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Field Measurement of Fluorescent Dissolved Organic Material as a Means of Early Detection of Leachate Plumes

P. W. Graham · A. Baker · M. S. Andersen · I. Acworth

Abstract Early detection of landfill leachate plumes may minimise aquifer degradation and financial expenditure for the landfill operator. Current methods of landfill leachate monitoring typically include analysis of groundwater field parameters such as electrical conductivity (EC), coupled with laboratory analysis of a selection of major cations and anions. In many instances, background influences can mask the impact of leachate, which only becomes apparent once a significant impact has occurred. Here, we investigate the potential for changes in fluorescent dissolved organic material (FDOM) concentration to be used as an indicator of leachate impact. The research was undertaken in a fractured rock aquifer located downgradient of a local government-operated putrescible landfill in Central West NSW, Australia. Field measurement of groundwater FDOM was undertaken using an in situ fluorometer (FDOM probe) which provides a relative measurement of FDOM. To quantify the FDOM values, a bench fluorescence spectrophotometer was used to collect excitation/emission spectra. A plume of elevated FDOM and EC levels within the fractured rock system up to 600 m downgradient of the landfill was identified, whereas analysis of major cations and anions from boreholes within the plume did not detect leachate impacts above background. Excitation/emission matrices of groundwater from these locations confirmed that similar fluorescence signatures to those collected from the landfill were present. Photodegradation experiments were conducted to determine if fluorescent whitening agents (FWAs) were a component of the fluorescence signal. Observed photodegradation of 40 % compared to background (8 %) suggests that a component of the fluorescence signal can be attributed to FWAs. FDOM in groundwater therefore provides an indicator of low-level (up to 98 % dilution) leachate influence, and the identification of FWAs within groundwater can be considered confirmation of a leachate signal.

Keywords Optical fluorescence · Landfill leachate plume · Fluorescent whitening agents · Fluorescent dissolved organic material · PARAFAC · Photodegradation

1 Introduction

Worldwide, municipal landfills are the most common method of waste disposal and have proven to be a source of groundwater contamination in numerous geologic settings (MacFarlane et al. 1983; Kjeldsen 1993; Christiansen et al. 2001; Rapti-Caputo and Vaccaro 2006). Landfill leachate is the liquid produced when soluble organic and inorganic liquid components of the waste mix with infiltrating precipitation and groundwater (where groundwater interaction occurs) (Fetter 1999). The contaminants present within landfill leachate and the extent of leachate migration are dependent on numerous factors such as age of the landfill, landfill content, geological setting, environmental setting,

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attenuation and dilution. When constructed in recharge areas such as in upper catchment areas or valleys, the leachate emanating from uncontrolled landfills pose a considerable threat to groundwater and surface water resources in downgradient residential and agricultural areas (Lee et al. 2006). The World Health Organisation (2006) considers waste disposal to landfill to be responsible for pollution of groundwater resources under a wide range of conditions around the globe. Lee and Jones (1991) suggest that groundwater adjacent to sanitary landfills is polluted in more than 55,000 of the 75,000 monitored landfills within the USA. Numerous other studies have been undertaken across the world attempting to address various groundwater pollution issues associated with landfill waste (Christensen et al. 1998; Mikac et al. 1998; Afzal et al. 2000; Allen 2001; He et al. 2011, 2014a, b), and ongoing management of groundwater pollution is a matter of controlled management of leachate rather than prevention of leachate creation (Allen 2001).

The quality of landfill leachates varies over time as a result of new and emerging compounds such as perfluorinated compounds, *N,N*-diethyl toluamide (DEET), alkyl phosphates, pharmaceuticals, personal care products and xenobiotic organic compounds (Eggen et al. 2010; Preiss et al. 2012), and as a result, landfills are now viewed as a source of a new generation of emerging contaminants.

Traditional methods of monitoring landfill leachate are based on organic and inorganic geochemical processes and monitoring of the reaction products. Major cations and anions Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, PO_4^{2-}, SO_4^{2-}, NO_3^- and NH_4 combined with pH, EC and redox state are the typical suite of analytes used to characterise and identify leachate impact to groundwater surrounding a landfill (Baedecker and Back 1979; Basberg et al. 1998; Fetter 1999). These methods have been applied and refined over several decades and have proven useful for leachate plume characterisation. The methodology is however limited by the proviso that leachate must have impacted the groundwater and significantly altered the groundwater chemistry to allow detection of a leaking landfill, and that interpretation is based on a detailed understanding of regional groundwater chemistry and redox environment (Basberg et al. 1998). To this end, an evaluation of the effect of recharge from the surrounding catchment and of the natural vertical and horizontal distribution of groundwater quality in the recharge area is required to enable a suitable understanding of the resulting redox zonation and distribution of groundwater quality parameters caused by the landfill leachate (Park et al. 2008).

New methods for improving characterisation and monitoring of groundwater at potential landfill leachate-impacted sites utilising analysis of microbial populations have been proposed. These include the use of microbial diversity in groundwater and soil around a landfill site coupled with a nonparametric decision making process (Pearce et al. 2011) and identification of iron-oxidising bacteria at the surface water groundwater interface (Yu et al. 2010; Stuart et al. 2014). However, these methods require intensive sampling to determine microbial distribution and detailed statistical analysis to define areas of influence and results may be skewed by natural fluctuations in microbial populations.

The utilisation of optical fluorescence as a tool for characterising organic compounds within water is a well-established method. In 1991, Senesi was able to distinguish and identify humic and fulvic acids using fluorescence spectroscopy (Senesi et al. 1991). Further development of fluorescence analysis methods has resulted in more frequent use and broader application. Yunnis et al. (2012) applied laboratory measurement of UV absorption and fluorescence spectroscopy as a rapid and accurate method for monitoring of organic compounds in leachate samples from within a landfill. This methodology was compared to traditional laboratory methods for leachate characterisation such as dissolved organic carbon (DOC), chemical oxygen demand (COD) and major cations and anions. The research demonstrated that laboratory measurement of UV absorption and fluorescence spectroscopy was able to characterise different leachates, identifying the relative concentrations of aromatic, humic-like and fulvic-like compounds. The biodegradation rates of these components within the leachate could then be monitored. The study was limited to analysis of samples brought back to the laboratory and was not applied to the identification of leachate interaction with groundwater. Yunnis et al. (2012) stated that the advantages of the technique were "the rapid methodology and the demonstrated reliability".

The organic constituents within landfill leachates include a wide range of potentially fluorescent molecules and compounds (Vadillo 2006). Past findings have identified intense fluorescent peaks at λ_{ex} 220–230 nm and λ_{em} 340–370 nm, which were considered to be derived from the fluorescent xenobiotic organic matter

(XOM) fraction and fluorescence peaks at λ_{ex} 320–360 nm and λ_{em} 400–470 nm from a higher-molecular-weight fulvic-like fraction. Based on the level of fluorescence intensity, the potential leachate detection limit using optical fluorescence methods is <0.1 mg/L total organic carbon (Baker and Curry 2004). The fluorescent peaks associated with landfills have further been shown to be detectable at dilutions of up to 10^2–10^3 (Baker 2005).

One component of landfill leachate is likely to be stilbene-type fluorescent whitening agents (FWAs) such as the distyryl biphenyl (DSBP) and the diaminostilbene types (DAS), which are used in textiles, detergents, plastics and papers to make products whiter and brighter. Studies of FWA have suggested minimal potential for associated human health or environmental hazards (Burg et al. 1977). As a significant component of most landfills is paper, plastics and other compounds that contain FWAs, it is possible that FWAs could be used as a tracer for landfill leachate. Laboratory analysis of FWAs requires high-performance liquid chromatography with detection limits of between 0.12 and 0.24 mg/kg (Poiger et al. 1996; Jiang et al. 2015).

Riediker et al. (2000) analysed FWA from within four Swiss landfills using ion-pair liquid chromatography coupled to UV absorption. The landfills contained unsorted demolition and domestic wastes, and it was considered that FWAs identified were sourced from a combination of consumer and industrial products common in municipal waste, in particular dyes applied to paper and textiles. The analysis identified FWAs within the landfill leachate ranging from a few microgram per litre to several milligram per litre. The FWA concentrations identified were dependent on the landfill composition. No FWA was identified within samples from a monofill cell containing only municipal solid waste incineration residues. Low concentrations of FWAs were identified within landfill sections containing only industrial and demolition wastes, whereas the highest concentrations of FWAs were identified within leachates from landfills containing municipal solid waste (Riediker et al. 2000). It therefore seems reasonable to hypothesise that most landfills receiving general municipal waste would have some level of detectable FWAs.

As FWAs are produced to perform different functions, their physical and chemical characteristics are highly variable. A study of seven stilbene-type FWAs undertaken for the USEPA found the water solubility of the seven compounds varied between 1.9 and 400 g/L at 20 C, noting in particular that many FWAs are used as commercial products that are purposefully soluble in water. The USEPA report also discussed the potential for migration of FWAs within surface water, soils or groundwater; influencing factors included the partition coefficient (Log K_{ow}) which in the seven FWAs studied ranged between 3.23 and −3.89. It was noted that the presence of methyl groups in the FWA resulted in strongly positive Log K_{ow} while FWA molecules with sulphonate salts were found to have strongly negative Log K_{ow}. Fugacity mass percent values were typically air 0 %, water 60.8 %, soil 39 % and biota <1 %. Biodegradation rates were found to vary between 1.2 and 98.8 % over 28 days depending on the form of FWA (Ciba 2005).

Most FWA compounds are not readily biodegradable, but due to their ability to absorb part of the terrestrial sunlight, they can be photochemically degraded (Leaver and Milligan 1984; Kramer et al. 1996; Managaki and Takada 2005; Mostofa et al. 2010). A study of the degradation of DSBP and DAS dissolved in lake water and exposed to sunlight found half-lives of 63 min for DSBP and 245–302 min for DAS (Kramer et al. 1996). Studies of FWA in river sediments have found varying rates of degradation depending on the wavelength of the fluorophore (Mostofa et al. 2010; Yamaji et al. 2010). Baker (2002) identified fluorescence intensity peaks correlating with likely fluorescent whitening agents (FWAs) in river water collected downgradient of pulp mills. The identified fluorescence peaks were noted to decrease by ~40 % when the water samples were exposed to sunlight over a 24-h period. This decrease in fluorescence was considered a good indication of the presence of a mixture of FWAs within the water samples (Baker 2002). Sewage disposal is also typically high in FWAs, and numerous studies have utilised these characteristics to trace sewage impact in rivers and lakes (Close et al. 1989; Stoll et al. 1998; Mostofa et al. 2010; Yamaji et al. 2010), and the presence of FWAs in sewage is expected to be similar to FWAs which may be present in landfill leachate. The fate of FWAs in groundwater has not been documented in detail.

This suggests that FWAs will have highly variable properties in the environment and that there is potential for some of the FWAs present in large quantities in landfills to have high water solubility, a moderately low partition coefficient and be relatively mobile in groundwater, resulting in a chemical landfill tracer which is detectable using fluorescence.

The recent production of portable submersible fluorometers has made it possible to measure the concentration of FWAs in groundwater samples in situ. The aim of this research is to demonstrate that FWAs are a detectable component of landfill leachate which will be present at the front of most leachate plumes. The research also demonstrates that a landfill leachate plume could be identified and delineated in situ using an FDOM probe. The research therefore addresses two novel concepts: (1) a new tracer for landfill leachates and (2) a new method for identification and monitoring landfill leachate plumes.

2 Materials and Methods

2.1 Hydrogeological Setting

Research was undertaken at the University of New South Wales (UNSW), Australia Wellington Research Station (UNSW-WRS), which is located at Wellington in the central west of New South Wales (Fig. 1). The area is described by the Australian Bureau of Meteorology (BOM) as hot and dry, but with cool winters. This area is characterised by an average January temperature of >30 °C, the average 3 p.m. January water vapour pressure <2.1 kPa and the average July mean temperature <14 °C (BOM 2012). The annual average rainfall in the area is approximately 650 mm.

The site is located on the western side of the Macquarie River and is set within the Lachlan Fold Belt (Fig. 1). Burrendong Dam is located approximately 15 km to the South East of the UNSW-WRS. The Macquarie River runs approximately 25 km between Burrendong Dam and the site. The Macquarie River at the UNSW-WRS is located in a narrow low valley and overlies an assumed fault zone, with Ordovician metamorphic units outcropping on the eastern side of the river and Devonian metamorphic units on the western side (Scott et al. 1999). Both units outcrop as small hills with the Ordovician units rising steeply on the eastern side and the Devonian units rising on a more gentle slope to outcrop as a hill (approximately 40 m above the normal river level) approximately 600 m from the river bank. The area between the river and the outcropping Devonian units is infilled with Quaternary alluvial units which vary in texture from silts and clays to gravel and cobble units.
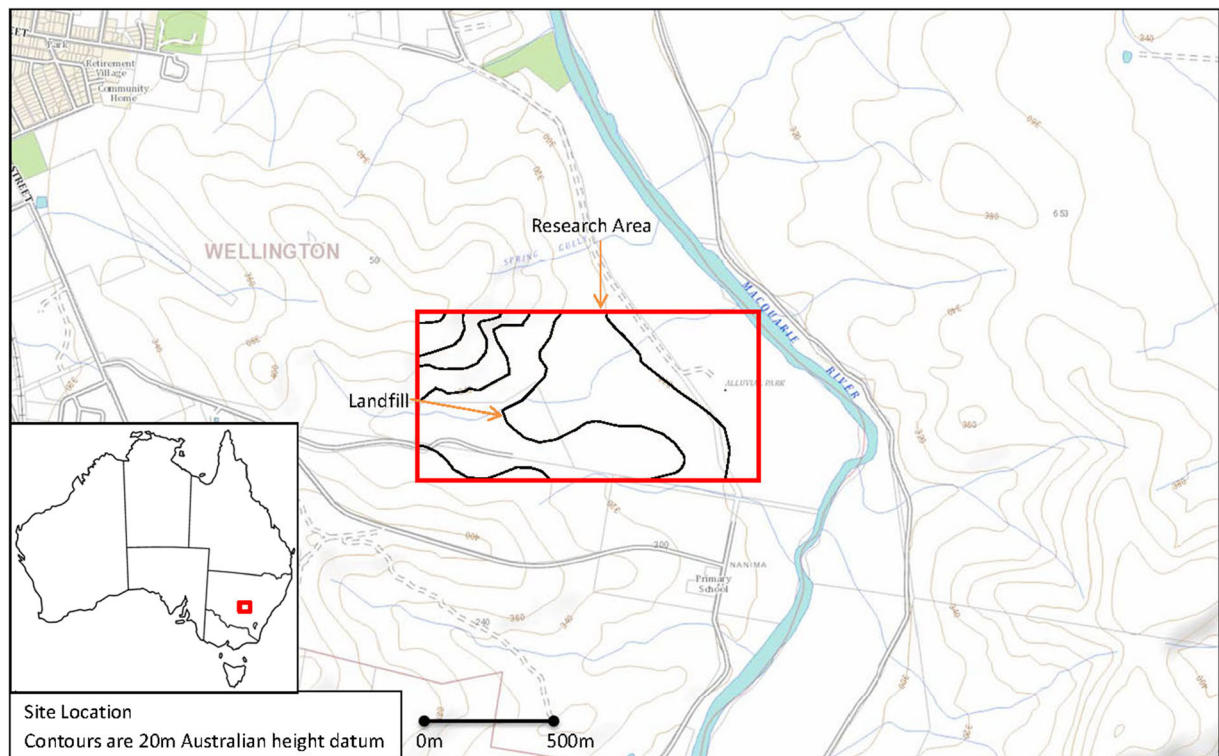

Fig. 1 Site location and regional topography

The landfill is situated halfway up a side valley on the Devonian metamorphic units. These valley slopes to the east and a combination of residual and alluvial clays and sands have filled in the valley below the landfill with the depth increasing towards the Macquarie River which is approximately 1.2 km from the landfill (Fig. 2).

A fractured rock aquifer is present below shallow alluvium within the Devonian units at an approximate depth of 8 m below ground level (mbgl) at the landfill and increasing to 18 mbgl at a distance of 500 m to the east of the landfill. A permanent water table was not detected in the alluvial aquifer within 900 m of the landfill. Current understanding (based on an unpublished detailed drilling and hydrogeological study undertaken by the authors) is that there is some connectivity between the alluvial and fractured rock system; however, the full extent of this connectivity has not yet been determined. A cross section of the study site is presented on Fig. 2.

The landfill is approximately 20 years old and has been installed on a liner composed of locally sourced clays compacted to 95 %. The cell of interest was decommissioned approximately 8 years ago and was covered by placement of a compacted clay. There is no leachate management system in place for the cell. During operation, the landfill accepted general household waste (including putrescible materials) and inert

building materials. It is understood that material from an older landfill (constructed circa 1960) previously located approximately 100 m to the south west of the current landfill was relocated into the current cell. There is also a sealed cell located approximately 300 m to the north-west of the current cell which was in the past used for disposal of animal carcasses. The cell is monitored and maintained by the local Municipal Council. This style of landfill (construction, geographical location, waste type and management) is typical of Australian landfills, and until mid-2000s (when local waste transfer stations were established), these landfills were present in almost every small to large Australian rural town.

2.2 Methodology

The fractured rock aquifer was characterised through a drilling program including installation of 23 boreholes using a combination of Tubex and air hammer drilling methods. In addition, three existing boreholes located around the perimeter of the landfill were used for the study. The location of the boreholes in relation to the landfill is shown in Fig. 2.

Samples were collected over a 7-month period between December 2012 and June 2013 using a 12-V centrifugal groundwater pump. Prior to use, a sample of the
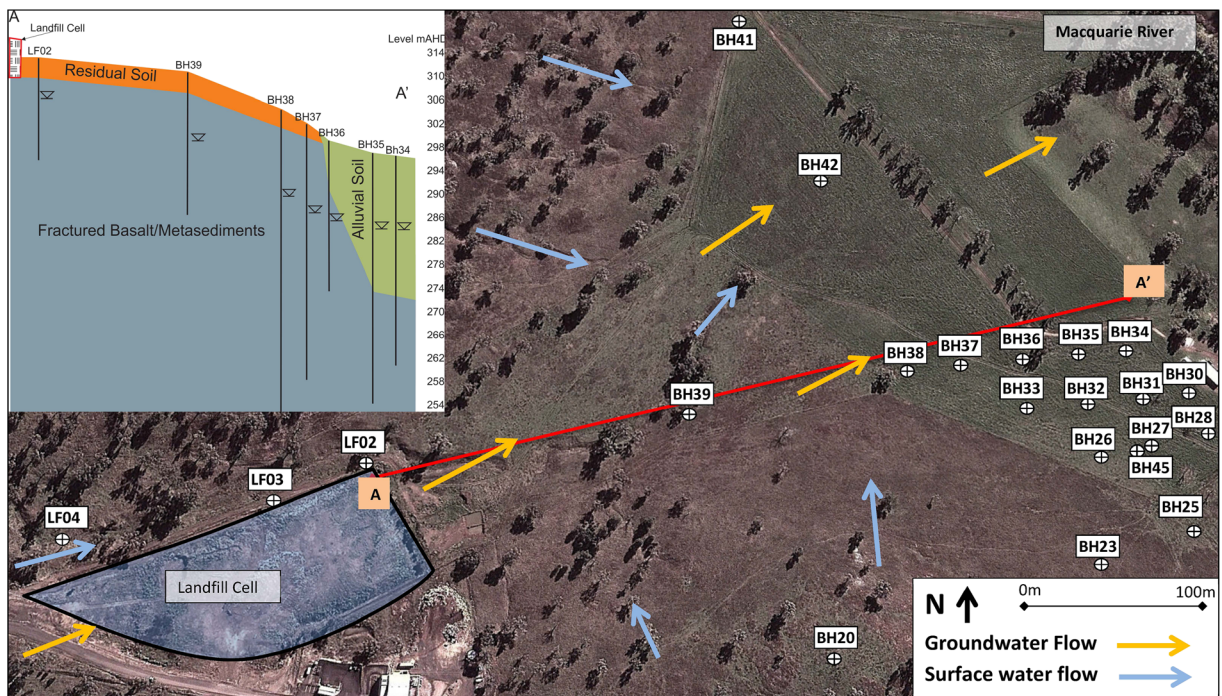

Fig. 2 Site features, borehole locations and cross section A–A′ (vertically exaggerated)

groundwater pump tubing was soaked in distilled water and a sample of the soak water was subjected to all analysis methods to ensure that it would not be a source of fluorescent materials. Prior to sampling, all locations were dipped to measure the standing water level and hence calculate the stagnant volume of the borehole and three borehole volumes were then purged from the boreholes. Groundwater was pumped through a flow cell measuring pH, EC, DO and temperature. The water was then passed through a darkened flow cell to prevent sunlight exposure and interference in the FDOM readings.

The submersible in situ fluorometer (Turner Designs, FDOM fixed sensor range excitation 350/390 nm, emission 440/500 nm (FDOM probe)) was mounted in this flow cell. During pumping, especially around the landfill, bubbles were observed to accumulate on the optical window of the FDOM probe, resulting in erroneous readings. Therefore, a revised sampling method was developed, where once the field flow cell values had stabilised, the pump was switched off, the optical window cleared of accumulated bubbles and an FDOM reading collected.

Samples were also collected for laboratory analysis using an Aqualog (Horiba) Spectrofluorometer (ASF) and HACH pocket colorimeters. These samples were collected directly from the pump tubing and field filtered using nonpyrogenic 0.45-μm disposable filters. New filters were used for every location.

Following field sampling, excitation/emission matrix (EEM) spectra were collected using the ASF. Scans were conducted using excitation wavelengths from 240 to 400 nm at 10-nm steps. Emission wavelengths were collected from 210 to 600 nm at 2-nm bandwidth and 1-s integration time. The intensity of all EEM spectra was normalised by dividing the integrated intensity area of the Raman water curve at 350-nm wavelength excitation from the 370- to 450-nm emission wavelength range. Initial EEMs for Borehole LF02 were found to be influenced by the presence of significantly elevated FDOM, and as a result, samples from this location were diluted to 50 % of the initial concentration using distilled water. Inner filter correction was undertaken, and scatter lines were masked. The EEM data was then used to build a model using parallel factor (PARAFAC) analysis (Leurgans and Ross 1992; Bro 1997; Coble et al. 2014). Absorbance data was also collected at the wavelength of 340 nm (Table 1).

Samples were analysed for nitrate, ammonia and phosphate colorimetrically, using the cadmium reduction method for NO_3^-, the indophenol method for NH_4^+ and the acid persulphate digestion method for PO_4^{3-}. In addition, a round of samples was collected in April 2013 and analysed for major cations and anions. Samples were analysed by the UNSW Analytical Centre, cations were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES); anions, nitrate and phosphate were analysed using ion chromatography; and N-NH$_4$ was analysed using flow injection analysis (FIA).

To determine the relative leachate concentration in downgradient boreholes, a leachate dilution experiment was undertaken on groundwater collected from borehole LF02, which was located immediately adjacent to the landfill. Unfortunately, a borehole specifically sampling the landfill cell itself was not available; however, the concentration of leachate within borehole LF02 was sufficiently high to provide dilution estimates relative to this borehole. A bulk sample of groundwater from borehole LF02 was collected, and field measurements of FDOM were taken. A filtered sample was also collected for analysis using the ASF. The bulk sample was immediately returned to the laboratory, and dilution samples were prepared with a mixture of the groundwater from borehole LF02 and distilled water. These samples were then analysed using both the FDOM probe and the ASF (following filtering).

Assaad et al. (2014) and Kramer et al. (1996) confirmed that FWA was present within river and lake waters through measurement of photodegradation rates, with rapid (<200 min) photodegradation and reduction in fluorescence intensity indicating the presence of FWA. As this method is an established diagnostic test for the presence of FWAs which can be implemented in the field, it has been applied in this study to determine if part of the FDOM detected was likely to be FWAs. The experiment included a series of photodegradation experiments which were undertaken on (a) groundwater from boreholes considered likely to be impacted by leachate and (b) boreholes which were known to be outside the leachate plume. The experiments were undertaken using natural sunlight on three separate dates, and the experiment dates were selected based upon weather conditions to ensure that there was no cloud cover and constant sunlight was present during the experiment. On 23 April 2013, a 150-min experiment was undertaken on boreholes BH36, BH26 and BH28. On 14 May 2013, a 2880-min experiment was undertaken on boreholes BH36 and BH39, with duplicate samples run for both

Table 1 Average ($n=6$) nutrient concentrations and PARAFAC components

	Metres from LF02	α OD 340 nm ($-$Log T)	C1 (QFI)	C2 (QFI)	C3 (QFI)	EC (μs/cm)	FDOM (FI)	NO_3 (mg/L)	P-PO_4 (mg/L)	N-NH_3 (mg/L)
LF4	-290	0.0098	129	77	55	1172	466	0.50	0.53	0.12
LF3	-110	0.0311	779	468	731	1708	1681	0.40	0.40	0.28
LF2	0	0.1805	5336	3359	1762	2038	13,590	0.57	1.09	0.83
BH39	290	0.0745	1600	1260	942	1783	4549	0.57	0.50	0.29
BH38	510	0.0197	388	320	269	1271	1258	2.30	0.65	0.14
BH42d	560	0.0122	242	202	204	931	902	2.83	0.69	0.05
BH37	560	0.0135	328	241	228	1364	1114	2.10	0.46	0.10
BH33	600	0.0118	142	93	125	1048	525	2.80	0.30	0.17
BH36	610	0.0174	296	209	222	1321	910	2.48	0.68	0.02
BH41	620	0.0155	121	70	95	1093	417	3.25	0.45	0.18
BH32	671	0.0118	97	61	94	998	430	3.35	0.33	0.06
BH23	685	0.0084	41	21	35	651	189	1.30	0.45	0.15
BH35d	693	0.0043	93	62	82	924	308	3.40	0.42	0.15
BH26	700	0.0053	34	14	24	618	172	2.91	0.33	0.12
BH31d	739	0.0159	202	132	530	683	447	1.85	0.56	0.08
BH34d	739	0.0042	49	32	64	673	220	4.10	0.58	0.00
BH45	748	0.0093	57	32	49	742	214	4.39	0.48	0.09
BH27d	755	0.0042	56	32	57	762	227	3.72	0.52	0.04
BH25	770	0.0032	54	27	52	634	254	3.93	0.55	0.11
BH29	770	0.0098	58	32	53	821	188	3.16	0.44	0.06
BH30d	790	0.0030	35	18	29	804	119	4.50	0.25	0.05
BH28	810	0.0055	82	45	80	807	346	3.68	0.70	0.02

Shaded boreholes are considered to be influenced by landfill leachate, and borehole BH33 is at the margin of the plume

QFI quantitative fluorescence intensity, *FI* relative fluorescence intensity, α UV absorbance at 340 nm

boreholes during this experiment. On 5 June 2013, a 360-min experiment was undertaken on boreholes BH26 and borehole BH33. The experiments were undertaken by extracting representative groundwater from each location and holding the water in a clear 15-L plastic container. The containers were then placed in direct sunlight, and samples were collected at specified intervals. Collected samples were analysed using the FDOM probe mounted within the darkened sampling bottle; these samples were then filtered, and excitation emission matrices were collected using the ASF. The water temperature in the plastic containers was monitored, and the temperature increased by between 4 and 5 °C during the experiment. As the filtration of samples could potentially change the fluorescence signal (Baker et al. 2007), during the sunlight degradation experiment undertaken on 23 April 2013, both filtered and unfiltered samples were analysed using the ASF. Sixteen

pairs of filtered and unfiltered samples were analysed, and the results run through the PARAFAC model.

3 Results

The aim of the experiment was to demonstrate that the FDOM probe could identify a landfill leachate plume utilising measurements of fluorescence intensity collected in the field (FDOM probe) and validated through laboratory analysis (ASF). This was done by comparing fluorescence of DOM background groundwater to the fluorescence of DOM and leachate within leachate-impacted groundwater. The composition of the leachate component being detected was then confirmed to be FWA by application of an established diagnostic method for measurement of FWA in surface waters.

3.1 Correlation of ASF to FDOM using PARAFAC Model

Groundwater samples were collected on a monthly basis between December 2012 and June 2013. Field data suggests a groundwater gradient of between 0.015 and 0.05 m/m running from the landfill in a general easterly direction (towards the sampled bore field) (Fig. 2). No temporal trends could be discerned, and average values for field-measured EC and FDOM are therefore presented in Table 1.

Through the course of the study, a total of 480 EEMs were collected. A three-component model was derived by applying the PARAFAC method to the 480 EEMs. The three-component model had a core consistency of 85, and a four-component model was developed; however, core consistency dropped significantly to 59 indicating an over-specified model (Coble et al. 2014). The three components were characterised by the following ranges: C1 300–350/400–450 nm Ex/Em and <260/400–450 nm Ex/Em, C2 240–270/430–500 nm and 360–400/430–500 nm Ex/Em and C3 270–280/350 nm and <250/350 nm Ex/Em, corresponding to peaks M/C (terrestrial-derived humic material), C^+ (reprocessed, allochthonous humic material) and T (tryptophan, microbial/protein like), respectively, as described by Coble (1996). Modelled EEMs for the three components are presented in Fig. 3.

The three-component PARAFAC model outputs (a quantitative measure of FDOM for each component) were averaged across the sampling period for each location (Table 1). Contours of the measured FDOM, C1, C2, C3 and EC values have also been presented on Fig. 4. Table 1 has been ordered based on the distance from borehole LF02 (at the base of the landfill). The locations considered to be influenced by leachate have been shaded. This shows a general trend of decreasing concentration of EC, FDOM, humic and microbial components with increasing distance from borehole LF02. In situ FDOM data shows a significant decrease away from the landfill monitoring borehole LF02 towards the east. The FDOM gradient as measured by the FDOM probe (Fig. 4d) ranged from 13,000 relative fluorescence intensity immediately adjacent to the landfill to approximately 1000 relative fluorescence intensity at borehole BH36. The relative fluorescence intensity in all boreholes east of borehole BH36 dropped significantly to levels ranging between 100 and 500. These levels are considered to be representative of natural background FDOM in the area.

Borehole BH31d is an outlier in this data set and has been noted during sampling to be recharging very slowly and have poor water quality. We consider this borehole to be in a low permeable zone and not well connected to the aquifer. Borehole BH20 is also an outlier, as it is located at the peak of a hill which is thought to be strongly influenced by direct rainfall recharge through fractures and thus being hydraulically up-gradient from the landfill.

Correlation between the FDOM probe and the absorbance (at 340 nm), C1, C2, C3 and EC has been calculated using the data presented in Table 1. The R^2 of FDOM to absorbance, C1, C2, C3 and EC was 0.99, 0.99, 0.99, 0.87 and 0.55, respectively. The correlations between FDOM data collected using the in situ probe and laboratory-derived C1 and C2 values confirm the applicability of the field probe for leachate detection.

To assess the extent of any inner filter effect (IFE), absorbance data was compared to C1, C2 and C3 results. The absorbance data correlated to the C1, C2 and C3 data sets with a 0.987, 0.994 and 0.942 R^2, respectively. A plot of the absorbance data against FDOM, C1 and C2 data sets is presented in Fig. 5a–c. The relationship was linear in each instance with no obvious outliers in the absorbance vs C2 plot. Borehole BH39 was slightly displaced in the C1 and C3 plots, and BH31d was an outlier in the C3 plot, but as explained above, this borehole is not well connected to the aquifer.

3.2 Photodegradation

The results of the photodegradation experiments are presented in Fig. 6. The figures show fluorescence intensity vs time for the PARAFAC components C1, C2 and C3 and the FDOM probe results for each degradation experiment. Table 2 shows a summary of the degradation measured between 150 and 160 min into each experiment.

The relative fluorescence intensity was found to decrease between 20 and 70 % in borehole BH36, approximately 30 % in borehole BH39 and approximately 40 % in borehole BH33. Boreholes outside the area of impact showed an early decrease of approximately 10 % of the initial intensity within the first 30 min; following this, relative fluorescence intensity remained constant.

Fig. 3 EEMs of PARAFAC model components, **a** component 1, **b** component 2 and **c** component 3. The *grey-shaded area* represents the excitation and emission wavelengths detected by the FDOM probe (Ex 350–390 nm Em 440–500 nm)
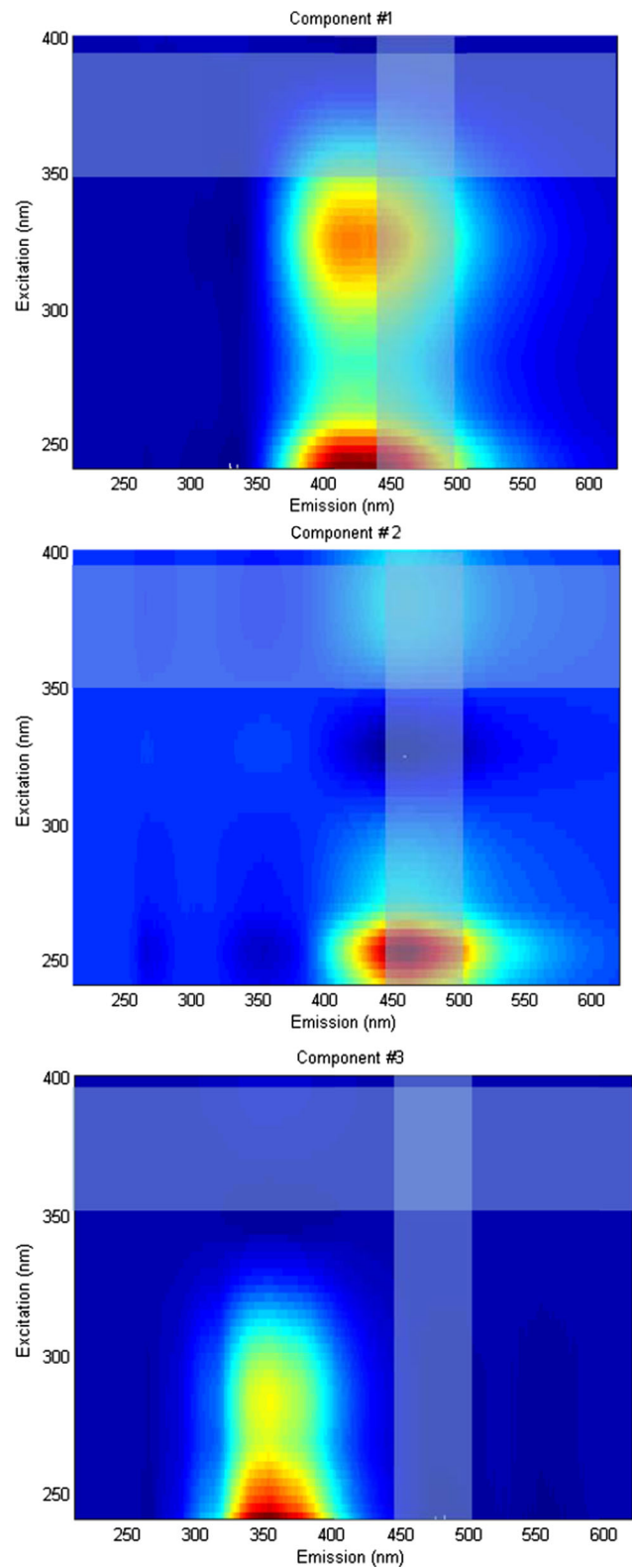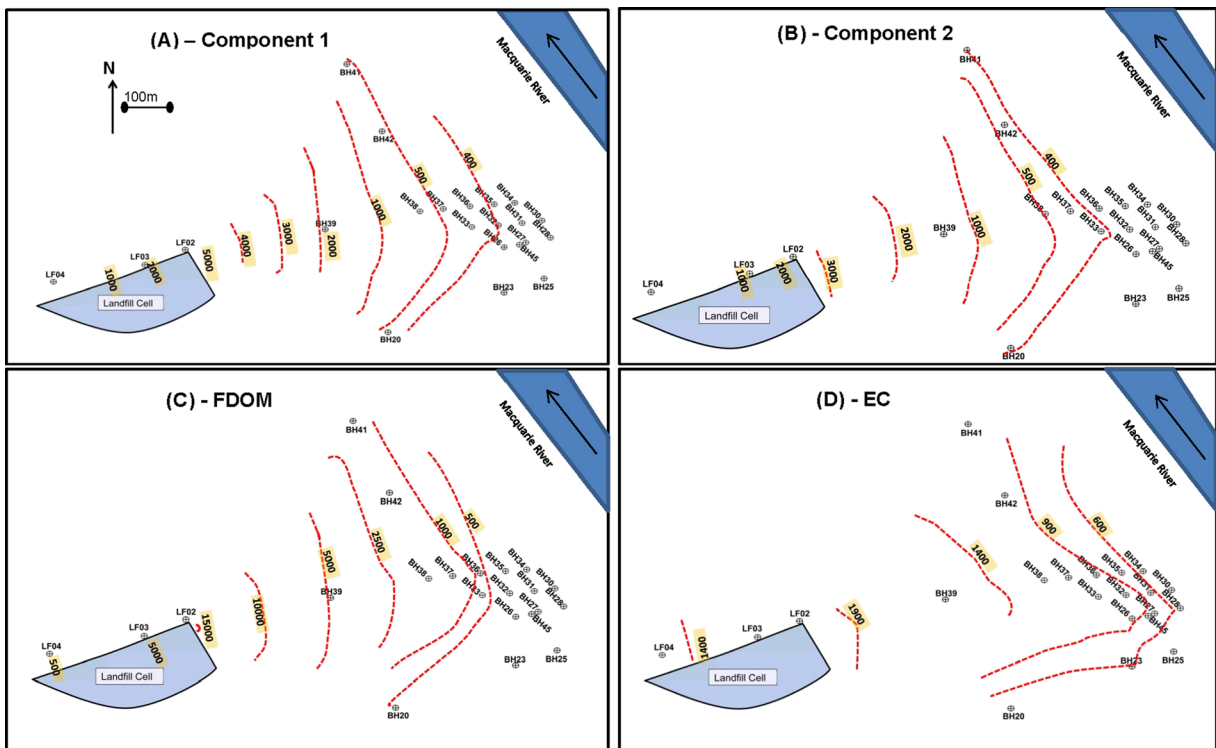
Fig. 4 Contours of **a** component 1, **b** component 2, **c** FDOM and **d** EC

Filtered and unfiltered samples were collected and analysed using the ASF during the April 23, 2013, sunlight degradation experiment. Relative percentage difference (RPD) was calculated for the three model components within each pair. The RPDs are presented in Table 3.

The experiment considered the potential for oxidation of the groundwater during sampling, to affect the redox chemistry resulting in precipitation of iron oxyhydroxides and potentially co-precipitation of DOM, which could influence the fluorescence. Use of suboxic chambers such as those described in Lapworth et al. (2013) may be applicable on some sites where the groundwater samples are anoxic and UV treatment is required to confirm if FWA is present. However, the FDOM probe is able to be employed in the borehole; therefore, field FDOM analysis can be completed with minimal risk of impacting the redox conditions. Measurement of DO and Fe^{2+} during sampling (Table 4) on this site suggests that the water was highly oxidised and significant redox reactions were only occurring in boreholes LF02 and BH39 which were in the immediate vicinity of the landfill where fluorescence signals were at the upper point of instrument detection limits and loss of DOM due to precipitation is not considered an issue.

3.3 Leachate Dilution

The results of the leachate dilution experiment are shown in Fig. 7. The figure shows the FDOM, C1, C2 and C3 landfill dilution values for 100, 50, 20, 10, 5, 2 and 1 % along with the same values for specific boreholes. These data sets have been ordered based on FDOM relative fluorescence intensity values with the x axis the estimated percentage of leachate (Log). It should be noted that ordering the samples in this manner has also resulted in all samples within 650 m of the landfill being placed in order of distance to the landfill. The figures show the relative fluorescence intensity in each borehole against a 0 to 100 % dilution slope. Borehole BH39 is located between 30 and 40 % leachate concentration; borehole BH38 is approximately 5 %; and boreholes BH37, BH36, BH42d and BH33 are all within the 5 to 1 % range. Other boreholes on site can be seen to be placed at levels of less than 1 % or what would be considered to be natural background FDOM relative fluorescence intensity concentrations.

The data sets in Fig. 7 have been ordered based upon data collected in the field by the in situ probe. It can be seen that the laboratory-derived data correlates to the field data, confirming the accuracy of the field FDOM data.

Fig. 5 Absorbance data compared to **a** component 1, **b** component 2 and **c** FDOM. Data presented is monthly collected over 6 months between January and July 2013
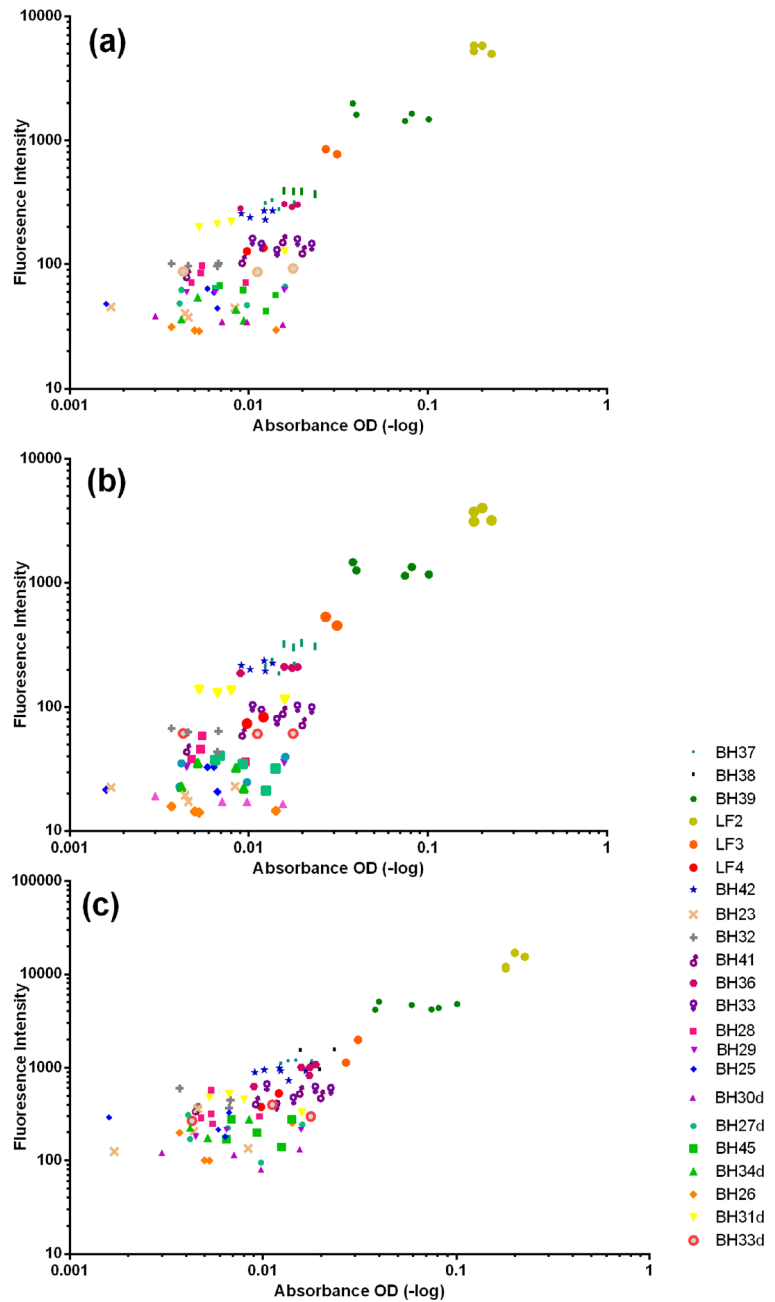

3.4 Correlation of Fluorescence Data to Chemical Data

The major cation and anion data collected in April 2013 was analysed and is presented in Table 5; note that due to site restrictions, samples were not collected from LF02 and BH39 at this time. The boreholes have been ordered based on the distance from the landfill, and locations which (based on fluorescence analysis

reported later) are considered to be influenced by leachate have been shaded. Correlation between distance from landfill and each major cation and anion was calculated as was the correlation between FDOM measurements and the major cations and anions, and R^2 values for each are present in the first two rows of Table 5. Correlation of the major cations and anions to the distance of the sample from the landfill is poor with

Fig. 6 Results of photodegradation experiment: (a) component 1, (b) component 2 and (c) FDOM
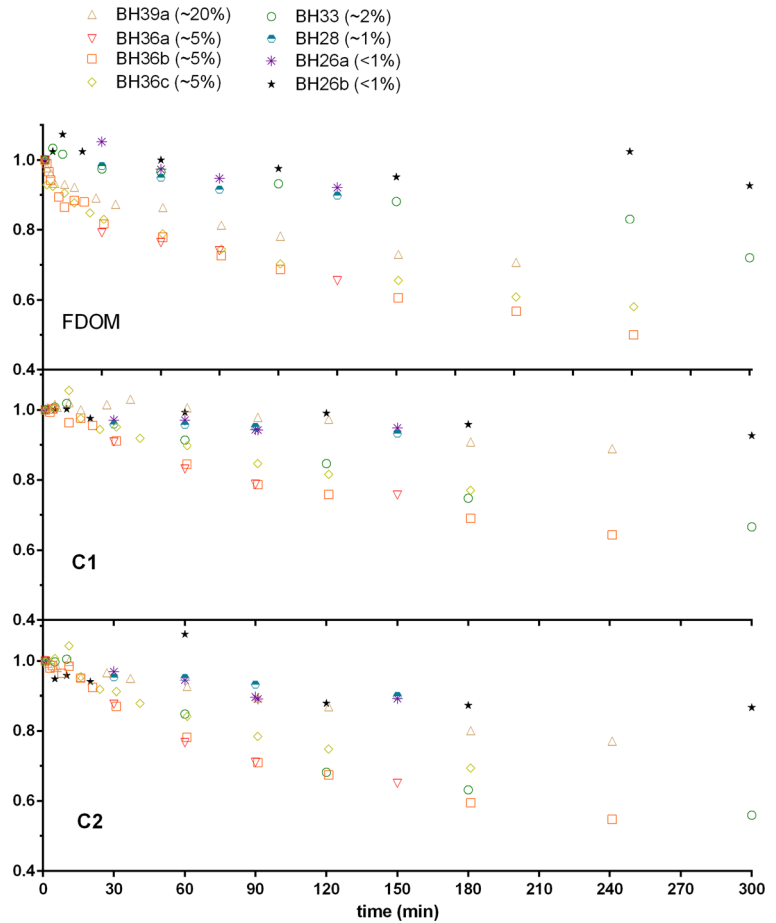
the highest correlation being 0.36 for alkalinity. The correlation to FDOM values is also poor with no R^2 value exceeding 0.33.

It was noted that EC and alkalinity were correlated with a R^2 value of 0.73. This suggests that there is some mineralisation of organics occurring within the landfill

and in the plume. However, any mineralisation in the plume would be dependent on reducing conditions which were only identified in close proximity to the landfill (boreholes LF02 and BH39). The elevated background alkalinity is considered to be a combination of mineralisation of natural organic matter in the unsaturated zone and dissolution of carbonate minerals.

4 Discussion

Generally, groundwater was found to flow in an easterly direction, with the borefield placed down gradient of the landfill. A large northward groundwater gradient was observed from the hill to the south of the landfill. This indicates that the aquifer is also being recharged by rainfall infiltration into fractures on this hill, which could provide a source of dilution.

The experiment was undertaken to demonstrate that the field application of the FDOM probe provides

Table 2 Photodegradation

	A (340 nm)	FDOM	C1	C2	C3
Fraction of initial concentration remaining at 150–160 min					
BH26 23 April 2013	0.83	0.92	0.94	0.89	1.26
BH26 05 June 2013	1.10	0.95	0.95	0.87	1.05
BH28 23 April 2013	1.23	0.89	0.93	0.89	0.81
BH33 05 June 2013	0.96	0.88	0.63	0.63	0.64
BH36 23 April 2013	0.46	0.65	0.75	0.65	0.99
BH36b 14 May 2013	0.46	0.65	0.69	0.59	0.88
BH36c 14 May 2013	0.39	0.60	0.77	0.69	0.97
BH39 14 May 2013	0.74	0.73	0.90	0.80	1.00

Table 3 Relative percentage difference between fluorescence components analysed by ASF on filtered and unfiltered samples

		C1 RPD	C2 RPD	C3 RPD
BH26	0 h	5.33	9.18	28.80
	0.5 h	5.95	9.10	23.90
	1 h	6.18	5.64	12.56
	1.5 h	6.71	8.85	21.68
	2.5 h	7.63	5.67	13.06
BH28	0 h	1.30	2.08	6.08
	0.5 h	3.40	2.83	6.32
	1 h	2.39	2.34	4.89
	1.5 h	2.94	3.04	5.68
	2.5 h	5.29	3.98	9.71
BH36	0 h	0.77	0.90	3.66
	0.5 h	0.28	0.49	4.09
	1 h	0.40	1.67	5.74
	1.5 h	0.57	1.57	6.91
	2.5 h	0.36	0.78	3.51

The shaded rows are within the area considered to be influenced by leachate, and BH33 is considered to be at the margin of the plume

meaningful data for measurement of landfill leachate. Field readings were compared to laboratory EEM and absorption data collected using the ASF to confirm the suitability of the field data collected. Correlation between the field data and the laboratory collected data was high and suggests that the field method is an accurate and robust method for rapid data collection.

The in situ FDOM probe results were not filtered, and therefore, we assessed the potential for sample filtration prior to analysis on the ASF to affect the fluorescence intensity. Therefore, during the 23 April 2013 sunlight degradation experiment, both filtered and unfiltered samples were analysed by the ASF, and RPDs were

Table 4 Dissolved oxygen and Fe^{2+} field measurements

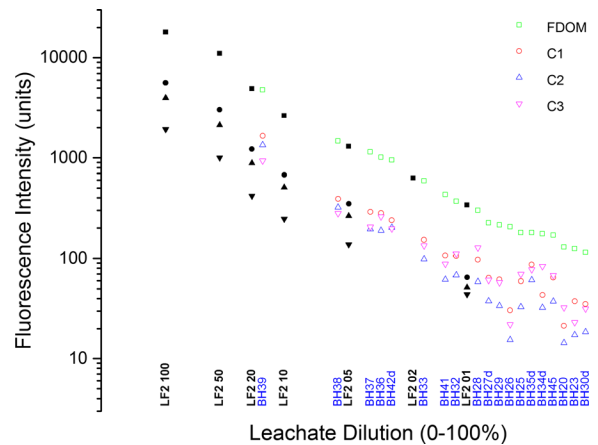|	BH25	BH26	BH27	BH28	BH29	BH30
Fe^{2+} (µg/L)	1.3	0.4	0	0	0	0
DO (mg/L)	2.73	5.68	4.93	1.72	6.53	6.77
	BH31	BH32	BH33	BH34	BH35	BH36
Fe^{2+} (µg/L)	–	0	0	0.1	0	0.8
DO (mg/L)	2.5	6.24	>6	3.73	3.98	4.33
	BH37	BH38	BH39	BH41	BH42	LF02
Fe^{2+} (µg/L)	1	1.2	31.6	0	1.1	–
DO (mg/L)	4.49	4.59	0.04	4.12	0.06	0.8

Fig. 7 Fluorescence intensity of diluted landfill leachate with FDOM and ASF data included. X axis is a Log 10 scale of leachate content, and field data has been ordered based on FDOM values

calculated for each filtered/unfiltered pair (Table 3). The RPDs for components 1 and 2 ranged between 0.36 and 0.9 for borehole BH36 (within the plume). The RPDs for components 1 and 2 for boreholes BH26 and BH28 (outside or at the fringe of the plume) ranged between 1.3 and 9.1. The RPD for component 3 ranged from 3.5 to 6.9 within the plume and 4.8 to 28.8 in the samples outside or at the fringe of the plume. Within the plume (borehole BH36), the relative fluorescence intensity was approximately ten times higher than the background samples. The higher RPDs for points outside the plume therefore represent only small changes in fluorescence intensity. The low RPDs for components C1 and C2 in samples collected from borehole BH36 (0.36–0.90) suggest that sample filtration did not significantly alter the fluorescence intensity and the experimental results, and these results are consistent with those reported by Baker et al. (2007) for freshwater DOM.

He et al. (2014a) demonstrated through fluorescence spectroscopy that one of the major sources of DOM within landfill leachate is microbial by-product-like material such as protein-like components produced by enhanced microbial activity stimulated by compounds within the leachate. The experiment undertaken here was able to distinguish protein- and microbial-like DOM in the fluorescence analysis. The FDOM probe, due to its specific wavelength, is not sensitive to microbial- and protein-like components. The PARAFAC analysis undertaken on EEMs from the ASF was able to distinguish three specific components, of which component C3 targeted microbial- and protein-like FDOM. The C3 component was therefore not considered in the photodegradation analysis.

Table 5 Major cation and anions relative to distance from landfill and FDOM values

	Metres to LF02	FDOM (FI)	Na$^+$ (mg/L)	Ca^{2+} (mg/L)	K$^+$ (mg/L)	Mg^{2+} (mg/L)	Cl$^-$ (mg/L)	F$^-$ (mg/L)	SO$_4$$^{2-}$ (mg/L)	Alk (meq/L)
R^2 distance to LF02	0.78	0.08	0.03	0.33	0.00	0.02	0.01	0.01	0.36	
R^2 FDOM		0.33	0.24	0.33	0.10	0.02	0.08	0.01	0.27	
BH39	290	4549	na	na	na	na	na	na	na	13.6
BH38	510	1258	68.3	122	0.79	82.2	131	0.6	43	14.2
BH42d	560	902	70.1	77.5	0.88	55.9	77	<0.1	29	6.9
BH37	560	1114	64.1	127	0.76	79.7	122	0.5	42	11.1
BH33	600	525	57.6	103	0.85	52.0	84	0.3	25	9.0
BH36	610	910	64.5	128	0.65	81.8	127	0.5	40	11.1
BH41	620	417	69.2	100	0.47	73.3	65	0.5	17	11.5
BH32	671	430	54.1	99.6	0.57	58.2	79	0.3	21	9.0
BH23	685	189	38.3	63.9	0.70	38.6	18	0.4	1.2	na
BH35	693	308	57.0	110	1.09	60.3	137	0.2	20	8.4
BH26	700	172	49.9	72.2	0.44	26.9	21	0.4	8.3	6.9
BH31	739	447	77.5	63.9	1.17	12.1	38	<0.1	12	na
BH34	739	220	65.5	75.3	0.79	35.2	41	<0.1	11	7.5
BH45	748	214	44.3	77.7	0.73	50.4	48	0.5	13	6.6
BH27	755	227	45.3	81.3	0.67	51.8	50	0.6	15	7.3
BH25	770	254	47.8	60.3	1.19	27.5	22	0.2	3.5	6.4
BH29	770	188	45.6	84.9	0.72	53.7	57	0.3	15	7.8
BH30	790	119	45.3	83.8	0.58	52.3	54	0.3	22	7.7
BH28	810	346	48.2	81.6	1.21	49.5	54	0.3	38	7.4

na not analysed, *Alk* alkalinity measured by field titration, *FI* relative fluorescence intensity

The photodegradation component was undertaken to confirm the presence of FWA (and, therefore, leachate) within the groundwater. Photodegradation of FDOM, C1 and C2 components was generally shown to be consistent over a 150-min period for boreholes considered to be within the area of leachate impact (boreholes BH39, BH36, BH33). The majority of FWAs are most likely to be detected within the C2 component (as defined in Fig. 3). It was therefore interesting to note that the degradation of the C2 component was typically observed to be 10 % higher than the C1 component.

There was a discrepancy noted between the photodegradation recorded in borehole BH39 using the FDOM field probe and the ASF. At 300 min, the photodegradation identified in borehole BH39 using the FDOM field probe was 30 % while using the ASF, the C1 component degradation was 12 % and the C2 component was 23 %, suggesting that the FDOM probe recorded a higher level of photodegradation. Although not shown in Fig. 6 (for consistent scale purposes), this

experiment was continued for 2880 min at which time, the degradation recorded in borehole BH39 using the FDOM field probe was 41 %, and the C1 and C2 recorded using the ASF were 39 and 51 %, respectively. The actual cause of this variation has not been confirmed during this experiment; however, there are several factors which are likely causes. The variation was only noted in borehole BH39 which is in close proximity to the landfill and is estimated to contain up to 20 % leachate. Ziyang and Youcai (2007) found that the colloidal fraction (1.2–0.45 μm) constitutes a large fraction of landfill leachate; therefore, it is likely that the groundwater/leachate composition in this location contains a higher concentration of fluorescent material sorbed onto colloidal particles. Based on these likely leachate characteristics at borehole BH39, filtration of the ASF sample may be resulting in detection of a complex desorption-photodegradation reaction. Based on the comparison of FDOM and ASF data to absorbance data, the variation is unlikely to be a result of IFEs

(i.e. absorbance in the unfiltered FDOM measurements). Future research should focus on identifying factors causing this discrepancy through undertaking longer photodegradation experiments and more detailed characterisation of leachate components.

A comparison of the field data FDOM with the dilution experiment showed a clear relationship between distance from the landfill and relative fluorescence intensity within groundwater. Based on the distance of borehole locations from the landfill, the relative fluorescence intensity was shown to decrease with the equivalent of between 2 and 5 % landfill influence identified in boreholes BH37, BH38, BH42 and BH36. Differentiation between landfill-influenced fluorescence intensity at intensities lower than 1 to 2 % of the value in LF02 is not discernible from background intensities. Borehole BH33, at approximately 2 % dilution, is considered to be on the outer edge of the plume. However, the boreholes where intensities fell below 2 % of the landfill FI were all located further than 650 m from the landfill.

The in situ FDOM gradient showed an order of magnitude change in fluorescence intensity from LF02 through to borehole BH36, which is considered to be the edge of the detected plume. This trend was also replicated with the C1 and C2 PARAFAC components and the EC readings (Fig. 4). Correlation coefficients were calculated for FDOM, C1, C2, C3 and EC against the distance from the landfill with R^2 values of 0.89, 0.86, 0.82, 0.67 and 0.74, respectively. However, with the exception of a high leachate concentration zone immediately surrounding the landfill (i.e. LF02, BH39 and LF03), no trend was identified in other field characteristics measured including PO_4, NO_3 and NH_4 (R^2 values of 0.25, 0.72 and 0.31, respectively). Note that the NO_3 correlation was due to increasing concentrations of NO_3 with distance from the landfill which are considered to be due to a combination of elevated background NO_3 concentrations generally across the site (which was considered to be a relic of farming practices on the site) combined with a reducing zone in the immediate vicinity of the landfill (LF03, LF02 and BH39) causing denitrification. These data are considered to demonstrate that a plume of groundwater with elevated fluorescence intensity is present on the eastern side of the landfill. Based on the range of fluorescence intensity identified across the site, the source of FDOM is the landfill.

An inverse correlation between EC and distance from the landfill was also identified. It could be argued that the measurement of EC is a well-established method and

thus preferable to the measurement of FDOM. However, EC is influenced by the variation in dissolved ion concentrations relating to geology, water-rock interactions, residence time, dust and dry deposition and up-concentration of dissolved salt by variable evapotranspiration (Appelo and Postma 2005). In contrast, the field FDOM probe specifically targets low concentrations of fluorescent material such as FWAs. In many instances, background EC variations can therefore be difficult to distinguish from EC increases at the fringe of a suspected landfill leachate plume. For example, in this study, the background EC was approximately 800 μs/cm while the EC measured within the boreholes at the fringe of the plume (boreholes BH33, BH36, BH37, BH42d and BH38) ranged from 1000 to 1300 μs/cm, within the natural range expected in a heterogeneous fractured rock aquifer. Acworth and Brain (2008) measured electrical conductivity ranging from 3000 to 12,000 μs/cm within boreholes positioned less than 500 m apart within an unpolluted fractured rock aquifer on a site approximately 60 km west of the UNSW Wellington research station. Utilisation of the field FDOM probe allowed identification of the elevated DOC and, more specifically, the presence of FWAs. This, in conjunction with the EC, enabled the leachate plume to be identified and delineated with a higher degree of certainty. Therefore, we suggest that the FDOM method described here provides a more specific tool, but, as with most tracer investigations, is should be used in conjunction with other methods.

Due to the accuracy of the method with reported detection levels of 10^{-3} (Baker 2005; Coble et al. 2014), FWA is not required to be a major component of the leachate plume and can be detected at very low concentrations at the plume front; however, as demonstrated here, once leachate concentrations are less than 1 to 2 %, background fluorescence causes interference and the method would not be considered applicable at these levels.

The correlation of FDOM and ASF measurements confirms the accuracy of the FDOM probe. The correlation of the FDOM readings and the distance from landfill combined with the photodegradation and dilution results confirm that the variations in relative fluorescence intensity measured using the FDOM probe are representative of landfill leachate and the field method is a suitable standalone procedure capable of identifying leachate impact in groundwater at concentrations as low as 2 % with ASF methods only required for calibration-

or site-specific initial method validation. The method is a simple procedure which requires minimal maintenance or calibration and can be easily applied in the field for immediate collection of data. The collection of instantaneous data provides confidence that collected samples are representative and have not undergone chemical change prior to laboratory analysis due to oxidation or chemical changes resulting from excessive holding periods. The method shows great potential for rapid delineation of landfill leachate plumes and as a means of ongoing monitoring of leachate migration or remedial works. Furthermore, confirmation of FWA presence can be completed in the field and requires only sunlight, clear plastic containers and a 2- to 3-h degradation period.

Typically, the C3 component showed highly variable levels of fluorescence intensity during the degradation experiment. This variability is considered to be an experimental effect due to microbial breakdown and cell lysis due to exposure to UV light. The C3 data is not considered further. As the florescence responses of microbial populations fall within the C3 component and are not within the set wavelengths of the turner probe, any potential influences of microbial populations on interpretation of the experimental results are considered to be negligible.

5 Conclusions

We demonstrate that measurement of fluorescence intensity in groundwater using a handheld FDOM probe has repeatedly and accurately identified variations in relative fluorescence intensity in an aquifer impacted by landfill leachate. Photodegradation experiments have demonstrated that the elevated fluorescence intensity identified within the plume is degraded by exposure to sunlight as opposed to the natural background fluorescent material and that FWAs sourced from landfill materials are likely to be a significant component being photodegraded. A dilution experiment using leachate from near the landfill was done to estimate the fraction of leachate at each borehole location.

The fluorescence intensity variations measured using the handheld FDOM probe were confirmed by analysis with an ASF. Analysis of excitation emission matrices produced by the ASF using PARAFAC has resulted in a three-component model. Components C1 and C2 of this model were found to be the most prevalent within

groundwater collected, and component C2 was found to be the most susceptible to photodegradation, suggesting that component C2 contained a greater proportion of FWAs.

We suggest that a handheld FDOM probe can be applied for field measurement of landfill leachate. Furthermore, the use of FWAs as an early indicator of leachate impact seems a plausible method with the field results identifying a definite plume up to 650 m from the landfill where other common field indicators had shown no positive response. Further research is required to demonstrate the method applicability to other sites. The system is also considered to have potential applications for field delineation of organic contaminant plumes.

Compliance with ethical standards   The research did not involve testing on human participants or animals. All parties involved in the research have been informed of the paper and consent to the publication.

Conflict of interest   The authors declare that they have no conflicts of interest.

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