Seasonal variations in the composition of major ions in deep groundwater. Na, K, Mg, Ca, and Cl (in mg/L) of deep groundwater (Well **3**), near the Lukutan River. Error bars represent the propagated uncertainties in the measurement.

the significant increase in tritium and in the electrical conductivities of water from the Lukutan River. A significant increase in the concentrations of Na, K, Ca and Cl similarly occurred in the groundwater from well **4** in the same period. The increase in tritium in wells **2** and **4** can be due to the rapid infiltration and percolation of leachate impacted surface water induced by the flooding that occurred then. The flooding may also have induced pollutants from other sources, particularly those being discharged to the Marikina River, infiltrating the shallow permeable alluvial aquifer. Direct loading from the landfill of the underlying aquifer could also be considered, made possible by migration through the fractured rocks that characterizes the landfill geology. Well **3**, which unfortunately, has no tritium data available for 2003, has constantly shown tritium that is modern from 2005 to 2008.

Assessment of the concentrations of the leachate related ions, in well **3** reveals a consistent increase in these ions in the aquifer as the rainy season ensues as seen in Fig. 6. Notwithstanding seasonal variations, a general increase in the major ion concentrations, with the exception of K, from 2003 to 2009, is noted. Relating this to the increase in the concentration in this well of most of the signature ions in the leachate (Na, Ca, Mg, Cl), we can infer that this is due to diffusion of the leachate plume in the aquifer to this point. K has a high affinity for ion exchange and will typically be the most retarded of the cations in the leachate plume. Although Ca and Mg have high affinity for ion exchange, they typically are the dominating base saturation ions, thus, will move with the leachate front (Christensen et al., 2001). Water quality trends observed in wells **2** and **4** lacked the consistency observed in Well **3**. The migration of leachate within the fractured rocks appears to be sporadic.

4.6. Stable isotopes in freshwater and leachate

The stable isotope compositions of water in the freshwater sources and leachate (δ^2H and $\delta^{18}O$) are plotted against the local meteoric water line (LMWL), (Castañeda et al., 2007). The LMWL shows the correlation between the isotopic composition of hydrogen and oxygen in local precipitation. Deviation from the line indicates mixing or isotopic exchange with other sources. In Fig. 7, the leachate from the pond is highly enriched in deuterium and moderately enriched in ^{18}O compared to the river water. Enrichment in the hydrogen isotopic signature in leachate during the methanogenesis process has been observed (Hackley et al., 1996; Humprey, 2004; North et al., 2006) It was observed that methanogenesis does not affect the oxygen isotopic composition (Morasch et al., 2002]). Isotopic fractionation occurs with the preferential association of lighter hydrogen isotope with the gas phase, CH_4, leaving the heavier isotope in the liquid phase.

Hydrogen isotope ratios, δ^2H, determined in the leachate were +16‰ in the dry season and +6‰ in the wet season. Because it is highly enriched compared to that in freshwater, δ^2H can be a good tracer for leachate contamination. However, due to the dilution of leachate with stream water, the isotope signature of the leachate is typically masked. As seen in the Fig. 7, the leachate impacted river water is hardly distinguishable from the unaffected waters.

The observed trend in the stable isotopic compositions of groundwater in 2003 can be related to the chemical and tritium data. In Fig. 8, the observed variation in the isotopic composition of the deep groundwater strongly indicates the impact of leachate signature on these wells, particularly wells **2**, **3**, and **4**. In the previous section, we have shown wells 2 and 4 to exhibit spikes in tritium concentrations in the wet season in 2003. The vertical displacement above the LMWL (enrichment dominantly due to deuterium) indicates leachate migration directly from the landfill within the fractured bedrocks. It is further noted that the magnitude of displacement is directly related to the magnitude of tritium spikes (comparing wells **4** and **2**). Leachate transported through the river will not give this distinct signature due to dilution as noted earlier. The isotopic compositions of the Lukutan River in the rainy season still lie along the LMWL even if leachate signature was

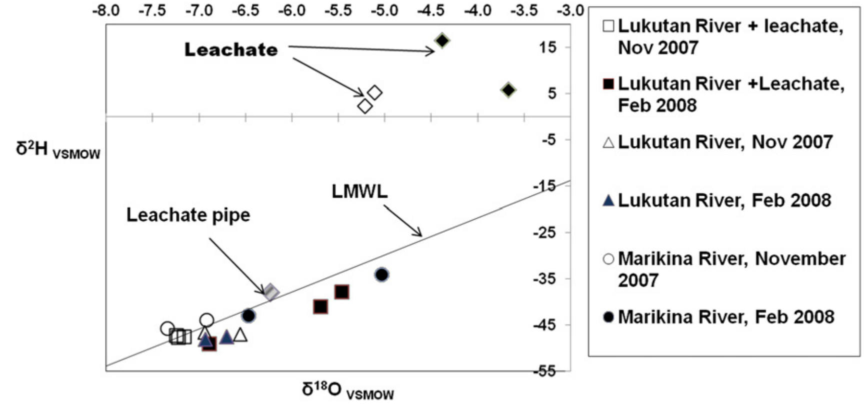

Fig. 7. Hydrogen and oxygen isotopic composition of freshwater and leachate in relation with the local meteoric water line (LMWL). Isotopic compositions are given as δ values, the relative deviations with respect to the standard value, the Vienna Standard Mean Ocean Water (VSMOW). δ is reported in ‰ (permil, equivalent to 10^{-3}). Filled diamonds represents leachate from the pond while unfilled diamonds represents leachate runoff directly from the garbage mound, obtained in the wet and dry seasons. The less negative values are obtained for samples collected in the dry season.

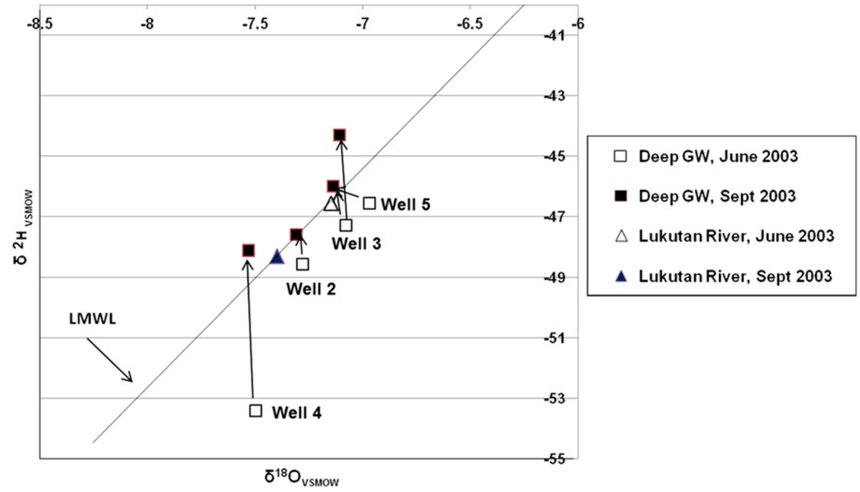

Fig. 8. Hydrogen and oxygen isotopic composition in relation with the local meteoric water line (LMWL) of deep groundwater in Rodriguez and the Lukutan River in 2003. Isotopic compositions are given as δ values, the relative deviations with respect to the standard value, the Vienna Standard Mean Ocean Water (VSMOW). δ is reported in ‰ (permil, equivalent to 10^{-3}). Arrows connect samples from the same boreholes to show the displacement affecting the hydrogen isotope composition, from early to late monsoon. Enrichment in deuterium in the late monsoon is attributed to infiltration of leachate contaminated water. Numbers in parentheses refer to the sampling points.

strongly seen from the tritium value. This provides evidence of leachate migration to the southeast of the landfill site to about 5 km possibly along major fractures oriented in that direction. It has been possible to estimate groundwater velocities of about 100 m/day for fractured basalt rocks.

The isotopic compositions of water from the deep wells in the drier months are generally below the LMWL, most apparent for well **4**. Such displacement has been explained to be caused by methane migration from the landfill to the groundwater through fractures in the underlying rocks (Brizmohun and Sacchi, 2009). Methane degassing will occur when total gas pressure exceeds hydrostatic pressure and capillary effects can be overcome (Yager and Fountain, 2001), thus, the observed signature in the drier months. The characteristic δ^2H of methane formed in landfill was reported to be highly depleted in deuterium, −304‰ (van Breukelen et al., 2003). Exchange with methane will cause depletion in deuterium in the groundwater and consequently, a negative vertical displacement in the δ^2H - δ^{18}O plot.

5. Summary and conclusions

The major ion composition, elevated tritium levels, and the signature isotopic composition of leachate have facilitated the tracing of leachate transport in the affected environment. The results obtained from these tools corroborated and provide useful evidence of leachate migration in the surface water and the vulnerability to contamination of groundwater in the vicinity of the municipal landfill. While the signals from the conservative inorganic parameters may be obscured due to geogenic and anthropogenic sources, as well as other processes such as dilution and retardation, the tritium signature in the leachate provides a sensitive and confirmatory evidence of leachate contamination owing to the lack of other tritium generating sources. It can be used further to calibrate and fine tune contaminant flow models in the river that may be useful for management and mitigation purposes. The detection of tritium in concentrations similar to and even above the present day concentrations in the deep groundwater indicates hydraulic connection with surface water and its susceptibility to contamination from the surface including leachate from the landfill.

While the stable isotopic signature of leachate is obscured in surface water and less useful in understanding contaminant transport in this medium, it has provided a better understanding of leachate migration to the groundwater. The sporadic occurrence and the apparent rapid infiltration in the groundwater can be attributed to the inherent complex nature of flow in fractured rocks. Further work in the area is required to evaluate the use of isotope data to quantitatively assess the relative contributions of leachate and landfill gas contaminant to groundwater contamination. Further evaluation of the spatial and temporal variability in the isotopic composition of leachate tritium and isotopic composition of dissolved inorganic carbon in leachate would be useful in making quantitative assessments.

This work should provide impetus for regulatory agencies to evaluate further the impact of long term operation of the facility.

Conflict of interest

None declared.

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