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Note

The Use of Tritium as an Environmental Tracer of Leachate from a Landfill Site in Ireland

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In 2014, tritium was detected in the groundwater leachate at a landfill site in Kerdiffstown, County Kildare, Ireland. The objective of this work is to determine the tritium activity concentrations in the groundwater leachate at the Kerdiffstown Landfill in order to determine the leachate flow. Thirty-seven boreholes both on and off-site at Kerdiffstown landfill were sampled for groundwater leachate from September 2014 to March 2015. The leachate samples were then double distilled and analysed for tritium using a low level Liquid Scintillation Counter. Through the use of the tritium in leachate measurements made in this study, the flow of leachate from the Kerdiffstown landfill site was determined. The maximum tritium activity concentration measured at the landfill was (458 ± 35) Bq/l. This measurement was made at a borehole located in the north-west of the site and has a depth of 70.45 mOD (meters above Ordnance Datum). Based on the measurements made in this study it is reasonable to assume that the primary source of tritium on this site is located in the north-western zone and a general flow of leachate from west to east is observed. The results of the study also indicate that leachate flow increased during periods of heavy rainfall.

Key words: tritium, leachate, landfill, Liquid Scintillation Counting, Triple to Double Coincidence Ratio

1. Introduction

Tritium (^{3}H) is one of the most widely used environmental tracers due to its ability to be measured at relativity low levels[1]. Multiple studies with tritium as an environmental tracer have been conducted worldwide[1-3]. Tritium is naturally produced in the earth's upper atmosphere when cosmic neutrons strike nitrogen (^{14}N) or oxygen (^{16}O) molecules in the air. Man-made sources of tritium have led to an increase in tritium levels worldwide. The annual addition of man-made tritium to the environment ranges from 50 to 70 PBq[4].

The largest artificial source of tritium is a result of nuclear weapons testing during the 1950s and 1960s. From 1945 to 1960, these tests released over 186,000 PBq[4]. The processing of spent fuel rods is another tritium source. The La Hague reprocessing plant in France releases about 10 PBq/y while Sellafield in the UK releases about 2 to 3 PBq/y[4].

Tritium in consumer and industrial items could be another potential cause of tritium in the environment.

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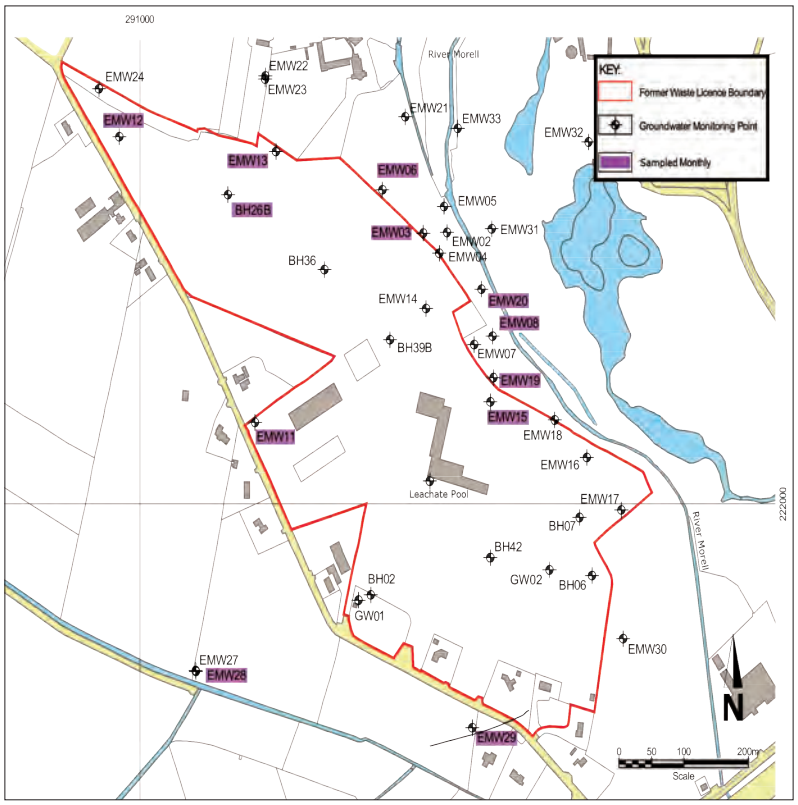

Fig. 1. Map of Kerdiffstown landfill illustrating the location of boreholes. Boreholes highlighted pink were sampled on a monthly basis. All other boreholes were sampled at least once.

The potential sources of tritium in landfills had previously been thought to be luminescent paint[5]. Recent studies indicate that the most probable cause of tritium in landfill leachate is as a result of disposed gaseous tritium lighting devices (GTLDs) which can contain up to 1TBq of tritium per device[5-6]. The typical lifespan of GTLDs is 10 to 12 years due to the half-life of tritium[5]. The sources of tritium in Irish Landfills are unknown. There are no nuclear power stations and no nuclear fuel cycle activities in Ireland. However, potential sources of tritium in Irish landfills could include the disposal of luminous devices such as watches, clocks (which both contain up to 7.5 GBq per device[6]), GTLDs and luminescent paint.

A landfill site in Kerdiffstown, Co. Kildare, Ireland was vacated in 2010 resulting in the Environmental Protection Agency, Ireland taking control of the site between 2010 and 2015 before management of the site transferred to Kildare County Council. The Kerdiffstown landfill site is located to the west of Dublin at GPS co-ordinates 53° 14' 28.9" N 6° 37' 48.48" W (Fig. 1). The site comprises of an area of approximately 0.3 km^2. The site was detailed by the EPA in the report, "Evaluation of Environmental Liabilities at Kerdiffstown Landfill"[7]. Prior landfilling commencing in parts of the site in the 1970s, the site was quarried for sand & gravel. It is believed that quarrying operation generally did not extend into the water table.

The quarrying operation was primarily in the north-eastern zone of the site. The landfill waste mainly comprises of construction and demolition waste. The vast majority of the site is not lined and the landfill is not capped.

The site has been split into two zones, the north-western zone and the south-eastern zone. Samples and historical data indicate that the north-western zone contains older waste; it is believed this older waste has reached absorption capacity. The south-eastern zone does not indicate that it has reached absorption capacity. A lined cell was constructed in the south-eastern zone of the site for the removal of leachate. For the past number of years there have being growing concerns about the direction of the leachate from the Kerdiffstown landfill. Initial surveys on the site have detailed the migration of leachate from northwest to east towards a river, the River Morrell, to the north-east of the site. This river was identified as a potential receptor for migrating leachate as it is approximately 40 m from the site boundary and 50 m from waste at its closest point. The river is a tributary system of the River Liffey, a large river that flows through the center of Dublin and supplies much of Dublin's water.

In order to assist the EPA in determining the contents of the groundwater leachate and to determine its flow thirty seven boreholes were constructed on and off-site site between the years of 2010 to 2012. The boreholes range in depth from 63.29 to 84.07 mOD. The locations of these boreholes are highlighted in Fig. 1.

Initial investigations by the EPA determined that measureable quantities of tritium were detected in some of these boreholes. As a result of these initial investigations, this study was carried out in order to determine the flow of leachate at the Kerdiffstown site by using tritium as a groundwater tracer.

The Triple to Double Coincidence Ratio (TDCR) feature of the Hidex 300 SL in conjunction with formula outlined in ISO11929 were used to determine the Activity Concentration, Decision Threshold and Detection Limit (see section 2.2)[8]. Measurement uncertainties were evaluated using the Kragten approach[9].

The influence of climate conditions (rainfall, atmospheric pressure and tidal patterns) plays a contributing role in the migration of gas and landfill leachate[2, 10]. The influence of rainfall was investigated as part of this study. The average monthly rainfall for the sampling period was (64.85 mm) the wettest month was November (138.9 mm), while the driest month was September (13 mm).

2. Materials and methods

2.1. Sample collection and preparation

Thirty seven boreholes and the leachate pool were sampled at the Kerdiffstown site. A total of 128 samples were analysed for tritium activity. Samples were collected on the first week of each month from September 2014 to March 2015. A total of 12 samples were collected on a monthly basis, highlighted pink in Fig. 1. An additional sample at BH39B was taken in October 2014. All thirty seven boreholes were sampled in December 2014 apart from BH39B (Fig. 1).

Leachate was pumped at a flow rate of 5 l/min from the boreholes with an inertial pump and a mechanical actuator (Waterra Power Pack PP1), from *in-situ*. Boreholes were purged prior to sampling. Approximately 1 l of each sample was collected. Samples were stored in Polyethylene Terephthalate 1 l bottles at room temperature.

Prior to counting by LSC, the samples were prepared via a two stage distillation process. For the first distillation 125 ml of sample was distilled and approximately 100 ml of distillate was collected in a 250 ml round bottom flask. This process removed the bulk of the organic matter contained in the sample. Approximately 0.4 g Sodium iodide, 0.4 g sodium metabisulphite and 1 g of anhydrous sodium carbonate were then added to the distillate to retain other vaporisable radioactive substances (i.e. carbon and iodine)[4]. The solution was checked to ensure it was alkaline, and a second distillation was performed, this further purified the sample and removed interfering radionuclides. The first 20 ml of the second distillate was discarded. The following 60 ml was retrieved in a 100 ml amber bottle. The 60 ml of distillate was stored at room temperature prior to analysis.

2.2. Tritium analysis

Tritium analyses were carried out on 8 ml of sample mixed thoroughly with 12 ml Ultima Gold LLT in 20 ml plastic vials. Samples were dark equilibrated for 3 hours prior to counting in the LSC. Samples were measured for a total of three hours. A total of eight blank samples were prepared with purified tritium-free water using the double distillation technique. The eight blank samples were placed intermediately for every four samples in the Hidex sample holder. Blank samples were counted regardless of the sample quantity counted. The average of the eight blank samples was evaluated for background counts per minute and background TDCR.

The activity of tritium (A) was determined using Eq. (1). The background counts per minute $\left(\frac{N_b}{t}\right)$ was subtracted from the net counts per minute $\left(\frac{N_n}{t}\right)$ and divided by the efficiency (ε).

$$A(\mathrm{Bq}) = \frac{\left(\frac{N_n}{t}\right) - \left(\frac{N_b}{t}\right)}{\varepsilon \times 60} \qquad (1)$$

The TDCR value of the sample ($TDCR_{sample}$) was calculated by Eq. (2).

$$TDCR_{sample} = \frac{\left[\left\{\left(\frac{N_n}{t} \times TDCR_{net}\right)\right\} - \left\{\left(\frac{N_b}{t} \times TDCR_{BKG}\right)\right\}\right]}{\left\{\left(\frac{N_n}{t}\right) - \left\{\left(\frac{N_b}{t}\right)\right\}\right.} \qquad (2)$$

Where $TDCR_{net}$ is the net TDCR count and $TDCR_{BKG}$ is the background TDCR count acquired from the purified tritium-free water samples.

The efficiency (ε) was determined by fitting the $TDCR_{sample}$ to a TDCR quench curve. The TDCR quench curve was constructed using a set of quenched standards, produced in the EPA using a certified tritium activity standard and varying amounts of Ultima Gold LLT scintillant[11]. The certified ^{3}H standard was obtained from LEA-Cerca, France.

The construction of the quench curve used 10 samples each containing 0.1 ml of (28.2 ± 8) kBq/l tritium standard. Various ratios of purified tritium-free water and liquid scintillation cocktail were added to achieve a quench curve (Efficiency versus TDCR) with a TDCR range from 0.201 to 0.514.

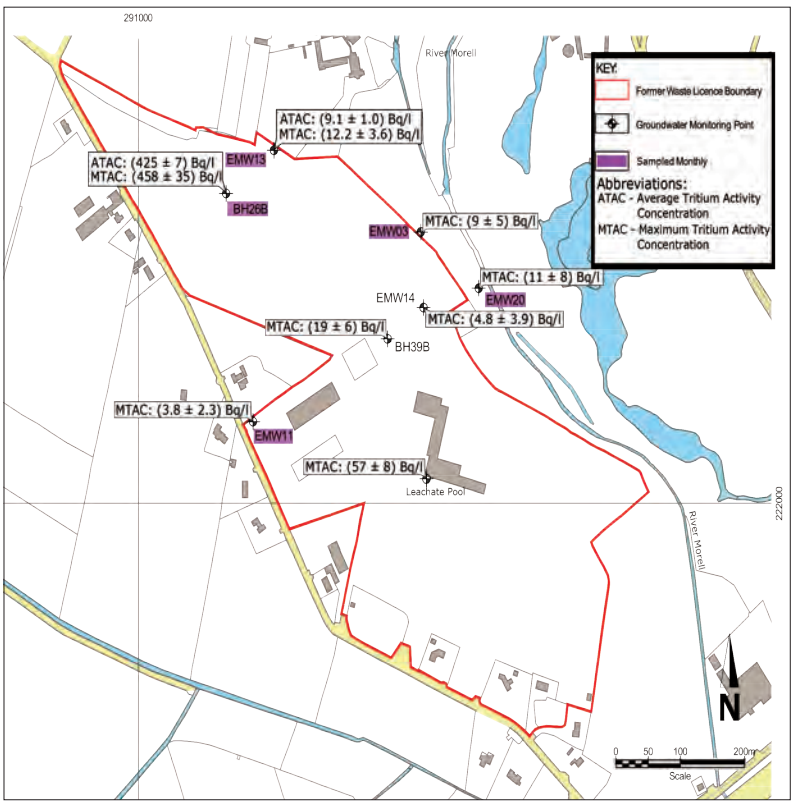

Fig. 2. Map of Kerdiffstown landfill illustrating the detectable tritium activity concentration. The maximum tritium activity concentration (MTAC) is calculated with an uncertainty of 2-sigma. The average tritium activity concentration (ATAC) is calculated with standard deviation.

Calibration consisted of analysis of tritium standards ranging in activity concentration from 3 Bq/l to 900 Bq/l. The Kragten approach was used to perform uncertainty analysis[9]. The decision threshold and detection limit was determined in accordance with ISO11929[8]. Where the decision threshold (y^*) was determined applying Eq. (3).

$$y^* = k_{1-\alpha}\,\tilde{u}\,(0) \qquad (3)$$

Where

$k_{1-\alpha}$ = The probability of the error of the first kind = 1.645.

$\tilde{u}\,(0) = u(A_0)$ = standard uncertainty of the measurand associated with the primary measurement result (activity of sample) when A_0 is 0.

The detection limit ($y^{\#}$) was determined applying Eq. (4).

$$y^{\#} = \alpha + \sqrt{\alpha^2 + (k^2_{1-\beta} - k^2_{1-\alpha})\;\tilde{u}^2\,(0)} \qquad (4)$$

With

$$\alpha = k_{1-\alpha}\,\tilde{u}\,(0) + \frac{1}{2}\left\{\left(k^2_{1-\beta}/A_1\right)\left[u^2(A_1) - \tilde{u}^2\,(0)\right\}\right.$$

Where

$k_{1-\beta}$ = The probability of the error of the second kind = 1.645.

A_1 = primary measurement result of the measurand (activity of sample).

$u(A_1)$ = standard uncertainty of the measureand associated with the primary measurement result A_1.

2.3. Gamma analysis

Gamma analysis was performed on a total of six samples at the Kerdiffstown landfill. These samples were for the month of September and were from boreholes EMW06, EMW11, EMW12, EMW15, EMW28 and BH26B.Gamma analysis was performed using a coaxial well detector (GCW4023, CANBERRA Industries Inc., U.S.A.) with a certified relative efficiency of 41.6%, and a resolution of 2.3 keV at 1.333 keV of ^{60}Co. The software used to analyse the spectra was Canberra Industries ApexGamma Spectroscopy software suite. 1 l of sample was analysed in a 1 l marinelli beaker for 24 hours.

3. Results and discussion

The tritium activity concentrations measured in this study above detection limits are indicated in Fig. 2. Figure 2, presents the average tritium activity concentration (ATAC) with standard deviation and the maximum tritium

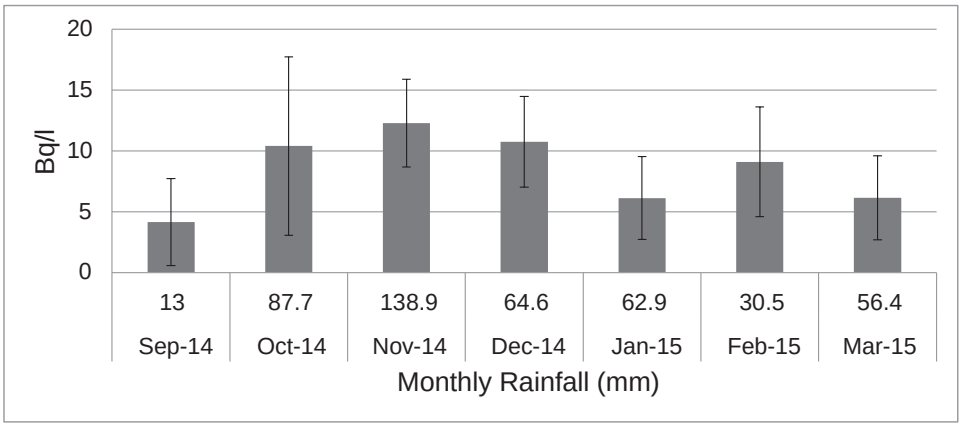

Fig. 3. A plot of tritium activity concentrations at EMW13 versus average monthly rainfall.

activity concentration (MTAC) with an uncertainty of 2-sigma. Of the 128 measured samples, 81% were reported as less than the detection limit. The average tritium activity concentration with associated standard deviation was determined for boreholes BH26B and EMW13. There were a total of seven measurements for BH26B. All measurements were distinguishable from background and an average with standard deviation of the seven was determined. There were a total of seven measurements for EMW13. Six of the seven measurements were distinguishable from background and an average with standard deviation of the six was determined. The variation of tritium activity concentration at EMW 13 in time series with monthly rainfall was determined and is presented in Fig. 3. The activity concentration of samples were not decay corrected to their sampled date due to the relatively short sampling period in comparison to the half-life of tritium, (12.312 ± 0.025) years.

The highest measured activity concentration of tritium within the landfill was (458 ± 35) Bq/l at borehole BH26B.

It is evident from the results that tritium concentrations are greatest at borehole BH26B. This would indicate that a tritium source or sources are present in the north of the site. The depth of BH26B is 70.45 mOD. The average depth of boreholes containing tritium was a depth of 72.91 mOD with the maximum recording at 76.44 mOD and the minimum at 68.76 mOD.

During the month of January tritium was recorded offsite at borehole twenty, EMW20. This indicates that leachate is leaving the site and is close to the River Morrell. Borehole twenty, EMW20, was measured on a monthly basis and for all other months the results were less than the detection limit.

The borehole with the highest tritium activity concentration measured in this study is above the parametric value of 100 Bq/l for EU standards for tritium in water intended for human consumption[12]. However, since this water is not been used as a drinking water source and the tritium activity concentration in the leachate is undergoing significant dilution before leaving the site there will be little or no concern of tritium from the landfill leachate affecting drinking water supplies in close proximity to the landfill.

Results from the gamma analysis indicate that no other artificial radionuclides are detectable at the measured locations.

4. Conclusions

Environmental analysis of tritium at the Kerdiffstown site has been identified as a potential environmental tracer for leachate flow within the site. The highest recorded tritium measurement for the sampling period was (458 ± 35) Bq/l. The highest measurement recorded on the site was less than half of the average of similar studies conducted[1, 3, 13]. The location of the highest tritium measurements was in the north eastern location of the site indicating the location of the tritium source.

By measuring the tritium source, there is potential to accurately determine the flow of leachate in the north-western zone of the landfill. By monitoring the tritium at the landfill, there is the potential to access the impact of weather conditions on the leachate plume. Additional studies could also determine the effects of the planned remediation on containing leachate plumes within the site.

Conflict of Interest Disclosure

All the authors report no conflicts of interest.

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