Identification of sources and processes in a low-level radioactive waste site adjacent to landfills: groundwater hydrogeochemistry and isotopes

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Multiple tracer-element and isotope approaches were applied at a 1960s-era low-level radioactive waste burial site located in the Lucas Heights area on the southwest urban fringe of Sydney, Australia. The site is situated among other municipal and industrial (solid and liquid) waste disposal sites causing potential mixing of leachates. Local rainfall contains marine-derived major ion ratios that are modified during infiltration depending on waste interactions. The local geology favours the retention of contaminants by ion-exchange processes within the clay-rich soils and the shale layer underlying the burial site. Local soils experience periodic infiltration and wetting fronts that can fully saturate the waste trenches (bathtub effect) while surrounding soils are mostly unsaturated with discontinuous perched lenses. Within the trenches, the degradation of organic matter results in localised methanogenesis, as suggested by enriched $\delta^2$H and $\delta^{13}$CDIC values in adjacent subsurface water. Movement of contaminants from the trenches is indicated by Na, Br and I concentrations, variations in $^{87}$Sr/$^{86}$Sr, enriched $\delta^{13}$CDIC values and evolution of $\delta^{34}$S of dissolved sulfate in perched water bodies above the shale. Although transport is limited by the low transmissivity of the clay-rich soils, migration and mixing processes are indicated by the variation of concentrations with distance from the trenches, disappearance of $\delta^2$H enrichments, mixing with other sources of Sr and sulfate isotope fractionations. The depth distribution of waste-derived contaminants (specifically $^3$H and Be) between the perched water surrounding the trenches, and the underlying shale and sandstone layers, indicates limited downward transport of contaminants. Past removal of the shale layer in an adjacent site, Harrington’s Quarry, has facilitated the mixing of some municipal waste leachates (characterised by circum-neutral pH, high alkalinity, low sulfate, high $^3$H, high Be, enriched $\delta^2$H and $\delta^{13}$CDIC) into the underlying groundwater system as suggested by high TDS, Cl/Br ratios, Be and $^3$H found in deeper wells. This study demonstrates the applicability of using trace elements, stable- and radio-isotopes to document the existing geochemistry and the contaminant transport from the waste trenches. The multiple tracer approach addresses the complexities of transport at the site and differentiates various municipal, industrial and radioactive waste sources.

KEY WORDS: low-level radioactive waste, Little Forest Legacy Site, landfill leachate, groundwater, stable isotopes, Hawkesbury Sandstone groundwater.

INTRODUCTION

A primary concern for low-level radioactive waste sites is the isolation of the wastes from the hydrological cycle. In order to achieve this objective, the engineering design of the site needs to be compatible with the local hydrogeological conditions (Bedinger 1989). This key requirement was not always fully understood in the case of older sites (e.g. Melton Valley, Oak Ridge, TN; Maxey Flats, KY; West Valley, NY; all in the USA) where high rainfall >1000 mm and variable geology led to subsurface saturation and movement of wastes, and eventually to closure and the need for remediation (Dayal et al. 1984; Bedinger 1989; Randall 1990).

Nuclear science in Australia has, since the late 1950s, centred on the Lucas Heights facility near Sydney, where a research reactor commenced operation in 1958. After an initial focus on the nuclear fuel cycle and...
development of power reactors, activities concentrated on other research applications and the production of radioisotopes for medical, research and industrial purposes. The associated low-level radioactive waste generated by those activities was disposed of between 1960 and 1968 in a nearby enclosure known as the Little Forest Legacy Site (LFLS) and formerly known as Little Forest Burial Ground (LFBG). A summary of the disposal operations at LFLS is given in Payne (2012).

Available disposal records at LFLS reveal that the waste contained various radionuclides including fission products (137Cs and 90Sr), tritium, activation products such as 60Co, actinides such as 238U, 235U and 232Th (with their decay products), and small amounts of 239+240Pu and 235U derived from the research into power reactor design. The site has been routinely monitored for radionuclides since its closure in 1968 (e.g. 3H, gross α, β and selected γ emitters) (e.g. Hoffmann et al. 2006; Hughes et al. 2011). Monitoring has shown no significant exposures to members of the public from the waste under the current management regime. However, there have been significant changes in land use around the site since its closure in 1968, with major industrial and municipal waste facilities installed nearby. Encroachment of Sydney suburbs into the areas surrounding the LFLS has occurred in recent decades, and plans exist for further developments that would place residences and recreational facilities closer to the site.

Given the prospect of continued residential, recreational and industrial activities proximate to the LFLS, a better understanding of the contaminant hydrology in the area is needed to document current and potential contaminant pathways, and the baseline geochemical conditions that may be impacted by a variety of future activities. Recent research at LFLS has focused on the hydrology of the site as indicated by tritium data (Hughes et al. 2011), the uptake of tritium in vegetation (Twining et al. 2011), assessing various methods of modelling the resulting doses to biota (Johansen et al. 2012), and the potential for surface dispersion of radionuclides owing to the impervious nature of trenches (Payne et al. 2013).

The present paper focuses on groundwater geochemical data collected during the period 2007–2009 at LFLS and aims to:

1. Differentiate between shallow (perched groundwater) and deeper groundwater, and identify the main solute contaminant sources;
2. Describe potential water–rock–waste mixing and geochemical processes affecting groundwater and their impact on water chemistry;
3. Determine major hydrogeochemical variations in response to rainfall patterns; and
4. Assess the major pathways for groundwater flow from the shallow to deeper systems including the possibility of contamination of deeper waters.

STUDY SITE BACKGROUND

Physiography and geology

The southern Sydney locality of Lucas Heights is situated within the Georges River catchment southwest of Sydney (Figure 1a). The LFLS site is a 5.5 ha fenced area adjacent to the 1.6 km radius buffer zone around the Lucas Heights Science and Technology Centre. The disposal area is situated on a hydrological divide between Mill and Barden creeks (Figure 1b) with surface runoff from LFLS flowing towards both creeks.

The dominant lithologies outcropping on the eastern Woronora Plateau are of Triassic age and consist of the Hawkesbury Sandstone, which extends to a depth of at least 192 m (Ellis 1977), with conformably overlying shallow remnants of shale and thin sandstone lenses. These were previously interpreted as Ashfield Shale (Lovering 1954; Herbert 1980) although now considered to be lenses within the Hawkesbury Sandstone (Urcoia 1981; Sherwin & Holmes 1986). The shale lens is laterally discontinuous at a regional level (Loughnan et al. 1962) but extends beyond the LFLS boundary in all directions (Mumme 1974). The shale lens dips towards the northeast and is closer to the surface in the southern area of the site. The maximum thickness of the shale lens is ~14 m in the middle of the lens in the vicinity of the burial trenches, and thins to as little as 4 m on the southeastern boundary of the site (AAEC 1966). This is corroborated by the reported thickness of shale excavated from the adjacent Harrington’s Quarry (HQ) and other nearby coring data (NSW Department of Mines 2012). Electrical resistivity data and drilling records indicate that the upper section of the shale lens consists of the soil zone and weathered shale material to a maximum depth of ~7 m (Supplementary Paper S1, Figure S1, 1–1’ profile). Electrical resistivity profiles suggest a low paleorelief feature beneath the burial site that could indicate a depression, with more conductive materials filling the relief over the sandstone and the shale layer sitting unconformably on top (Figures S1, 2). The electrical response of materials in the central area could be associated with either high clay content (laminites) or a preferential path for groundwater. Sandstone also outcrops outside the fenced perimeter along the bed of a small creek (referred to here as Turtle Creek; Figure 1c).

The soils at the site are highly weathered and derived from the shale, resulting in a profile from surficial red–brown clay soil, through mottled grey, silty kaolinite clay with numerous fine sandy partings. Immediately below the weathered material lies a light-grey leached silty shale grading to fresh dark carbonaceous parent shale with silty interbedding. The parent shale grades into shale/sandstone laminae above the basal Hawkesbury Sandstone. Kaolin is the most abundant mineral in the weathered shale (~30%) with interstratified illite–smectite (~28%), and the remainder being quartz and minor phases (hematite/goethite, anatase) (Raven & Self 2011) but no analyses are available for the parent shale materials.

The underlying Hawkesbury Sandstone consists primarily of laterally discontinuous quartzose sandstone units that generally range in thickness from 1.5 m to 3.0 m, with some siltstone/fine sandstone laminae, siltstone and claystone interbeds. The sandstone is composed mostly of medium-grain sand cemented with silica, clay and iron oxides or carbonates. The structure of the sandstone varies from massive to cross bedded.
Locally, the beds dip towards the northeast, which is also the direction of the cross-bedding dip.

**Climate**

The LFLS area has a warm temperate climate with maritime influences. Temperatures reach their maximum during February with average maximum and minimum being 25.9°C and 17.4°C, respectively. The coldest month is July with maximum and minimum at 15.7°C and 7.1°C, respectively (Isaacs & Mears 1977; Clark 2004). Mean annual rainfall at Lucas Heights was 1015 mm for the period 1958–2011 (BOM 2011) with annual average pan evaporation being ~1200 mm.

Most significant rainfall events in winter in this region involve air masses that have travelled from the Tasman Sea pushed by low-pressure systems. Inland troughs bringing moisture from the northeast also result in periodic large rainfall events. Alternating dry and wet periods are common and can be prolonged as they are linked to wider climatic events such as El Niño, La Niña and modulated by the Indian Ocean Dipole (Ummenhofer et al. 2009). Since 1958, based on yearly rainfall deviation from the average, we can differentiate four wet periods from 1958 to 1962, from 1971 to 1977, from 1983 to 1991 and from 2007 to 2012, alternating with intervening dry periods. Detailed groundwater sampling at LFLS commenced in 2007 after the break of the drought (Figure 3a).

**Hydrogeology**

Cores of weathered shale extracted from below and adjacent to the trenches have typically been unsaturated, with variable levels of moisture in perched horizons that appear to be discontinuous across the site. Periodic infiltration and lateral movement along perched horizons within the vadose zone have led to standing water accumulating in site wells, with levels being systematically recorded since 2007 (Figure 3b; Hughes et al. 2011). In general, most shallow wells within the vadose zone exhibit water-level increases immediately following large precipitation events indicating a clear connection to the surface via infiltration. Deeper wells show a parallel but dampened response compared with shallow wells. Isaacs & Mears (1977) reported an effective runoff coefficient of 20% and a soil porosity of 10% for the site. It is likely that infiltration into the trenches may be increased owing to the disturbance during trench emplacement. Isaac & Mears (1977) estimated hydraulic conductivities (K) between 1 and 130 mm day⁻¹, typical of clays in poor aquifers. Slug-test measurements in the MB series wells show higher hydraulic conductivities (9–66 mm day⁻¹) particularly after rain, owing to the
Figure 2  W–E and S–N geological cross-sections at LFLS showing stratigraphy and representative features (old quarry outline, fences, wells, and trenches). The colour coding on the wells follows the scheme shown in Figure 4a. The vertical bars in the wells show the screened interval, and triangles illustrate the standing water level in August 2007 (blue) and October 2008 (green). Dark dashed arrows represent general groundwater flow, and the light dashed arrow represents flow during dry conditions. The general site topography and quarry floor surface for HQ are derived from a digital elevation model (NSW Department of Primary Industries 2012). Modern surface at HQ has been taken from DASCEM Holdings (2000). All geological information has been compiled from several sources including MB series log reports (Bradd 2003), P well series and interpretations (PPK 2002), base to shale contours and extent of LFLS shale (Mumme 1974; Coffey Partners International 1991), other logs from wells around the study area (Coffey Environments 2010), and electrical resistivity survey and interpreted stratigraphy presented in Supplementary Paper SP1.
soil and weathered shale zone contribution (see Hughes et al. 2011 for well details). However, these estimates are of a qualified nature as they were derived assuming saturation of the soil above the shale, which is contrary to the generally dry soil conditions that have been observed during various coring and well drilling activities.

The parent shale is expected to minimise direct downward movement of groundwater into the Hawkesbury Sandstone below. A well that is screened through the shale zone (P1s) shows relatively high conductivities (370 mm day\(^{-1}\)), suggesting that this well may sample water from the weathered shale zone or intersects preferential paths along the contacts between the weathered and parent shale. Springs related to the transition between the shale–sandstone interface emerge at the limits of the shale outcrop southeast of LFLS (AAEC 1985) particularly along the Turtle Creek. To the northwest of the site, a well, screened within fine-grained sandstone, has a relatively high hydraulic conductivity (well CW, 420 mm day\(^{-1}\)).

The Hawkesbury Sandstone has been interpreted as a layered aquifer system with groundwater occurring in discrete horizons with occasional vertical connection (McKibbin & Smith 2000). Inspection of cores obtained in the local area infers relatively high permeability in some of the coarser grained, less cemented sandstone, which suggests that groundwater may travel through both the fissures in the rock and within the pore spaces in the sandstone (Knight et al. 1978). The upper sandstone units are generally weathered, strongly jointed and fractured resulting in a dual porosity aquifer in which flow may be dominated by the secondary porosity (McKibbin & Smith 2000). Primary porosity of medium-grained Hawkesbury Sandstone has been measured at 10–15% (Knight et al. 1978), but the average effective porosity in the semi-confined Hawkesbury Sandstone
aquifer nearby, has been reported as high as 51% (Coffey Partners International 1991), suggesting a high frequency of fractures and bedding planes. Hydraulic conductivity in the deeper wells (P1d, P2d) is generally lower than the shallower wells, in the range 27–120 mm day$^{-1}$ (Hughes et al. 2011). The site hydrological regime has been modified by various land uses including the removal of shales in quarried areas and operations of HQ leachate extraction systems as discussed below.

Neighbouring sites and land use

The neighbouring areas around the LFLS have had diverse land uses including: disposal site for liquid chemical waste, ‘night soil’ (human excrement) disposal, and municipal landfill sites (Figure 1b). All of these impose constraints on the future utilisation of the area and have the potential to affect LFLS hydrogeology and hydrogeochemistry.

Approximately 400 m NW of LFLS, the Industrial Waste Collection Pty Ltd (IWC) Liquid Waste Depot was used for the disposal of liquid and solid toxic wastes from 1969 to 1980 (Coffey Partners International 1991). This was used for the disposal of grease, paints, solvents, tannery wastes, as well as specific industrial chemicals including dioxin contaminated materials and residues from herbicide production (Coffey Partners International 1991). Disposal was concentrated in the excavations left by shale quarries and prospects. The area directly adjacent to the E–NE of LFLS was used for the disposal of night soil from 1947 to 1990.

Bordering the site along the west, the ~6 ha HQ was excavated for shale and sandstone between the mid-1950s and 1980s (Coffey Partners International 1991; GHD 2003). Excavations were deeper on the northern side of the quarry, where they reached 7 m below surface, and progressively shallower to the south where the shale layer was closer to surface. Before the cessation of the quarrying operation in 1980, seepage from the IWC site to the north had been identified in HQ (GHD 2003). Run-off drained into the quarry and pooled at various depths between the closure of the quarry and its filling with 450,000–600,000 tonnes of municipal waste in 1987. No clay seal was installed at the base of the landfill, with waste in direct contact with the underlying sandstone. This contact is confirmed by borehole logs from wells installed on the northern side of HQ (Douglas Partners 2006). A leachate drainage and pump-out system was installed prior to filling the area. However, the leachate sump is not located at the deepest section of HQ, therefore leachate derived from the waste material, particularly in the northern section of HQ, may not be effectively removed (GHD 2003). Leachate pumped between 2005 and 2008 averaged 9.7 m$^3$ day$^{-1}$.

Waste disposal at LFLS

A total of 79 trenches were used for waste disposal in the period 1960 to 1968 (Figure 1c). Each trench was approximately 25 m long, 0.6 m wide and 3 m deep and spaced at intervals of 2.7 m (AAEC 1985; Payne 2012). This arrangement allowed for all trenches to be placed above ~7 m of shale. The waste was not compacted, but was covered by about one metre of overburden and has been top-dressed as necessary, in part to compensate for the effects of settling.

The total volume of waste was estimated at 1675 m$^3$ (Ellis 1977). The total activity of radionuclides is indicated by records to be approximately 150 GBq at the time of disposal (AAEC 1985). The amount of radioactivity in various operational categorisations was recorded and these records provide a basis for estimating the total amounts of radionuclides buried. A major proportion of activity of the waste comprised short-lived isotopes including gamma emitters (e.g. $^{60}$Co and $^{137}$Cs), as well as $^{90}$Sr. However, the waste also included longer-lived isotopes including actinides, specifically several grams of $^{239}$, $^{240}$Pu, $^{238}$U and $^{235}$U and larger amounts of $^{238}$U and $^{232}$Th. The tritium amount disposed of is unknown but disposal records suggest several hundred waste drums containing residues from the processing and subsequent drying of sludge. Some ~1700 kg of beryllium was also disposed of at the site (Payne 2012).

The available disposal records tend to focus on the radioactive materials and provide little information on the codisposed organic and inorganic waste. In general, the bulk of the waste would have consisted of contaminated paper, obsolete equipment, laboratory consumables, packing materials, clothing, plastics, ion-exchange resins, solvents, scintillation vials, and decontamination fluids, similar to other contemporaneous low-level radioactive waste sites worldwide (Ellis 1977; Francis et al. 1980).

FIELD AND LABORATORY METHODS

Water sampling and analytical methods

Several generations of observation bores are present on the LFLS site, dating back to the 1960s (Figure 1c; Supplementary Paper SPI). Before sampling, all wells were pumped or purge-bailed either to dryness and/or to remove three well volumes, with all purged water removed from the site. After purging, all wells were allowed to recover to standing water level and then sampled immediately. The pump used during purging and sampling was either a 12 V centrifugal pump with flow controller, a low flow peristaltic pump (most shallow wells) or a subsensible pump for deeper wells.

Specific conductance (SC), dissolved oxygen (DO), temperature, pH and Eh were monitored in a flow cell for stabilisation before sample collection. All groundwater samples were collected from an in-line 0.45 μm, high volume filter. The different samples were treated accordingly to analytic requirements and refrigerated until analysed. Some unfiltered landfill leachate samples were provided by Waste Services (WSN), collected either from a pump located in a sump at HQ or from the influent streams to the Lucas Heights Landfill leachate treatment plant. This group of samples were only used to assess water stable isotopes and $^3$H in leachate.

MAJOR AND MINOR IONS

Total alkalinity was determined in the field by direct titration (Cendón et al. 2014) or in the laboratory with...
0.02 M HCl, prepared from a 0.1 M certified solution. Samples for major cations were taken in acid-cleaned 125 mL HDPE (High Density Polyethylene) bottles and acidified to ≈pH 2 using 70% double-distilled HNO₃. Samples for major anion analyses were collected in pre-rinsed (>18.0 Ml/cm⁻¹ type-water) 125 mL HDPE bottles, with no further treatment until analysis. Field blanks consisting of >18.0 Ml/cm⁻¹ type water, were filtered in the field and treated as samples, with contamination negligible for all analytes.

The chemical composition of water samples was characterised by ICP-AES for cations and selected minor elements (Al, Si, Mn and Fe). Ion Chromatography (IC) was used to analyse major anions. Major ions were assessed for accuracy by evaluation of the charge balance error percentage (CBE%) (Supplementary Paper SP3). Calculations, necessary to assess electrical neutrality, dissolved element speciation and saturation indices for common minerals phases were undertaken using the WATEQ4F thermodynamic database in the PHREEQC 2.4.2 programme (Parkhurst & Appelo 1999).

MINOR, TRACE ELEMENTS AND ⁸⁷Sr/⁸⁶Sr ISOTOPES
These samples were collected in a 250 mL HDPE bottles preconditioned to trace element level with successive HNO₃ and HCl acid baths followed by a final double sub-boiled HNO₃ bath and an ultrapure >18.0 MΩ·cm⁻¹ water rinse in a clean laboratory type 7 (ISO14644) within a laminar flow cabinet (type 5). Once dried, bottles were placed in double sealed plastic bags until used. Trace element and strontium isotope samples were acidified to ≈pH 2 with ≈70% double distilled HNO₃ in the laboratory fume hood upon return to the laboratory.

Trace-element concentrations were determined in the dissolved phase (<0.45 μm) by ICP-MS for the analysis of Be, Sr, I and U. In the case of iodide, concentrations were determined from non-acidified samples with NH₄OH-EDTA acid added in equal portion to water samples and standards for matrix matching. The pH was maintained above 8.0 to ensure minimum loss of iodide to iodine by oxidation with air: The accuracy and precision of the analytical method for ICP-MS was tested using SLRS-4, Riverine Water Reference Material. Strontium isotope analyses were performed from the trace element sample following the methods described in Cendón et al. (2014).

WATER STABLE ISOTOPES (δ²H AND δ¹⁸O)
Stable water isotope ratios were analysed in a Delta V Advantage Isotope Ratio Mass Spectrometer. In the case of δ²H, a 1 μL water sample was injected into the septum part of a dual inlet perpendicular using chromium metal at 900 C to produce H₂ gas from H₂O. The H₂ sample gas generated was introduced to the mass spectrometer and its isotopic composition measured relative to a pure hydrogen gas. In-house standards, established by runs with VSMOW2 and SLAP2, were run as samples to allow the results to properly be reported against VSMOW. Results are accurate to ±1%. For δ¹⁸O analysis water samples were allowed to equilibrate in a sealed vial flushed with 0.3% CO₂, the oxygen in the water exchanges with oxygen in the CO₂. Multiple injections of the sample oxygen (as CO₂) were measured vs a pure CO₂ monitoring gas. Standards were as per δ¹⁸O with precision for δ¹⁸O measurements being ±0.2‰.

DISSOLVED INORGANIC AND ORGANIC CARBON (δ¹³C DIC AND δ¹³C DOC)
The δ¹³C DIC and δ¹³C DOC samples were collected in preconditioned gas sealed 12 mL glass vials (Exeterm) after 0.45 μm filtration without any additives (Doctor et al. 2006). To avoid any other problems derived from the filtration size, samples were kept in dark refrigerated conditions and analysed shortly after collection. The first two sets of samples were processed in an Aurora 1030 TIC/TOC interface for the measurement of inorganic and organic carbon in water, attached to a mass spectrometer. For the rest of the samples only δ¹³C DIC was measured in a Delta V Advantage mass spectrometer. The water samples were added to a helium flushed vial and then acidified. The CO₂ released by the acid was allowed to equilibrate and then sampled for analysis. In-house standards, established by runs with NBS18, NBS19 and LSVEC, were run as samples to allow the results to be properly reported relative to VPDB. Results are accurate to ±0.3‰.

DISSOLVED SULFATE ISOTOPES (δ³⁴S AND δ¹⁸O)
Most samples had HS⁻ concentrations below detection limits with maximum values of 0.03 mg L⁻¹ for all LFLS samples. Groundwater with very low DO and Eh was not sampled to avoid any sulfur fractionation between the different aqueous species. Dissolved sulfate from <0.45 μm filtrates was converted to BaSO₄ and analysed for sulfur and oxygen isotope compositions.

Sulfur isotope ratios (δ³⁴S/³²S) were analysed using a Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS) with an elemental analyser interfaced to a VG PRISM II mass spectrometer. The results are reported against VCDT (Vienna Canón Diablo Troilitte) with measurement precisions being ±0.25‰. The ¹⁸O/¹⁶O ratio of BaSO₄ is determined using a high temperature reactor coupled to an isotope ratio mass spectrometer in continuous flow mode. Oxygen-containing compounds are quantitatively converted to CO at temperatures between 1350 and 1500 °C. After GC separation, the CO gas is swept by a carrier gas into the mass spectrometer. Results are expressed relative to the international VSMOW (Vienna Standard Mean Ocean Water) standard. Accuracy and precision of δ¹⁸O of BaSO₄ is generally better than ±0.3‰.

TRITIUM ANALYSIS (³H)
Samples were collected in 1 L Schott glass bottles and prepared using Eichrom™ Tritium columns. Detailed analytical methods can be found in Hughes et al. (2011), together with a detailed account of all ³H data collected at the site from 1975 to 2008.
RESULTS

Physico-chemical parameters, major and minor ions

Total dissolved solids (TDS) in groundwater vary across the site depending on well location, depth and preceding climatic conditions (Supplementary Paper SP3). In general, shallow samples have low TDS with minimum values of 135 mg L\(^{-1}\), while samples screened partially, or totally, within the shale have higher values, with P1s having an average value of 3473 mg L\(^{-1}\). The deeper well P2d (screened in the sandstone) has higher TDS than P1s only in 2007, while P1d consistently has high TDS values with an average of 6847 mg L\(^{-1}\). Samples from the HQ leachate pumping system recorded the highest TDS value (7838 mg L\(^{-1}\)) (Supplementary Paper SP3; Hancock & Jewell 1999).

The pH of groundwater across site varies between 3.9 and 8.0 with an average of 5.4 (±0.7), similar to average values of 5.8 observed in the 1960s during disposal (Mumme 1974). Average dissolved oxygen across the site is low (2.4 mg L\(^{-1}\)), compared with shallow samples in non-contaminated sites elsewhere (Cendón et al. 2014). Dissolved oxygen results place most of the LFLS in a reducing zone near trenches, night soil area and HQ. Measurements of Eh relative to the Standard Hydrogen Electrode, while interpreted with caution, show relatively oxygenated conditions with an average of +0.29 V. A few samples to the north outside the LFLS fenced area (BHA) show reducing values (−0.07 V; Supplementary Paper SP3), while leachate samples show slightly oxidising conditions (+0.07 V), as do samples in the night soil, north of LFLS and some samples near trenches (D14).

Most groundwater in the vicinity of trenches is of the Na–Cl type (Supplementary Paper SP4), with samples in the southern and western side generally of the Na–SO\(_4\) type. Samples around the eastern side (e.g. MB20) and HQ leachate are of the Na–HCO\(_3\) type, similar to major ion chemistry observed in landfills worldwide (Baedeker & Back 1979; Grossman et al. 2002). There is no apparent change in water types between wetter or dryer conditions.

Minor, trace elements and \(^{87}\)Sr/\(^{86}\)Sr isotopes

Minor and trace element concentrations are reported for Al, Be, Fe, I, Mn, Sr and U (Supplementary Paper SP5). In general, trace-elements across the site are more abundant in those samples with higher TDS (P1d, P2d). Iodine concentrations in LFLS samples are above natural levels and increase with proximity to trenches with concentrations of up to 27,100 μg L\(^{-1}\) for CH31. Beryllium in groundwater samples ranges from 0.004 (OS2) to 29.28 (P1d) μg L\(^{-1}\), indicating non-natural inputs. Uranium concentrations in groundwater samples are low with a maximum value of 0.22 μg L\(^{-1}\) in MB22.

Results for Sr in the MB-series bores are affected by interaction with basalt gravel used in the filter packs. Only results from the other bore series are considered and these range from 3 μg L\(^{-1}\) to 700 μg L\(^{-1}\) in BHB. A total of 24 groundwater samples were analysed for \(^{87}\)Sr/\(^{86}\)Sr isotope ratios (Supplementary Paper SP6). However, all MB-series samples (9) had low Sr-isotope ratios (0.706663 ± 0.000284) and relatively higher Sr concentrations, both consistent with mixing of basalt derived Sr and local groundwater. Those results are not incorporated. The remaining data range from 0.709519 (CW) to 0.717520 in CH21.

Water stable isotopes (δ\(^{2}H\) and δ\(^{18}O\))

The stable water isotope distribution at LFLS generally follows the Local Meteoric Water Line (LMWL) and is similar to results in groundwater from other coastal localities in the Sydney Basin (Cendón et al. 2014) indicating it is of meteoric origin and has experienced no significant evaporation prior to recharge. The average for all groundwater samples (Supplementary Papers SP6, SP7), excluding those showing clear effects of δ\(^{2}H\) methanogenic enrichment (leachate samples and CH30, CH21 and MW13), is δ\(^{2}H\) = −23.10% and δ\(^{18}O\) = −4.80% with a deuterium excess (d = δ\(^{2}H\) – 8 δ\(^{18}O\)) of 15.00%. This compares closely with weighted average values from Lucas Heights rainfall from October 2005 to September 2009 of δ\(^{2}H\) = −20.20% and δ\(^{18}O\) = −4.50% with a deuterium excess (d = δ\(^{2}H\) – 8 δ\(^{18}O\)) of 15.90% (Hughes & Crawford 2013). Leachate samples ranged from δ\(^{2}H\) = −15.80% near LFLS trenches to δ\(^{2}H\) = +15.70% in leachate from HQ. The δ\(^{18}O\) being very similar to the rest of samples.

Carbon stable isotopes (δ\(^{13}\)C\(_{\text{DIC}}\) and δ\(^{13}\)C\(_{\text{DOC}}\))

Dissolved inorganic carbon isotope (δ\(^{13}\)C\(_{\text{DIC}}\)) values range widely from −1.92% in MB301 (HQ) to −29.07% in P1d (Supplementary Paper SP6). Shallow groundwater in non-contaminated sites within the Sydney basin (Cendón et al. 2014), have typical δ\(^{13}\)C\(_{\text{DIC}}\) values of ~25‰, as expected for groundwater interacting with soils from C3-vegetated areas (Vogel 1993).

Dissolved organic carbon isotopes (δ\(^{13}\)C\(_{\text{DOC}}\)) in 2007 groundwater ranged from −27.16% (MB20) to −11.08% (OS3) compared with March 2008 with a range from −25.80% (P1d) to −18.71% (MB20). There is a marked difference in results and trends for the two samplings for both isotopic ratios and DOC concentrations (Supplementary Paper SP6). Expected natural background isotopic values are ~27%, while groundwater affected by interaction with waste will vary depending on the type of waste, time since disposal (maturity) as well as processes involved.

Dissolved sulfate isotopes (δ\(^{34}\)S and δ\(^{18}O\))

Sulfur isotopes (δ\(^{34}\)S\(_{\text{SO}}\)) in dissolved sulfate for March 2008 samples ranged from +20.00% to +27.60% with an average value of +22.20% (±1.8). The same wells in October 2009 ranged from +19.30% to +22.60% with an average value of +21.30% (±0.7), suggesting fresh sulfate inputs after rains had flushed the system (Supplementary Paper SP6). Golab (1998) reported sulfur isotope values ranging from +11.8% to +19.4% for coastal rainfall south of Sydney, with lower values associated with coal fired
metallurgic emissions. Most groundwater results are close to values expected from sulfate dissolves in seawater (+20.0 ± 0.25‰; Longinelli 1989) with no other values reported for groundwater elsewhere in the Sydney area to our knowledge. Oxygen isotopes (δ18OvsSMOW) in sulfate from March 2008 ranged from +4.6‰ to +15.4‰ with an average of +12.55‰ (±2.9). Values for the same wells in October 2009 ranged from +11.7‰ to +16.8‰ with an average of +14.6‰ (±1.2). Similarly to sulfur isotopes the second sampling had more constrained results. In general, the sulfate-δ18O values are much higher than those expected from marine derived aerosols (seawater-SO₄: δ18O = +9.5‰; Longinelli 1989).

**Tritium results (3H)**

Tritium activities in the LFLS site are generally several orders of magnitude above those expected in modern rainfall (~0.24 Bq L⁻¹) with values up to 12489 Bq L⁻¹ (CH30) and an average across the site (2007–2009) of 750 (± 2027) Bq L⁻¹. Recently, Hughes et al. (2011) reviewed all ³H data available for more than 1000 groundwater samples (1975–2008) from the LFLS site and its vicinity. Over that period of monitoring, the maximum tritium activity was 3.9×10⁶ Bq L⁻¹ in a shallow sample from D10, near well MB16, taken in 1975. Prior to the construction of CH30, well MB16 registered the highest activity during our sampling with 3290 Bq L⁻¹ in 2009. Radioactive decay has resulted in a significant reduction in activity over time. Generally, tritium activity decreases with distance from the trenches and depth with well construction and dilution from shallower soil water further affecting results.

**DISCUSSION**

**Sources of dissolved constituents**

**SHALLOW PERCHED GROUNDWATER AT LFLS**

Owing to the close proximity to the ocean and the low reactivity of local lithologies, most natural solutes in groundwater in the vadose zone of LFLS are derived from atmospheric deposition via rainfall, aerosols and dry deposition. There is a considerable variation in groundwater chemical composition from well to well across the LFLS. This was first observed in major-ion analyses from 1961 and 1974 (Mumme 1974; Isaac & Mears 1977). However, since 1974 a general decrease in concentrations is also apparent for analyses from the same wells (BH10, OS2 and OS3). The clearing of trees, prior to trench excavation in 1960–1968, would have diminished local evapotranspiration in the unsaturated zone and potentially raised shallow groundwater levels hindering salt accumulation and favouring flushing of previously retained salts towards lower areas (Ruprecht & Schofield 1991). Some lower areas around LFLS still retain forest with evapotranspiration and major ions accumulation is expected to take place. This may partially explain the considerable variations in major ion concentrations across the site, suggesting a post-clearing equilibrium in elevated areas around the trenches (Figure 4; Supplementary Paper SP3), while lower areas behave similarly to pre-clearing times or are still affected by mobilisation of salts from upgradient unsaturated zones.

Na⁺/Cl⁻ ratios in shallow groundwater from the LFLS trenched area tend to depart from the marine ratio (Figure 4a). Silicate mineral dissolution is unlikely owing to slow dissolution kinetics and quick response of groundwater levels to rainfall events (Hughes et al. 2011); therefore the Na⁺ excess is partly attributed to cation exchange of Ca²⁺ and/or Mg²⁺ in groundwater for Na⁺ in the clay minerals (e.g. Simunek & Suárez 1997). The cation-exchange capacity of LFLS samples ranges between 73 meq kg⁻¹ in the topsoil and 83 meq kg⁻¹ in weathered shale, typical for the abundant kaolinite (Temple & Smith 1958; Appelo & Postma 2007). Furthermore, the Ca²⁺/SO₄²⁻ groundwater ratio, generally below 1, also suggests Ca²⁺ uptake by clays resulting in a relative Na⁺ and SO₄²⁻ enrichment compared with other major ions (Figure 4b).

Departures from expected natural trends are evident even in shallow, low-TDS, perched groundwater (Figure 4a). These anomalies depend on the proximity of the wells to the trenches and neighbouring contaminated sites, as well as the depth to groundwater and position with respect to the weathered and parent shale materials. The release of some Na⁺ from the waste is suggested by higher Na⁺ concentrations and by low Cl⁻/Br⁻ ratios in samples close to the trenches (Figure 4a, c). Surface and very shallow samples away from trenches lie close to the Cl⁻/Br⁻:Cl⁻ seawater ratio, while shallow samples close to trenches show an increase in Na⁺ and Br⁻ that can only be related to the waste, as Br⁻ is not affected by exchange or uptake by precipitating mineral phases. Groundwater from the newly developed well CH21, directly down-gradient from the trenches, exhibits a clear enrichment in Na⁺ and Br⁻ suggesting the link between Na⁺ and Br⁻ excess and the LFLS waste.

Further interactions with other contaminants and clay minerals are evidenced by the departure of K⁺/Cl⁻ from marine ratios (Figure 4d), with K⁺ generally enriched in leachates (Kjeldsen et al. 2002). Samples close to trenches have a K⁺ excess with an increasing trend towards the night soil area (e.g. MB21, MB20). Whether a source of K⁺ is present in the night soil area or corresponds to movement of K⁺ originated in the trenches cannot be differentiated. A Cl⁻ excess is identified in deeper samples along the north flow path, in shale, sandstone and evolved HQ leachate. These samples have interacted with weathered and potentially parent shale where K⁺ could be sorbed by illite (Griffioen 2001). The observed K⁺ concentrations suggest shale strongly controls the removal of K⁺ from the HQ leachate with slopes depending on the original Cl⁻ source, interaction with clay and therefore individual flow paths.

Major ions sources show seasonal variations in some samples (e.g. BH10; Figure 4e) where the sample collected in 2009 has Mg²⁺/Cl⁻ ratios significantly different to seawater, with groundwater samples derived from wetter periods closer to expected marine-derived ratios. The SO₄²⁻/Cl⁻ ratios are generally enriched in SO₄²⁻ and, contrary to the Mg²⁺/Cl⁻ ratios, drier samplings are closer to seawater ratios. If SO₄²⁻ were only associated with the direct incorporation of atmospheric deposited...
Figure 4 (a, d, e) Variation of Na⁺, K⁺ and Mg²⁺ concentrations vs Cl⁻. (b) Variation of Ca²⁺/SO₄²⁻ ratios vs Na⁺ concentrations. (c) Variation of Cl⁻/Br⁻ concentration ratios vs Cl⁻. (f) Variation of I concentrations with ³H activities in groundwater and Turtle Creek samples. Seawater ratio is shown for reference when appropriate. The colour scheme and sample locations can be seen in Figure 2; see Supplementary Paper SP3 for details.
salts, a similar trend for Cl\(^-\) and SO\(_4\)^{2-}\) would be expected. The relative SO\(_4\)^{2-}\) increase in groundwater is consistent with the uptake of Ca\(^{2+}\) by clays and pre-concentration in the unsaturated zone owing to evapotranspiration, leading to localised gypsum (CaSO\(_4\cdot2\)H\(_2\)O) precipitation in the slightly acidic soils around forested areas during dry periods, and gypsum dissolution during wet periods. Sulfate concentration in soil samples (0.6 to 8.0 m depth) from the north of the LFLS, averaged 73 mg/kg (n = 14), confirming the presence and accumulation of sulfate in the soil zone (DASCEM Holdings 2000). Only samples from very shallow wells (OS2) and night soil areas (MB20, BHB, BHA) show SO\(_4\)^{2-}/Ca\(^{2+}\) ratios similar to those expected from gypsum dissolution. All groundwater samples are unsaturated with respect to gypsum precipitation and most to calcite (except BHA and leachate; Supplementary Paper SP8).

The origin and accumulation of sulfate at LFLS can be further investigated with dissolved sulfate isotopes in groundwater. Dry deposition (e.g. windblown dust) in eastern Australia has been measured to comprise up to \(\sim 50\%\) by weight soluble salts (Kiefert 1995) with important contributions from gypsum-coated playa lakes in inland Australia. However, isotopic signatures from inland gypsum dust sources are expected to have lower \(\delta^{34}\)S with increasing distance from the coast (Chivas et al. 1991) and are therefore not likely to be a major sulfate source at LFLS. Cycles of partial precipitation of gypsum within the soil during dry periods and dissolution during wet conditions would produce a sulfur isotopic enrichment, with values close to those observed in the groundwater (\(\sim +21.6\%\)). Sulfate\(-\delta^{18}\)O fractionation during gypsum precipitation is \(\sim +3.5\%\) (Lloyd 1968), with a resulting isotopic value for gypsum sulfate of \(\sim +13\%\), close to observed values. Further dissolution\(\)-precipitation cycles would explain some of the more enriched values with sulfate\(-\delta^{13}\)O of \(+16.8\%\) found closer to forest areas (MB12).

**DEEP GROUNDWATER AT LFLS**

The Na\(^+\)/Cl\(^-\) ratios from deeper wells follow the seawater ratio closely (Figure 4a), similarly to other samples in the Sydney area (Cendon et al. 2014). Despite a similar depth and close proximity, P1d has a significantly higher TDS than P2d, particularly when compared with P1s (screened within the shale), suggesting potential mixing with another high TDS source.

Leakage from HQ is a feasible source of solutes to deeper groundwater and has been identified in base-flow samples from Mill Creek (Hancock & Jewell 1999). High HCO\(_3\)\(^-\) is common in landfill leachates as a by-product of bacterial reduction and will also shift \(\delta^{13}\)C\(_{DIC}\) values to more enriched values (Cartwright et al. 2010). The major changes in HCO\(_3\)\(^-\) concentration in P2d from 44.6 mg L\(^{-1}\) in 2007 to 124.8 mg L\(^{-1}\) in late 2008 are coupled to dry\(-\)wet periods and variations in the \(\delta^{13}\)C\(_{DIC}\) from depleted to slightly enriched values. As groundwater infiltrates deeper into fresh Hawkesbury Sandstone, dissolution of dispersed carbonates (particularly siderite, average \(\delta^{13}\)C = \(-5.1\); Cendon et al. 2014) can raise HCO\(_3\)\(^-\) and shift to more \(^{15}\)C enriched isotopic values than soil-derived HCO\(_3\)\(^-\). However, the sharp and seasonal (dry\(-\)wet) variations suggest that during wet periods some HCO\(_3\)\(^-\) is leaking into the vicinity of P2d; this is not noticed in P1d to the same extent, probably owing to the more acidic conditions and/or a longer flow path from HQ. The leachate from HQ could potentially mix with regional groundwater in the Hawkesbury Sandstone as it flows east below LFLS, channelled along the identified paleorelief morphology (Figure 2). The transfer of leachate contributions to shallow or deeper groundwater may be episodic, possibly coinciding with times of high rainfall when leachate pumps may not remove all extra leachate generated. The limited number of samples and dilution with other groundwater sources are likely to mask these variations. This is confirmed by the absence of a methanogenic-derived \(\delta^{13}\)C\(_{DIC}\) from depleted wells between HQ and LFLS.

There are no major sources of sulfate in the Hawkesbury Sandstone with depth and HQ leachate has low sulfate concentrations (2.7 mg L\(^{-1}\) \text{d}(-) owing to bacterial sulfate reduction (BSR) processes. Therefore, the low SO\(_4\)^{2-}\) concentration in the leachate would not affect the overall SO\(_4\)^{2-}/\(\delta^{34}\)S observed, as sulfate isotopic composition and concentration is controlled by sulfate accumulated and transferred from the soil column.

**SOURCES OF MINOR AND TRACE ELEMENTS**

Concentrations of selected minor (Al, Mn, Fe, Sr and I) and trace elements (I, Be and U) at LFLS generally increase with TDS, with natural compositions modified by different contaminant sources in the area. Iodine occurs in multiple oxidation states and in organic and inorganic compounds, with iodide and iodate being the most common inorganic species. Iodine is produced in the nuclear industry and also found in X-ray contrast media, disinfectants, reaction catalysts and medical products (Panno et al. 2006). Concentrations in rainfall are low (\(<1.5\) \(\mu\)g L\(^{-1}\)) while surface and groundwater have higher concentrations closely linked to the regional lithologies (Moran et al. 2002; Neal et al. 2007). Iodine concentrations in LFLS samples are above natural levels, correlate with \(^3\)H activities and increase with proximity to trenches (Figure 4f). The movement of I\(^-\) in perched groundwater is away from the trenches in all directions; CW is the exception, where high concentrations suggest mixing with other available I\(^-\) sources (HQ). Groundwater from wells CW, BHA, CH17 and MB21 shows an increase in Br\(^-\) compared with I\(^-\) in other bores. This may be related to the preferential uptake of iodine by vegetation (Hu et al. 2005) and/or higher mobility of Br\(^-\) away from trenches. Leachates have an excess of halogenated compounds compared with natural samples (Haarstad & Borch 2008); HQ leachate has similar Br\(^-\) but lower I\(^-\) concentrations compared with groundwater at LFLS. The deepest groundwater (P2d) has lower I\(^-\) and Br\(^-\) concentrations that P1d, also screened in the sandstone, suggesting a mixing with regional Hawkesbury groundwater with depth.

Beryllium is of special interest at LFLS because burial records report that \(<1700\) kg of Be (mostly BeO) were dispersed in the trenches (Ellis 1977; Bradd 2003). Beryllium metal and Be-oxides are mostly insoluble in water, and concentrations in water are expected to be
quite low particularly at circum-neutral pH. However, Be mobilisation increases under acidic or alkaline conditions with a 100-fold increase in concentration for freshwater between pH 7 and pH 4 (Neal 2003). Beryllium concentrations in UK rainfall showed weighted concentrations of 0.007 μg L⁻¹ (Neal et al. 1992) with groundwater generally showing higher concentrations depending on local geology. The average Be concentration of the upper continental crust is ~1.9 μg g⁻¹ with shales showing higher concentrations of ~3.5 μg g⁻¹ (Hu & Gao 2008). Groundwater samples at LFLS ranged from 0.004 μg L⁻¹ (OS2) to 29.28 μg L⁻¹ (P1d) (Figure 6a) with elevated Be concentrations also found in groundwater samples from shallow wells in neighbouring contaminated sites. Be concentrations in the IWC site averaged 5.8 μg L⁻¹ (n = 57) with the highest value being 37 μg L⁻¹ and most values down gradient from the site exceeding 4 μg L⁻¹ (DASCEM Holdings 2000). High levels are also found in groundwater from wells around HQ, with average values of 4.3 μg L⁻¹ for groundwater in the NE section and values of up to 13 μg L⁻¹ in the NW of HQ (GHD 2003).

In general LFLS Be results are quite consistent between sampling periods with concentrations near the trenches (e.g. MB16) quite low, even when samples have an elevated ³H activity (Figure 6a). If Be were leaching from the LFLS waste materials, then MB16 would be expected to show a higher Be concentration. Thus, it appears probable that Be is not leaching from the waste trenches into the groundwater to any significant extent. The higher Be content found in P1d can be interpreted as leaching of Be from shales, enhanced by localised low pH in shallower groundwater, and possibly also transport of Be from HQ.

Uranium concentrations (Supplementary Paper SP5) are generally low and similar to those found in regional groundwater elsewhere in the Sydney basin (Cendón, unpublished data). In general, all wells along the SW of the site have lower values, while deeper wells and those down-gradient from the trenches show higher values (OS3, MB17, BHA). A relatively high concentration (0.22 μg L⁻¹) is found in MB22 in a very shallow well (~1 m), located along the drainage line for LFLS runoff to the SE. The lack of an elevated concentration of total uranium, which could be attributed to LFLS is significant given that uranium was emplaced at the site. However, more sensitive isotopic studies are under way to determine whether uranium of unusual isotopic composition occurs.

Description of processes

PROCESSES IN THE TRENCH AREA

The elevated relative position of most trenches with respect to other potential sources of contaminants means that infiltrated water will first interact with trench contents. Waste in the LFLS trenches, being mostly organic, is expected to evolve similarly to a landfill, but trenches are separated, and waste was not compacted. The shallow nature of the trenches, low pH (~5.2) of surrounding perched groundwater compared with that of leachate at HQ (~7), relatively high dissolved oxygen (~1 mg L⁻¹) and high SO₄²⁻ concentrations show a generally oxidising environment. However, the comparison of closely located wells (CH30 and MB16) shows that well construction introduces some bias with mixing and dilution clearly affected by the long screens in the MB well series. Enriched δ³⁴S values near trenches indicate that degradation of organic matter produces δ¹³C-enriched CO₂ that mixes with natural soil CO₂ shifting...
Figure 6 (a) Variation of Be concentrations with $^3$H activities in groundwater and Turtle Creek samples. (b) HCO$_3^-$ concentration vs $\delta^{13}$C of dissolved inorganic carbon (DIC = H$_2$CO$_3$ + HCO$_3^-$ + CO$_3^{2-}$). (c) Variation of $\delta^{13}$C in DOC (dissolved organic carbon) vs $\delta^{13}$CDIC (see Supplementary Paper SP6 for details). (d) DOC concentrations vs $\delta^{13}$CDIC showing seasonal variations and trends during 2007–2008. (e) Tritium activities vs TDS. (f) $^{87}$Sr/$^{86}$Sr isotopic ratios vs the inverse of Sr concentration. The blue line corresponds to modern seawater $^{87}$Sr/$^{86}$Sr.
the $\delta^{13}C$ of DIC. This process is detected in all near-trench samples, suggesting organic matter degradation within the trenches still controls trench groundwater $\delta^{13}C_{DIC}$ values after ~50 years of trench closure and several drought–wet cycles.

Microbial degradation of organic matter in landfill leachates leads to the production of methane (methanogenesis) with a significant part of hydrogen forming CH$_4$ taken from surrounding water. The associated isotopic fractionation is linked to the metabolic pathway and can enrich considerably the remaining water fraction (Whiticar et al. 1986; Hackley et al. 1996). A group of leachate samples from or near HQ, and to a lesser extent wells close to LFLS trenches (CH21, CH30), show an enrichment in $\delta^2$H from ~25‰ to +15‰ without any observable enrichment in $\delta^{18}O$ values, resulting in an unusually high $d$-excess of up to 58‰ (Supplementary Papers SP6, SP7). Reducing methanogenic conditions may occur in deeper parts of the trenches, seasonally or along the flow path; samples from CH21 and CH30, down-stream from the trenches, show a high deuterium excess, typical in methanogenic processes (Figure 5a). Tritium activity is higher near LFLS trenches with accompanying high Br$^-$, Na$^+$, K$^+$ and I$^-$ concentrations (Figure 4a, c, f). Departures from background $\delta^{13}C_{DIC}$, $\delta^{13}C_{DOC}$ and radiogenic $^{87}Sr/^{86}Sr$ ratios near trenches further demonstrate the interaction of shallow groundwater with trench contaminants (Figure 6f).

Soluble contaminants originating in the waste trenches may be transported by water downward and laterally away from the trenches (Figure 2). However, their rate of transport is limited first by the low permeability of the clay-rich soils surrounding the trenches, and second by the lower shale aquitard. However, the unconsolidated material in the trenches can be saturated after rainfall. This has been identified and described as a ‘bathtub’ effect at other low-level waste facilities like West Valley (New York, USA; Bedinger 1989), in burial sites 4, 5 and 6 at the Oak Ridge National Laboratory (Tennessee, USA; Webster 1987), and also recently at LFLS (Payne et al. 2013). In the trenches, the saturation can enhance degradation processes in the waste and subsidence, forming cracks that in turn increase the permeability of the capping material. These cracks and differential settling at LFLS have been addressed with top-dressing when required. Other sites like Maxey Flats (Kentucky, USA) have adopted alternative solutions, such as PVC-covering all trenches minimising any vertical leakage into trenches (Lyverse 1987). The potential importance of a surficial pathway for dispersion of contaminants from LFLS is under study but is beyond the scope of this paper.

**MIXING OF LFLS AND HARRINGTON’S QUARRY WATERS**

Under natural and non-pumping conditions, shallow groundwater from HQ should flow towards LFLS with a small gradient (Figure 2). The quarrying and disposal of municipal waste in the HQ area have resulted in artificially high permeability, rapid infiltration, drainage and pumping of leachate. The combined effect is a change of the natural groundwater gradient, favouring flow from LFLS to HQ.

The HQ site contains leachates representative of a landfill at the anaerobic stage of decomposition, with a pH of ~7, high HCO$_3^-$, low sulfate concentration and $^3$H enriched water (Supplementary Papers SP3, SP6, SP7). This is evidence of bacterial activity where most sulfate has been reduced (BSR) and methanogenic processes are taking place. Leachate is actively pumped; however, sumps are not at the lowest point in the landfill, and there is no lining to prevent leachate movement to the underlying sandstone.

Groundwaters in other parts of the Sydney basin, from similar depths to P2d and under shale layers, have $^{14}$C residence times in the order of 2000 years with no $^3$H activity. However, tritium groundwater activities at LFLS with depth are quite constant with an average of 126 and 87 Bq L$^{-1}$ for Pid and P2d, respectively; for samples between 2003 and 2009 (Hughes et al. 2011; Supplementary Paper SP6). This indicates a good connection with a $^3$H reservoir and residence times on yearly or shorter time-scales. A small decrease in activity over the 6 years of sampling is observed, but this, apart from decay, could be related to the rate of mixing/dilution with regional groundwater ultimately controlled by seasonal fluctuations.

High $^3$H activities in municipal landfills are common and have been described elsewhere in the world (e.g. Hackley et al. 1996; Robinson & Gronow 1996; Castaneda et al. 2012) and are attributed to the disposal of radioluminescent materials containing tritium. The HQ leachate exhibits elevated tritium and is therefore a tritium source, although not as significant as the LFLS trenches. The observed $^3$H levels in deeper groundwater are consistent with either HQ or LFLS as potential sources. However, activities in P1s, screened within shale, downstream from the trenches and following the natural drainage have an average of 35 Bq L$^{-1}$ (Supplementary Paper SP6), suggesting that the shale layer at the PIs area allows only minimal transmission into the underlying sandstone. This suggests that no major leakage is occurring through the shale below the LFLS given that these levels are very low (~105 Bq L$^{-1}$) compared with those above the shale (up to 12 489 Bq L$^{-1}$).

**MIXING WITH IWC AND NIGHT SOIL AREA WATERS**

The Industrial Waste Collection (IWC) site is located to the NW of LFLS. The natural gradient of the site would move any IWC contaminant away from LFLS, therefore no impact to the shallow groundwater around LFLS is expected. However, IWC leachates could be important in deeper systems where inputs from unlined waste facilities maybe relatively more important than those from LFLS.

At the east and NE sides of LFLS shallow perched groundwater interacts with the night soils. The $^3$H activities, I$^-$ and K$^+$ concentrations show that water derived from LFLS has reached the eastern side of night soil area while the generally low $^3$H levels suggest dilution with locally recharged water (Figure 4f). Tritium activities at MB20 are low but above natural background with values in MB21 initially low but much higher during the last sampling, perhaps indicating a breakthrough in the flow. In general, conditions are more reducing with
bacterial sulfate reduction products (elevated HCO$_3^-$ and enriched sulfate $\delta^{34}$S) and enriched $\delta^{34}$C$_{\text{DIC}}$ detected along the flow path. While the number of samples is limited, sulfate $\delta^{34}$S enrichments and higher HCO$_3^-$ concentrations suggest BSR is taking place along the north. The sulfate-$\delta^{18}$O for the same samples is depleted suggesting a partial reduction of SO$_4^{2-}$ to HS$^-$. A potential HS$^-$ re-oxidation along the flow path would take oxygen from H$_2$O and atmospheric dissolved O$_2$ to form the new SO$_4^{2-}$ molecules. This process could explain the variation in sulfate-$\delta^{18}$O values observed (Mizutani & Rafter 1973).

**Groundwater response to rainfall at LFLS**

**WATER STABLE ISOTOPES**

Hughes & Crawford (2013) observed that winter rainfall at Lucas Heights, during the period September 2005 to September 2009, the $\delta^2$H and $\delta^{18}$O values were generally more depleted than summer rainfall. A dependence on the amount of rainfall was observed in summer, with large events showing greater depletion than small events. However, there was very little variation in the average groundwater $\delta^2$H and $\delta^{18}$O values between sampling periods, indicating that rainfall generally does not have a significant short-term effect on groundwater stable water isotopes at LFLS. The standard deviation for the four samplings was highest for BH10, MB13, MB20 and MB21 indicating the biggest temporal variability. These four sites also exhibit a moderate to strong correlation with rainfall ($r^2 = 0.53$ to $0.86$ for $\delta^{18}$O and $r^2 = 0.41$ to $0.91$ for $\delta^2$H) indicating a relatively stronger influence of recent rainfall. Samples from wells MB12, 14, 17, 18 and 19 have the lowest standard deviations suggesting that while these are open wells, rainfall may not be significantly diluting the groundwater samples at these sites. This could be linked to the proximity of the shale lens to the surface hindering recharge. Screened wells, in particular the P-series wells, do not have a noticeably lower standard deviation despite evidence from the hydrograph data that they have a lagged response to rainfall (Figure 3b). At these sites there is a trend toward more depleted stable isotope values with time possibly indicating a piston flow recharge from the large depleted rain events in 2007 and 2008 associated with the break of the drought.

The frequency of groundwater sampling is not sufficient to observe any seasonal patterns in groundwater stable isotope signatures at LFLS. However, we compared the average isotopic values ($\delta^{13}$C, $\delta^2$H and $\delta$-excess) of the set of wells sampled during all the sampling campaigns with the rainfall in the 6–8 week period leading up to and during each sampling period and found a moderate correlation for all parameters ($r^2 = 0.58$ to $0.77$).

**DIC, DOC AND CARBON STABLE ISOTOPES**

Sharp variations in carbon stable isotopes suggest a dynamic and complex system with observed isotopic values near trenches interpreted as the result of mixing of soil-derived CO$_2$ with enriched HCO$_3^-$ generated during methanogenesis and BSR (Grossman et al. 2002; Cartwright et al. 2010; Cozzarelli et al. 2011). Unfortunately, no concentration or isotopic values are available for CH$_4$ but the general correlation of HCO$_3^-$ and $\delta^{13}$C$_{\text{DIC}}$ and the observed deuterium excess, particularly in screened wells near trenches (CH31, CH21), supports the presence of limited methanogenic processes near trenches (Figure 6b).

Seasonal variations, depth and location of groundwater with respect to waste sources can impact on DIC processes. In 2007, after a prolonged drought, 387 mm of rainfall occurred in the month preceding a sampling event; this is expected to have transferred the accumulated negative $\delta^{13}$C soil-CO$_2$ signal into the groundwater samples (Figure 6b, c; Supplementary Paper SP6). The relatively wet conditions prevailing during 2008 would have enhanced saturation-induced degradation of the remaining organic matter and methanogenesis. During drier periods, with declining water levels, the waste can be partially exposed to unsaturated conditions stopping methanogenesis. However, the bottom of the trenches could retain sufficient methanogenic communities so that transition to methanogenic conditions can develop quickly when conditions are favourable. In general, $\delta^{13}$C$_{\text{DIC}}$ fluctuates according to wetter or drier conditions. Deeper wells (e.g. P2d) also commonly follow the same patterns, further suggesting short residence times for groundwater and mixing of shallow and deeper regional groundwater in localised areas.

The range of DOC concentrations observed for 2007–2008 is also consistent with wet–dry variations. High DOC concentrations increase in groundwater during dry conditions within trenches; this groundwater can be flushed as trenches fill up with fresh rainfall infiltration (Figure 6d). The lack of increase in DOC concentration along the flow path leaving LFLS trenches suggests a limited DOC reservoir and an episodic release from the trenches. Bacterial degradation of organic compounds generally favours $^{13}$C uptake, resulting in enrichment of $\delta^{13}$C in the residual DOC (Faure 1986). Farther from the trenches, $^{13}$C-enriched values also suggest DOC degradation; whether degradation takes place along the flow path (van Breukelen et al. 2003) or within trenches is more difficult to assess. As trench water is diluted owing to rainfall infiltration during wet periods, groundwater will eventually approach isotopic signatures closer to expected natural values, while enriched $\delta^{13}$C$_{\text{DOC}}$ values in groundwater will be displaced down gradient from trenches. Overall this highlights the impact of trenches in shallow perched groundwater recharge at LFLS.

Deeper wells show a different trend (Figure 6d) with CW showing higher DOC concentrations and more isotopic enrichment than deeper samples. This suggests the presence of another source of DOC with higher concentrations. We hypothesise that HQ is that source, with isotopic values being transferred in depth with mixing and dilution by other shallower groundwater sources. In general, the shift from 2007 to 2008 suggests that groundwater recharge to the deeper Hawkesbury Sandstone could operate at monthly or even shorter time-scales.
Groundwater flow at LFLS

LFLS trenches are located on a ridge that divides shallow flow and runoff between the N and SE of the site. Shallow perched groundwater flow is expected to broadly mimic topography; however, the underlying geology imposes certain constraints on groundwater movement at the site. The depth of the shale lens is greater to the north than the SE resulting in greater capacity to transport shallow groundwater to the north than the SE, where topography, seepage and surface runoff lead to drainage towards Turtle Creek.

The shallow and deeper systems are mostly well isolated by the presence of shale at LFLS (Figure 6e), as indicated by differences in deeper groundwater major ion ratios (K+/Cl−; Cl−/Br−:Cl−), concentrations (I−, H+), and isotopes (87Sr/86Sr, δ13CDOC). However, the removal of the shale to the west at HQ has allowed connection between the shallow and deeper systems. Deeper groundwater is also constrained by an apparent depression feature favouring a west to east flow below LFLS. While deeper aquifer data are limited, P1d suggests the possibility of excess HQ leachates flowing below LFLS to the east. Connection between deeper and surface systems is present beyond the boundaries of LFLS. Two recent analyses of the short-lived radon-222 (222Rn) isotope (half-life 3.8 days) in Turtle Creek confirmed it to be fed in part by groundwater, with 222Rn activities of up to 3.9 Bq L−1, similar to non-contaminated sites elsewhere. 87Sr/86Sr in Turtle Creek spring water is very similar to that found in deeper sandstone aquifers (P1d), reinforcing the link between springs along the Turtle Creek and the underlying sandstone aquifer (Figure 6f).

Hughes et al. (2011) showed that 3H (which is highly mobile) has radiated from the trenches following topography in a northerly direction to BH10, CW and beyond the fenced area over the past 50 years. This is also observed in I− concentrations generally decreasing with distance from the trenches. Results along the NW corner of LFLS (CW) confirm mixing with other sources (HQ) suggesting some preferential flow in that area, probably enhanced by the mining of the shale layer.

Flow to the north is enhanced by the presence of trenches but does not appear to be continuous. We hypothesise that during very wet conditions trenches fill, diluting any pre-existing leachates, and then hydraulic gradients drive the rapid shallow transport of a contaminated pulse away from the trenches through the more conductive surface layer, which occurs over a time-scale of weeks. This would explain the variation in 3H concentrations observed at BH10 from 159 Bq L−1 in August 2007 and 288 Bq L−1 in March 2008 (both diluted following big rainfall events) to 1924 Bq L−1 in November 2008 (after dry conditions). Continuing wet conditions shifted 3H values to 275 Bq L−1 in 2009.

Similarly, DOC concentrations show a dilution during wetter conditions, with DOC changing from 6.28 to 2.02 mg L−1 while δ13CDOC values became more depleted showing the dilution of the system and increasing influence of soil organic matter. Further, we hypothesise that following the initial shallow flushing of the trenches by rainfall, the lower hydraulic conductivity of the deeper lithologies reduces the flow rate from the trenches, and the concentrations of contaminants increase. This more highly contaminated water discharges slowly from the trenches near their base through a saturated layer seen during coring around the trenches (Hankin 2012).

CONCLUSIONS

The groundwater hydrochemistry of the LFLS and its environs is controlled by wet–dry rainfall patterns, evapotranspiration, local geology and land uses. Rainfall-infiltration controls the presence of water in the trenches, while evapotranspiration modulates the accumulation of solutes in the unsaturated zone. The main lithological factor controlling hydrochemistry and flow is the position, extent and heterogeneities of the local shale layer. The shale layer is intact in the trench areas but has been mined in neighbouring quarries, opening a recharge pathway of contaminants into otherwise locally protected deeper groundwater.

Solutes in groundwater are mostly sourced from marine-derived rainfall as shown by dissolved major ion ratios and dissolved sulfate stable isotopes. Shallow groundwater in elevated areas is generally of the Na−Cl type with low TDS, while in lower areas there is an increase in SO4− concentration and TDS, resulting in areas with Na−SO4-type waters. Further interaction with landfill contaminants tends to produce localised Na−HCO3-type water. Modified evapotranspiration processes, owing to localised vegetation removal from the LFLS area, have resulted in flushing of salts from higher areas, while in lower areas, solutes can be preconcentrated in the unsaturated zone, probably reaching gypsum precipitation during dry periods. Rainfall can partially dissolve and transport accumulated solutes, while interaction with clays occurs through cation exchange processes; these alter marine SO4−/Ca2+ ratios by uptake of Ca2+ (Mg2+ and K+) by clays, and release of Na+. Interactions with contaminants also take place in the trench area with release of Na+, Br− and I− from residues.

The LFLS is particularly sensitive to dry–wet cycles with a ‘bathtub’ effect developing in trenches during periods of high precipitation, causing trenches to saturate to various levels, and at times to the ground surface when rainfall is sufficient. Apart from the radionuclides dispersed by this surface route, contamination from trench materials is primarily limited to the shallow perched groundwater bodies above the shale layer (as indicated by major ions, I−, 3H, 87Sr/86Sr, δ13CDOC) with some low levels detected in the underlying Hawkesbury Sandstone consistent with either minor leakage through the shale, or inputs from other land uses around LFLS.

There is no evidence that the beryllium disposed of at LFLS has been leached into the local groundwater, with consistently low Be concentrations in samples near trenches. The slightly elevated result from one deeper groundwater well probably results from enhanced leaching of Be from shale owing to localised low pH in groundwater. Total uranium concentrations in groundwater are generally not increased by the presence of the LFLS wastes, but there may be a surface or near-surface
pathway for localised transport following intense rainfall and surface runoff.

The DIC, DOC and their carbon isotope values indicate the importance of organic degradation processes in the HQ leachate, night soil area and within the LFLS trenches. This is further reinforced by H enrichment in water linked to methane production, particularly observed in the HQ leachate and in some samples within trenches. Interaction with organic degradation processes is also observed in sulfur isotope trends consistent with bacterial sulfate reduction in groundwater along the north of the site.

The existence of competing sources (LFLS trenches, HQ, night soils) provides avenues for mixing, particularly in the deeper Hawkesbury groundwater system. A small proportion of HQ leachate enters below the shale mixing with regional groundwater and flows southeast as suggested by TDS, HCO and δDDOC and δD. This flow may be favoured by a paleorelief that would direct deeper flow to the southeast where some water can reach the surface in springs along Turtle Creek.

The present paper illustrates how groundwater geochemical and isotopic data can help illuminate a complex contaminated system, particularly in terms of the influence of various contaminant sources, describing the impact of geochemical processes and mixing on water chemistry, the response to rainfall patterns and the major pathways for groundwater flow. In conjunction with other studies, this information will assist in the understanding and management of the area.

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Bradd improved this final manuscript.

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