

# Fluorescence of leachates from three contrasting landfills

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Received 5 May 2003; received in revised form 30 January 2004; accepted 16 February 2004

## Abstract

Landfill leachates are composed of a complex mixture of degradation products including dissolved organic matter, which includes a wide range of potentially fluorescent organic molecules and compounds. Here we investigate the excitation–emission matrix fluorescence of landfill leachates from three contrasting landfill sites. Landfill fluorescence properties are all characterized by intense fluorescence at  $\lambda_{\text{ex}} = 220\text{--}230\text{ nm}$ , and  $\lambda_{\text{em}} = 340\text{--}370\text{ nm}$  which we suggest derives from fluorescent components of the Xenobiotic Organic Matter fraction such as naphthalene, as well as at  $\lambda_{\text{ex}} = 320\text{--}360\text{ nm}$ , and  $\lambda_{\text{em}} = 400\text{--}470\text{ nm}$  from a higher molecular weight fulvic-like fraction. Landfill leachates are characterized by intense fluorescence, with  $\sim 10^2$  intensity units of fluorescence at  $\lambda_{\text{ex}} = 220\text{--}230\text{ nm}$ , and  $\lambda_{\text{em}} = 340\text{--}370\text{ nm mg}^{-1}$  of total organic carbon, demonstrating leachate detection limits of  $< 0.1\text{ mg l}^{-1}$  total organic carbon. We demonstrate that for all landfill sites, leachate fluorescence intensity has a strong correlation with ground water quality determinants ammonia, total organic carbon and biochemical oxygen demand. We investigate both within-site and between-site leachate fluorescence properties, and demonstrate that although there is significant within-site variability, leachates from all 3 sites can be statistically discriminated using just fluorescence properties (65% success rate) or with a combination of fluorescence and basic geochemical parameters (85%). Our findings suggest that fluorescence can be used as a rapid and sensitive tracer of leachate contamination of ground water, as well as help discriminate, together with geochemical determinants, leachates from different landfill sources.

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**Keywords:** Fluorescence; Excitation–Emission matrix; Landfill leachate; Groundwater

## 1. Introduction

Landfill leachate is formed by excess rainfall percolating through waste layers. Leachate can be a source of pollution as it can leave the landfill site if it is unlined or if the lining fails. Many researchers have suggested that the most significant long-term pollutant from landfills is ammonia [1,2]. After leaving a landfill site, the leachate is attenuated by a number of processes that can be divided into physical (dilution), physiochemical (sorption), chemical (precipitation) and microbial (degradation); a review by Christensen et al. [1] gives more detail.

Leachate geochemistry is a function of the quality of the landfill input, which determines the relative importance of dissolved organic matter (DOM), xenobiotic organic matter (XOM), inorganic macrocomponents, and heavy metals, as well as landfilling technology and age. The latter is important as in many parts of the world, landfills must be monitored at least 30 years after closure, or until they are deemed stable and no longer a threat to the environment [2]. Hence, further research into leachate properties is needed to aid landfill monitoring.

Many studies have investigated the biogeochemical properties of landfill leachate. The (chemically defined) humic fraction of leachate is smaller in size and less aromatic than standard (Aldrich) humic acid, and leachate humic fraction aromaticity and size increases

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with leachate age, suggesting an increase in humification [3]. Older leachate has a wider range of molecular weight and with a high molecular weight fraction being present, whereas young leachate had a narrower molecular weight range at low molecular weight [4]. GC/MS analyses of both leachate and leakage water identified plant-material-derived compounds, degradation products of peptides, carbohydrates and lignin, and numerous XOMs from pharmaceuticals, plasticizers, pesticides and chlorinated aromatics [5]. Several XOMs have been detected in the leakage water, suggesting that they could be used as tracers of landfill leachate [5].

Of particular relevance to this study is that much DOM present in landfill leachate is fluorescent (fluorescence is often used as the detection method after GC/MS analysis), but the fluorescence analysis of in situ leachate has been rarely undertaken. In contrast to leachates, river, marine- and ground-water fluorescence measurement is becoming increasingly widespread; both as a method to characterize natural organic matter but also to fingerprint organic pollutants. In both respects, the development of excitation–emission matrix (EEM) techniques has been crucial in providing the optical resolution necessary to fingerprint individual or groups of fluorophores. Rapid analyses are now possible using fluorescence spectrophotometers such that an EEM can be generated in approximately 1 min, with analysis possible in situ. For example, the EEM fluorescence properties of marine waters have been widely analysed; (Coble [6] and subsequent papers). Fluorescence EEMs have been used as a fingerprint for coloured water inputs in an upland catchment [7]; as a technique to fingerprint waters from two different river systems [8]; and to fingerprint treated sewage effluent, farm wastes and pulp effluent, respectively in rivers in N England [9–12].

Little research has investigated the fluorescence properties of landfill leachates. One study has characterized leachate DOM using fluorescence EEMs [13], but their work was limited by the analysis of extracted rather than in situ DOM and a limited range of analytical fluorescence wavelengths (from 250–350 nm excitation). Unpublished data from groundwaters in Missouri [14] using a wider range of excitation and emission wavelengths demonstrated high fluorescence intensity in the range 200–260 nm excitation and 250–360 nm emission from leachate samples and landfill impacted springs (Fig. 1). Results demonstrated that even at 1:100 dilution, leachate can be distinguished from “background”, and that the success rate of identifying leachate impacted springs from clean springs was 87% when compared to wet chemical methods. Most importantly, this research posed the question whether the fluorescence at low wavelengths (high energy) provides a diagnostic fingerprint of landfill leachates.

Previous research, therefore, suggests that fluorescence has significant potential in the fingerprinting of

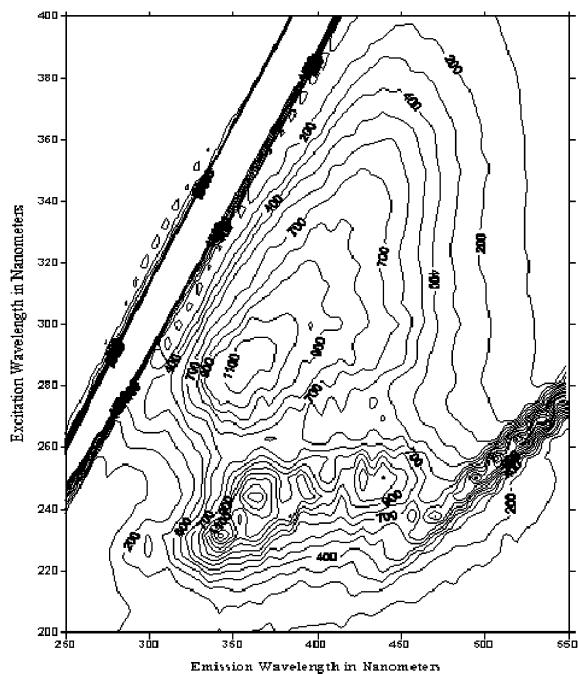


Fig. 1. Typical fluorescence EEM observed in a landfill leachate in a study of Missouri springs and landfill leachates [14].

landfill leachates, although further work is needed, both to verify previous findings and to apply them to a wider range of landfill sites. Here, we present first steps in this direction and present results of the analysis of fluorescence of landfill leachates both within landfill leachate boreholes and in adjacent ground water at three landfill sites in N England.

## 2. Materials and methods

We investigated the fluorescence properties of both landfill leachate within landfill sites as well as ground waters (both clean and contaminated) adjacent to the landfills. Sampling occurred between September 2002 and January 2003; with fluorescence samples taken paired with geochemistry samples taken as part of routine environmental monitoring obligations.

The three landfill sites are situated in N England. Site SB is situated in former clay pits and was in its last year of operation. Due to its commencement age and its location in thick clay deposits, the site is unlined. Ten samples covering both old and active sectors of the landfill, as well as treated and untreated leachate effluent, were sampled in September 2002. Landfill SB is located within a former brickclay pit which had an initial void space of 2,223,607 m<sup>3</sup>. Between 1970 and 1975 the northern half of the landfill was filled with a

high proportion of incinerator residues together with some domestic and industrial wastes. The southern half of the void has been landfilled with domestic, commercial and industrial, incorporating a proportion of special wastes between 1993 and 2003, with 160,000–570,000 tonnes input annually. The northern area has also received additional waste over the older landfill to produce a domed restoration landform. Landfilling operations ceased during March 2003. The geology of the area comprises thick laminated glacial clays that were deposited in a buried valley cut into the underlying Coal Measures. The laminated clays are overlain locally by more variable silty clays, which contain sands in places and areas of made ground. These shallow deposits of sands and gravels were removed during excavation of the clay pit; they are now only present around the perimeter of the site. The laminated clays, which are extensive both laterally and vertically, are of low permeability and form a non-aquifer. The only groundwater resource in the area is the Coal Measures, which is classified as a minor aquifer. It is likely that mining has resulted in poor groundwater quality. There are no licensed abstractions within 1 km of the site.

Site B is situated in sand and gravel workings actively operated by a gravel extraction company, and groundwater is being monitored prior to conversion to a landfill site. The western third of the site has been landfilled during the late 1970s and early 1980s. Due to the ongoing application for a waste disposal licence, no further site history details are available. Fifteen samples were taken from the surrounding ground waters in December 2002.

Finally, site JS is located within a former Magnesian Limestone Quarry with an initial void space of 3,349,116 m<sup>3</sup>. The site has operated since 1974. The quarry has been landfilled with a high proportion of domestic and commercial waste, with smaller proportions of industrial waste and sewage sludge. The site is also licensed for disposal of asbestos. The site is not lined, and has been licensed as a “dilute and disperse” landfill. Total annual waste input ranges from 28,000 to 381,000 tonnes. The geology of the area comprises weak and fractured dolomites and limestones (Magnesian Limestone) with a sand–silt matrix. The Magnesian Limestone formation overlies sandstones and siltstones belonging to the Coal Measures group. The Magnesian Limestone is classified as an aquifer; however, there are no licensed groundwater abstractions within 1 km of the site. Ground water samples adjacent to this site are essentially clean, although a small leachate plume is routinely detected at four monitoring locations. Fifteen ground water samples, including these four sites, were sampled in January 2003.

Ground water samples were collected in 50 ml plastic containers that had been previously cleaned by soaking in 10% HCl for 24 h and then triple rinsed in distilled,

deionized water. Samples were returned to laboratory and analysed within 24 h for spectrophotometric properties. Samples were filtered using Whatman GF/C glass microfibre filter papers that had been previously heated to 450 °C to remove any possible organic contamination. Fluorescence EEMs were generated using a Perkin Elmer LS50B Luminescence Spectrophotometer as described elsewhere [9]. The only modification was to scan a wider range of wavelengths with excitation from 200 to 370 nm and emission detected from 250 to 500 nm. Samples containing high concentrations of leachate were diluted to between  $\times 10$ –1000 dilution due to their high fluorescence intensity; this also avoided any inner-filtering effects [15]. The Raman peak intensity of water at 348 nm over the analysis period averaged  $23.6 \pm 0.8$  ( $n=20$ ); this value can be used to permit inter-laboratory comparison. Absorbance was measured using a WPA Lightwave UV/VIS spectrophotometer; absorbance was measured at 254, 340 and 410 nm. As well as providing water quality information, the measurement of absorbance permits the inner-filtering correction of fluorescence intensities, although this was not required as our diluted samples all fell below the necessary absorbance [15]. Geochemical parameters were measured in the laboratory using standard methods, ammonia colorimetrically using the distillation–nesslerization method, and pH was measured in the field.

### 3. Results

Results are presented in Table 1 for all three landfill sites. Table 1 demonstrates that landfill leachates sampled within the active landfill site at SB are characterized by high absorbance, high ammonia concentration, high total organic carbon concentrations and high BOD, as would be expected from such samples and described elsewhere [1]. Site B, with a historical unlined landfill, has similarly high geochemical parameters in its groundwater samples, whereas site JS groundwaters are essentially typical of uncontaminated groundwaters, with the exception of sites BH 33 and BH 34 and to a lesser extent GW3 and MH1, all of which are within the known leachate plume.

Typical fluorescence EEM results for leachate samples from within site SB (Fig. 2) demonstrate a distinctive and intense fluorescence peak at  $\lambda_{\text{ex}} = 220$ –230 nm, and  $\lambda_{\text{em}} = 340$ –370 nm, which is identical in location to the diagnostic fluorescence centre observed previously ([14]; Fig. 1). A peak is also present in both samples at  $\lambda_{\text{ex}} = 230$ –250 nm and  $\lambda_{\text{em}} = 400$ –440 nm, a poorly understood fluorescent centre widely attributed to a component of the humic fraction [6,8], but due to its poor characterization we will not consider it further here. A peak is present at  $\lambda_{\text{ex}} = 320$ –340 nm and

Table 1  
Geochemical and fluorescence data for landfill leachate and ground water samples

Site	Description	Ammonia (mg/l)	pH	BOD5 (mg/l)	Chloride (mg/l)	Iron (mg/l)	TOC (mg/l)	A <sub>254</sub> (/cm)	A <sub>340</sub> (/cm)	A <sub>410</sub> (/cm)	Fulvic-like fluorescence			Tryptophan intensity at 280 nm excitation (U)	Tyrosine intensity (U)	Fluorescence at 230 nm excitation, 340 nm emission (U)
											Excitation (nm)	Emission (nm)	Intensity (U)			
SB	BH 2	19	7.0	<1	140	16	55	0.199	0.093	0.0653	310	409	312	305	970	1487
	BH 7	75	7.0	5	510	48	68	0.572	0.160	0.0793	325	407.5	1073	713	1387	3812
	BH 22	2	7.3	<2	49	7.1	38	0.214	0.062	0.0249	340	423	271	285	1057	1021
	BH 38	nd	6.6	<2	50	66	18	0.218	0.213	0.2179	330	442.5	82	98	328	231
	GW 2	nd	6.9	<1	81	7.6	34	0.114	0.025	0.0083	320	418.5	189	191	478	710
	LMP 1	52	7.1	<1	370	3.5	130	0.780	0.153	0.0276	320	410.5	2054	1883	2360	5621
	LMP 2	170	7.4	10	440	11	170	0.926	0.206	0.0403	325	414	2438	1840	1534	6316
	LMP 23	300	6.8	41	1900	12	230	1.298	0.254	0.0418	325	409	1987	1949	3315	8469
	LEACHATE PLANT	1300	7.6	170	2100	5.2	1300	>2	>2	0.7805	335	426.5	23347	19335	21879	95551
	N.E. LEACHATE PUMP	190	6.9	20	780	22	250	0.825	0.178	0.0384	325	411	2497	2235	2512	7680
B	wa1	210	8.9	110	1500	43.00	380				310	415	25541	11039	27056	34199
	wa2	51	7.3	22	490	8.50	33	1.001	0.244	0.0744	300	412	953	317	1496	1792
	wa4	420	7.8	590	2300	28.00	560	>2	>2	0.5791	320	419	41905	23896	38095	80000
	wa6	1	7.2	9	370	12.00	36				300	417	3139	996	2879	4437
	wa8	3	6.7	26	970	3.90	7	0.185	0.057	0.0392	315	420	87	127	918	861
	cl1	270	7.7	88	2400	9.60	210	>2	>2	0.5851	310	420	13610	8909	18139	27255
	cl3	1	6.8	6	1700	17.00	33	0.776	0.439	0.3233	330	421	553	612	1573	5298
	cl4	1	6.8	<1	1200	29.00	2	0.069	0.034	0.0343	330	424	36	54	179	346
	cl5	nd	6.9	6	2900	16.00	11	0.700	0.036	0.0352	310	415	79	42	188	304
	cl6	nd	7.2	4	69	7.50	10	0.158	0.066	0.0542	310	418	317	126	158	363
	cl7	21	7.2	27	1200	3.60	130	>2	0.610	0.1556	310	416	10303	3853	13463	20476
	cl8	1	6.8	3	1300	13.00	2	0.094	0.036	0.0350	345	442	68	125	294	963
	cm1	nd	7.5	<1	18	0.78	2	0.051	0.023	0.0263	330	409	41	26	67	69

	cm2	1	7.3	<1	20	0.08	2	0.049	0.027	0.0220	315	404	22	24	76	85
	cm3	1	6.8	<2	410	2.70	2	0.101	0.035	0.0246	310	405	118	124	196	952
JS	GW 2	1	7.2	<2	65	0.037	0	0.049	0.025	0.0308	350	440	24	19	13	24
	GW 3	6	7.2	<2	150	0.76	13	0.076	0.033	0.0318	335	426	98	126	46	536
	GW 5	1	7.5	<2	40	0.25	10	0.039	0.021	0.0280	335	420.5	11	10	10	14
	GW 6	1	7.3	<2	40	0.035	11	0.051	0.023	0.0298	335	416	21	13	5	14
	GW 13	1	7.6	<2	39	0.12	12	0.073	0.031	0.0318	340	415.5	57	25	19	47
	GW 14	1	7.5	<2	44	0.045	10	0.062	0.028	0.0322	330	416	36	19	11	25
	GW 15	1	7.4	<2	49	0.27	8	0.048	0.025	0.0282	330	409	24	13	8	22
	GW 16	1	7.6	<2	39	0.07	10	0.047	0.023	0.0278	330	417	17	12	13	17
	GW 17	1	7.6	<3	47	0.038	9	0.043	0.021	0.0282	330	418.5	17	13	8	15
	BH 33	71	7.2	<10	420	3.3	9	0.265	0.074	0.0427	320	402.5	273	332	328	3151
	BH 34	110	7.2	<6	440	0.97	13	0.408	0.102	0.0425	325	404.5	693	861	1134	7290
	BH38	4	7.2	<3	56	0.029	8	0.052	0.023	0.0289	310	399.5	52	54	29	234
	BH 48	1	7.7	<3	38	0.28	9	0.043	0.022	0.0280	335	419	20	15	24	29
	MH 1	6	7.4	<3	120	0.18	9	0.106	0.030	0.0306	320	404.5	116	112	33	243
	MH 2	1	7.6	<3	74	0.073	8	0.045	0.023	0.0273	330	415	24	32	23	61

nd: Below detection limits.

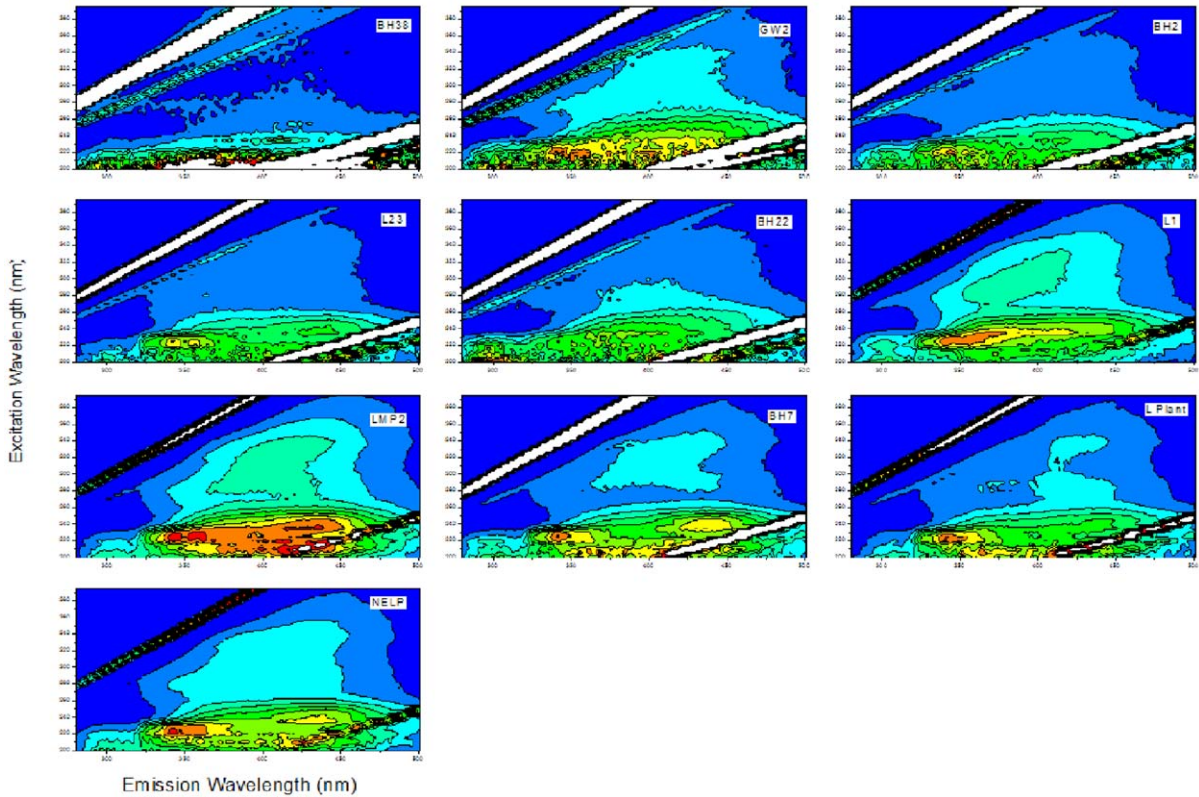


Fig. 2. Leachate fluorescence EEMs observed in this study from within the SB landfill site and which show the diagnostic fluorescence centres associated with landfill leachate. Colour reflects fluorescence intensity, low is blue, high is red. Each sample has been rescaled to show the relative peak intensities; in reality there are significant differences in intensity between samples although the same peaks reoccur in all samples.

$\lambda_{em} = 400\text{--}440\text{ nm}$ , that is attributed to aromatic and aliphatic groups in the DOM fraction and commonly labeled as fulvic-like [6]. A final fluorescence centre is observed with variable intensity at  $\lambda_{ex} = 275\text{--}280\text{ nm}$  and  $\lambda_{em} = 350\text{--}360\text{ nm}$ , attributed to the protein tryptophan, and widely observed in polluted river waters [9,11] and clean estuaries [16].

Comparison of Fig. 2 and Table 1 demonstrates that landfill leachates are characterized by intense fluorescence per gram of dissolved organic carbon. Intensity units of fluorescence  $\sim 10^2$  at  $\lambda_{ex} = 220\text{--}230\text{ nm}$ , and  $\lambda_{em} = 340\text{--}370\text{ nm}$  occur per milligram of total organic carbon, demonstrating leachate detection limits of  $\sim 0.1\text{ mg l}^{-1}$  of total organic carbon, and a lower actual detection limit of this leachate fingerprint as this fluorophore comprises only a fraction of this total carbon concentration.

Fig. 3 presents the correlation between the two most intense fluorescence centres, the peak at  $\lambda_{ex} = 220\text{--}230\text{ nm}$ , and  $\lambda_{em} = 340\text{--}370\text{ nm}$  and that at  $\lambda_{ex} = 320\text{--}340\text{ nm}$  and  $\lambda_{em} = 400\text{--}440\text{ nm}$  (fulvic-like). It clearly shows a strong linear relationship between the two at all

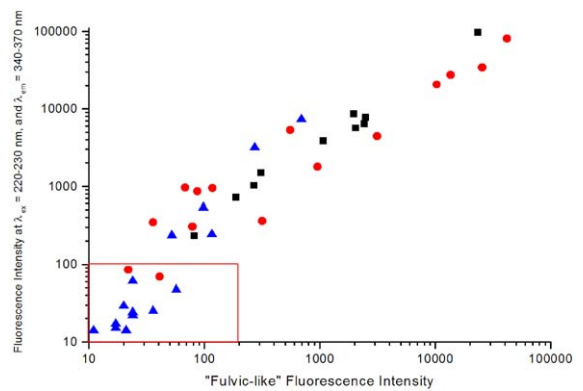


Fig. 3. Correlation between fluorescence intensity at the two main fluorophores. Black squares: site SB. Red circles: site B. Blue triangles: site JS. Red box is the range observed in ground and river waters (from [12,17]).

three sites. Site SB, with leachate samples taken within the landfill cells and leachate system, have the highest fluorescence intensities. Site B, which is contaminated by

a disused unlined landfill, has intermediate values, whereas samples from site JS, which include a large number of uncontaminated ground waters, have the lowest fluorescence intensities that are primarily within the observed range of river and ground waters [12,17]. At sites SB, B and JS the correlation coefficient between the two fluorescence centres is 0.999, 0.986 and 0.991, respectively, demonstrating that either can be used as a fingerprint of landfill leachate, although the lower wavelength (higher energy) centre has order of magnitude greater fluorescence intensity and will therefore have lower detection limits. For all three sites combined, the correlation coefficient between the two fluorescence centres is lower ( $r=0.83$ ), reflecting inter site variability in the relative proportions of the two fluorophores. In this respect, site JS has an 11:1 ratio of fluorescence at  $\lambda_{\text{ex}} = 220\text{--}230\text{ nm}$  and  $\lambda_{\text{em}} = 340\text{--}370\text{ nm}$  to fluorescence at  $\lambda_{\text{ex}} = 320\text{--}340\text{ nm}$  and  $\lambda_{\text{em}} = 400\text{--}440\text{ nm}$ , site SB a ratio of 4.1:1 and site B a ratio of 1.8:1. Interpreting these differences in terms of leachate geochemistry is difficult. Laboratory experiments using model compounds have demonstrated that the source of the fluorescence peak at  $\lambda_{\text{ex}} = 220\text{--}230\text{ nm}$ , and  $\lambda_{\text{em}} = 340\text{--}370\text{ nm}$ , is probably due to a mixture of fluorescent XOM that contains low molecular weight, high fluorescence efficiency molecules such as naphthalene (Baker, unpublished data) that are not normally observed at such high intensities in the natural environment. In contrast, the fluorescence centre at  $\lambda_{\text{ex}} = 320\text{--}340\text{ nm}$  and  $\lambda_{\text{em}} = 400\text{--}440\text{ nm}$  is more widely observed in river and ground water samples [6,12]: it is often attributed to ubiquitous, relatively stable and high molecular weight aromatic fulvic-like matter. The relative intensities of both fluorescence centres are likely to vary with both leachate age and landfill contents, but the site histories of our landfills do not enable us to draw detailed conclusions.

Fig. 4 shows the correlation between the fluorescence at  $\lambda_{\text{ex}} = 220\text{--}230\text{ nm}$ , and  $\lambda_{\text{em}} = 340\text{--}370\text{ nm}$  and am-

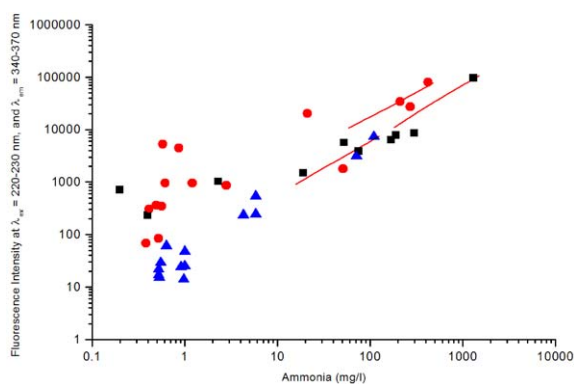


Fig. 4. Correlation between fluorescence intensity at  $\lambda_{\text{ex}} = 220\text{--}230\text{ nm}$ , and  $\lambda_{\text{em}} = 340\text{--}370\text{ nm}$  and ammonia concentrations.

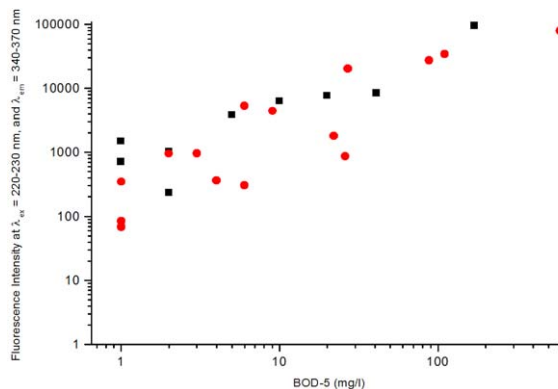


Fig. 5. Correlation between fluorescence intensity at  $\lambda_{\text{ex}} = 220\text{--}230\text{ nm}$ , and  $\lambda_{\text{em}} = 340\text{--}370\text{ nm}$  and BOD-5.

monia concentration, since the latter is often recognized to be a good determinant of leachate. Correlation coefficients are excellent between the two variables ( $r=0.98, 0.95, 0.98$  for sites SB, B, JS, respectively). The three sites in this case do have significantly different fluorescence intensity: ammonia ratios, with sites SB and JS having very similar ratios of fluorescence intensity: ammonia (60:1 and 73:1) whereas site B has much higher fluorescence intensity: ammonia ratio (160:1). Site B, situated in Quaternary sands and gravels, is much more aerobic than the groundwater and landfill sites JS and SB, which probably provides the simplest explanation of this contrast. The results suggest that where leachate contamination occurs in aerobic sites (rivers and shallow groundwaters) and therefore ammonia is more readily oxidized, fluorescence may be a more effective tracer than ammonia.

Fig. 5 shows the relationship between the 5-day biochemical oxygen demand and fluorescence intensity. At site JS, BOD-5 was below analytical detection limits and so no data is presented. For sites BS and B, as for the previous correlations, the relationship is strong and statistically significant, and the two sites have subtly different ratios of fluorescence: BOD ( $r=0.98, 0.94$  for sites SB and B, respectively). Given the time and effort required to analyse for BOD, the high correlation coefficients are encouraging as it suggests that a site by site correlation can be deduced and then used to predict BOD from fluorescence intensity. In our cases, 90% confidence limits suggest that BOD5 at site B can be predicted using fluorescence to  $\pm 30\text{ mg l}^{-1}$  over the range  $0\text{--}700\text{ mg l}^{-1}$ , and at site SB to  $\pm 13\text{ mg l}^{-1}$  over the range  $0\text{--}200\text{ mg l}^{-1}$ .

Results demonstrate a remarkable correlation between fluorescence intensity and geochemical determinants such as ammonia and BOD. Whilst there are between-site differences in the relationship between fluorescence and BOD and ammonia, we can show that

we can differentiate waters between the three sites using a combination of all the geochemical determinants measured (Table 1) and optical parameters. Fig. 6 demonstrates the within-site variability as expressed using principal components analysis for the SB landfill, which shows considerable variability best explained by a wide range of determinants including fluorescence intensity, BOD, ammonia, absorbance at 410 nm (colour) and iron

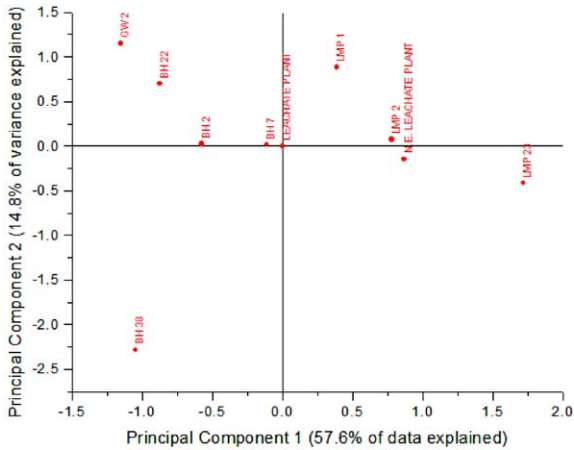


Fig. 6. Principal components analysis for leachate samples within the landfill at site SB.

concentrations. In particular, principal component 1 represents a trend of leachate concentration (left to right is low to high concentration of ammonia, BOD, absorbance and fluorescence intensity at  $\lambda_{ex} = 220\text{--}230\text{ nm}$  and  $\lambda_{em} = 340\text{--}370\text{ nm}$ ). Principal component 2 reflects differences in leachate quality (top to bottom is decreasing iron and absorbance at 410 nm). Note that the leachate plant falls at the centre of the plot, as would be expected if it is a mixture of all the other inputs.

Despite the within-site variation of Fig. 6, Fig. 7 shows that we can differentiate borehole and ground water at the three sites using discriminant analysis. Using fluorescence intensity at  $\lambda_{ex} = 220\text{--}230\text{ nm}$  and  $\lambda_{em} = 340\text{--}370\text{ nm}$ , fulvic-like fluorescence, absorbance at 410 nm (colour), pH, chloride and ammonia as discriminatory variables at the three sites (see Table 1), the first two discriminate functions explain 100% of the variability within the dataset. Discriminant function 1 reflects leachate concentration, with decreasing pH, increasing fluorescence at  $\lambda_{ex} = 220\text{--}230\text{ nm}$ , and  $\lambda_{em} = 340\text{--}370\text{ nm}$  and ammonia at high scores. Discriminant function 2 reflects leachate quality, with high scores at sites with a greater proportion of fulvic-like fluorescence, chloride and absorbance at 410 nm. Using just optical properties (fluorescence, absorbance) in the discriminant function, the analysis successfully discriminated the three sets of waters on 65% of occasions. However, 85% of all

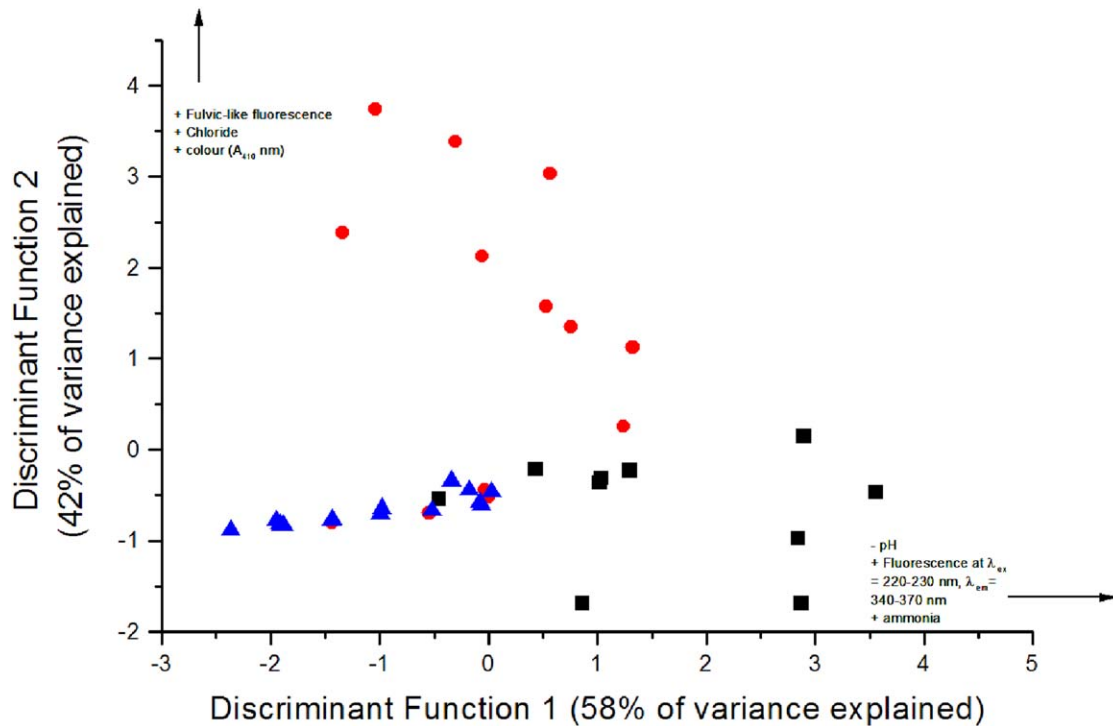


Fig. 7. Discriminant analysis of the three sites using all geochemical and optical parameters in Table 1. Black squares: site BS. Red circles: site B. Blue triangles: site JS.



samples are correctly classified to the correct landfill site when using just fluorescence, absorbance, ammonia and chloride, four parameters which are currently, or which soon will be, all measurable rapidly in the field. Such discrimination has important practical uses, for example at site B where there is pre-existing leachate pollution and where it is of operational interest to confirm that and new landfills are being managed sustainably.

#### 4. Conclusions

- (1) Landfill leachates are characterized by intense fluorescence, with  $\sim 10^2$  intensity units of fluorescence at  $\lambda_{\text{ex}} = 220\text{--}230$  nm, and  $\lambda_{\text{em}} = 340\text{--}370$  nm/ $\text{mg}^{-1}$  of total organic carbon, demonstrating leachate detection limits of  $< 0.1 \text{ mg l}^{-1}$  total organic carbon.
- (2) We demonstrate that for all landfill sites, leachate fluorescence intensity has a strong correlation with ground water quality determinants ammonia, total organic carbon and biochemical oxygen demand.
- (3) We investigate both within-site and between-site leachate fluorescence properties, and demonstrate that although there is significant within-site variability, leachates from all three sites can be statistically discriminated using just fluorescence properties (65% success rate) or with a combination of fluorescence and basic geochemical parameters (85%).
- (4) Our findings suggest that fluorescence can be used as a rapid and sensitive tracer of leachate contamination of ground water, as well as help discriminate, together with geochemical determinants, leachates from different landfill sources.

#### Acknowledgements

AB thanks Andrew Cowan and staff at Premier for site access and field support.

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