Isocratic LC methods for the trace analysis of phthalates and 4-nonylphenol in varying types of landfill and adjacent run-offs.

Reid, Antoinette M.; Brougham, Concepta A.; Fogarty, Andrew, M.; Roche, James J.*

Department of Life and Physical Sciences, School of Science, Athlone Institute of Technology, Dublin Rd., Athlone, Co. Westmeath, Ireland.

*Corresponding author. Fax: +353906424492

E-mail address: jroche@ait.ie

Abstract

To determine the levels of known endocrine disrupting chemicals such as phthalates and alkylphenols in environmental samples such as leachate water and sediment, suitable isocratic high performance liquid chromatographic method (HPLC) methods utilising a narrow bore column were developed. The study was an analytical challenge in terms of developing a method, which would be sensitive enough to detect trace levels of these compounds, while still retaining the advantages of being suitable for relatively inexpensive instrumentation and featuring reasonable throughput. Generally speaking, when the internal diameter of the HPLC column is decreased by a factor of two, the signal of a sample component increases by a factor of four, the square of the change in diameter. However, combining a narrower bore column along with the isocratic method enabled us to see 20-fold increases in peak signal. The detection of these compounds was further improved by using pre-concentrating techniques known as solid-phase extraction (SPE) and accelerated solvent extraction (ASE). Limits of detection in the ng/l range were reached for target analytes. Maximum values (μg l^{-1}) of 7.05 dibutyl phthalate (DBP), 7.37 diethylhexyl phthalate (DEHP), 5.56 diisononyl phthalate (DINP), 1.19 diisodecyl phthalate (DIDP) and 6.16 4-nonylphenol (NP) were found in sampled leachates, whilst maximum values (mg kg^{-1}) of 42.3 DBP, 49.8 DEHP, 36.2 DINP, 20.0 DIDP and 1.14 NP were found in sediments. Concentrated leachate contained up to 226 μg l^{-1} DEHP. The highest levels of NP were found to leach from an unlined landfill, with concentrations of 10.6 μg l^{-1}. The levels, which were quantified in the Irish midlands, are clearly linked to anthropogenic activity and were comparable to levels found in other pan-European studies.

Keywords: phthalates, nonylphenol, endocrine disruption, landfill leachate

1.0 Introduction

There is an extensive range of chemicals considered to have endocrine disrupting potential and it has been determined that substances do not need to be structurally similar to the prototypical endogenous hormone 17 β-oestradiol to produce a disrupting effect. Up to now, more than 50 non-steroidal anthropogenic chemicals are known to mimic the effects of the natural oestrogen[1]. More such agents are being identified with on-going research. For instance, oestrogen-mimicking effects have been observed for both phthalates and alkylphenols [2, 3, 4, 5] and recent reports also implicate metals [6, 7]. To date, most of the

substances of interest or concern are of relatively small molecular weight and these chemicals may mimic or antagonize small hormones, particularly the steroid and thyroid hormones [4].

Structural features of a compound may render it oestrogenic. Environmental oestrogens tend to consist of a *para*-substituted phenolic group, and more than one phenolic group on the structure can increase the oestrogenicity of the compound. The phenolic ring structure is typical of oestrogens and oestrogenic activity is produced by a number of synthetic compounds with this structural motif. Phenolic ring substitutions are common to most xeno-oestrogens, not only those that are synthetic pollutants but also natural compounds such as the phyto-oestrogens or the resorcilic acid mycotoxins. 17 β-oestradiol is an 18-carbon steroid with a phenolic A ring (**Fig. 1**). The phenolic A ring is the structural component responsible for high-affinity binding to the oestrogen receptor [8]. Preliminary screening for oestradiol and ethinyloestradiol confirmed that testing in leachates wasn't necessary. This was as expected as it is unlikely that they would be present in domestic landfilled waste, although oestrogens may be present in landfills accepting sewage sludge for disposal. This did not occur in the landfills tested in this study and a number of extractions were carried out in early experimental work just to confirm their absence.

[insert figure 1 about here]

For this study, the focus was on phthalates and nonylphenol due to their ubiquity in manufactured products and the successive extensive usage of these items. Nonylphenol was chosen due to its omnipresence in detergents and toiletries and its inevitable entry into the environment. According to a study carried out by Ternes *et al*., 1999,[5] in a range of rivers tested, only very low trace amounts of 4-tert-octylphenol were exhibited as it is less frequently used than 4-nonylphenol so it was not deemed necessary to test for 4-tert-octylphenol. Bisphenol A (BPA) is another phenolic compound known to exhibit oestrogenicity but was not tested for, as it was neither manufactured nor processed in the Shannon Region basin. However, deposited products made of epoxy resins and polycarbonates containing BPA as a monomer are potential sources for the leaching of BPA out of landfills.

Leachates from landfill, particularly from plastics such as PVC, also contain endocrine disrupting chemicals. Microbial decomposition of plasticisers is quite difficult and the common treatment applied to

landfill is not able to eliminate them [9]. EDCs can linger in the sediment for a long duration and may then pass on or be released by diffusion across the sediment-water interface or through sediment re-suspension at high water flows [10]. Among the substances of key interest to us, both phthalates and nonylphenol were shown to be oestrogenic in both *in vitro* and *in vivo* models in studies carried out by van den Belt, 2003 [11] and 2004 [12], amongst others.

One of the main objectives in this study was to develop a simple yet sensitive isocratic HPLC method for the determination of phthalates and nonylphenol in leachate, surface water and sediment without the need for any complex or costly equipment and which, would be capable of determining ultra trace quantities of our target analytes. Up to now, most studies regarding quantitation of phthalates or nonylphenol have been carried out using gas chromatography (GC) combined with mass spectrometry (MS). Such studies have included the analysis of phthalates [13, 14, 15, 16, 17, 18, 19, 20], BPA [21, 22] or NP [23, 24, 25, 26] individually or combinations of phthalates with BPA [9, 27], BPA with NP [28] or NP with phthalates [29], with extractions of these analytes from both water and sediment matrices. Our second objective was to identify and quantify the levels of the selected phthalates and 4-nonylphenol in landfill leachate, surface water and in sediments from those waters. It is only in more recent decades that landfills in Ireland are being more carefully constructed and managed. Typically, all solid waste in Ireland, particularly domestic waste, has been and is still deposited into landfills. Efforts to recycle from a low base have made a significant impact and coincided with a highly successful levy on usage of plastic bags.

Leachate and effluents from industrialised areas are potential locations for finding endocrine disruptors. Work carried out by the Lough Derg/Ree Monitoring and Management Program (2001) show that detectable levels of potential endocrine disruptors were found at a number of sites sampled in the Shannon catchment area[30]. Behnisch *et al*., 2001 [31], identified numerous xenoestrogenic compounds in a controlled landfill leachate treatment including ethinyloestradiol, NP and DBP to name but a few. Other studies analysed mainly for phthalates [9, 18, 19, 20, 27].

2.0 Materials and methods

2.1 Sampling leachate

In terms of landfill, the types of leachate and leachate sediment that were tested included a site of high leachate concentration (Derryclure) and two river locations beside two different landfill types; one an old, disused, unlined landfill facility in the urban centre of Athlone (Burgess Park), the other a lined and managed facility on the outskirts of the town (Ballydonagh). Burgess Park is situated on the east bank of the River Shannon and measures almost 8 ha. After 47 years, this landfill was finally closed in 1991 and following this the land was developed for commercial use where there now exists a shopping centre. Ballydonagh is situated 5 kilometres outside the Athlone conurbation. It opened in February 1991 and takes the majority of its waste from the county area. Ballydonagh is a fully lined engineered facility and is licensed to accept on average 40,000 tonnes per annum. The River Al, a tributary of the Shannon, is located at the north down-gradient of the facility. Samples taken at Burgess Park and at Ballydonagh consisted of river water mixed with leachate and not 'pure leachate' and the leachate sediments were from the river locations in question. At Derryclure (Co. Offaly), an installation of a leachate management system was carried out as a requirement for the Irish EPA in order to keep the existing landfill facility in operation. The landfill is situated 5 kilometres from Tullamore town and north, south and east of the facility is bounded by raised peat lands. It is also licensed to accept roughly 40,000 tonnes per annum. Liquid samples of surface and ground water were taken along with liquid samples from the silt traps, referred to as *concentrated leachate* in the results section. These samples were pure leachate and pure leachate sediment specimens. From the three types of landfill examined only the engineered facility at Tullamore allowed for collection of leachate for removal and subsequent treatment. Consequently, levels in this matrix, as expected, were many times greater than in the others tested. The procurement of liquid samples was synchronised with *in vivo* and *in vitro* work, which was being carried out in parallel by other members of the EDC group who were assessing the oestrogenicity of these samples.

[insert figure 2 about here]

2.2 Development and validation of analytical methodologies

In this study, once optimal methodology had been established, linearity and limit of quantitation testing were carried out. There was no existing isocratic method for determining our test chemicals prior to this and the method that was developed was far more sensitive than existing gradient methods due to

enhanced baseline stability. Much lower levels could be detected with the combination of a narrow bore configuration coupled with a chemically bonded phenyl phase exploiting aromatic π-π interactions.

2.3 Instrumentation and reagents

All chromatographic measurements were performed on a modular liquid chromatographic system consisting of Waters Autosampler 717, Waters Pump 510, and Shimadzu LC-6AD Detector. The column used was a Pinnacle™ II Phenyl (150 x 2.1mm, 5 μm) and an equivalent guard column was also purchased from Restek, Ireland. Two separate isocratic methods were developed, both using an optimum wavelength of 226 nm; a method employing a flow rate of 0.2 ml min^{-1} using an acetonitrile-water mix 70:30, (phthalates) and another employing a flow rate of 0.1 ml min^{-1} and using a methanol-25mM Na_2HPO_4 pH 4.8 buffer mix, 75:25 (nonylphenol). A Dionex 100 Accelerated Solvent Extractor with 66 mL extraction cells was used to perform pressurised liquid extractions of the solid samples.

All reagents were of analytical grade. The following were purchased from Sigma-Aldrich (Ireland); dimethyl phthalate (DMP) > 99% $C_{10}H_{10}O_4$; dibutyl phthalate (DBP) > 98% $C_{16}H_{22}O_4$; phthalic acid bis (2 – ethylhexyl ester) (DEHP) 99% $C_{24}H_{38}O_4$; bis (3,5,5 – trimethylhexyl) phthalate (DINP) $C_{26}H_{42}O_4$; and diisodecyl phthalate (DIDP) > 99% $C_{28}H_{46}O_4$, and 4-nonylphenol (4-NP) techn. Technical nonylphenol is a degradation product of nonylphenol ethoxylates (NPEOs), which are used as non-ionic surfactants (Braun et al., 2003). HPLC grade methanol, acetonitrile, dichloromethane and ethyl acetate were purchased from Labscan Analytical Ltd (Ireland). SPE disks from 3M-Empore™ and Chem Tube-Hydromatrix for ASE were purchased from Varian through JVA Analytical (Ireland) whilst 30 mm cellulose filters were purchased from Dionex, UK, and 47 mm microfibre glass filters GF/C (1.2 μm) and GF/F (0.7 μm) were purchased from AGB Scientific (Ireland). The bulking agent, known as Chem tube-Hydromatrix, required purification using a bake-out process at 850 ^{0}C for 24 hours to completely eradicate plasticiser contamination.

Serially diluted solutions of analyte mixtures of the primary stock solutions were carried out in the appropriate HPLC grade solvent as required on a daily basis. Primary stock solutions were prepared

individually from the pure compound at a concentration of 100 mg l^{-1} and solutions were stored in amber glass bottles at 4 ^{0}C, remaining stable for at least eight months.

2.4 Sampling and sample treatment

Both liquid and sediment samples were procured routinely at selected intervals close to significant conurbations in the border, midlands and western (BMW) region of the Republic of Ireland in the River Shannon Catchment area, the Shannon being the largest river in the British Isles. An organic modifier (5 % methanol) was added to liquid samples on commencing sample pre-treatment and before the extraction process was carried out, whilst sediment samples were dried to constant weight in an oven at 80 ^{0}C over a 48 hr period, cooled and stored in a desiccator. Samples were taken at consistent sampling points using an inert, stainless steel, telescopic sampling rod and cup followed by transfer to pre-cleaned 2.5 l amber glass bottles autoclaved and washed with methanol, which were also rinsed on-site with the river water to be collected, and were then stored in cool-bags with ice-packs and transported to the laboratory directly following physical characterisation.

2.5 Enrichment techniques and analysis

SPE reduces very small quantities of analyte into a more concentrated volume, which can then be analysed chromatographically. For solid-phase extraction of the samples, a three-station vent discharge, filtration manifold was assembled and a 47 mm extraction disc was washed and conditioned prior to use, ensuring that the disk was not allowed to go dry at any stage. Water samples were prefiltered using microfibre glass filters (0.70 µm) followed by filtration with a 0.45 µm nylon filter (confirmed as being contamination free) to remove particulate matter, which could block sorbent pores. Strong vacuum was avoided, as it would inhibit the formation of the non-covalent bonds between the analytes and the sorbent, so a flow rate of 8 ml/min or less was used. The water sample was then added to the reservoir and under tap-vacuum, was filtered as quickly as the vacuum would allow (<< 8 ml/min). The solvent rinse was applied followed by the elution process, which was carried out by triplicate additions of 5 ml portions of ethyl acetate. Drying down was carried out in a water bath at 37 ^{0}C under a constant, low velocity stream of nitrogen and reconstitution into 200 µl of mobile phase was accordingly carried out. The reconstituted

sample was vortexed for 30 seconds. The eluate was transferred into a vial with a contamination-free insert for subsequent analysis by HPLC or by alternative methods, depending on the nature of the analyte.

Extraction of sediment samples was carried out on a Dionex 100 Accelerated Solvent Extractor under elevated temperature (100 –110 ^{0}C) and pressure (1500 psi). The high pressure keeps the solvent liquidised at the high temperature and this means that the solvent can penetrate the matrix better and hence solubilise analytes to a greater extent. The completely dried sample was ground up and homogenised with pre-treated bulking agent and this was then packed into the extraction cell. Recovery experiments determined the most suitable solvent mix, temperature, number of static cycles and flush volume. The extractions were performed and the liquid extract was flushed from the extraction cell into the collection vial where it could then be manipulated to allow compatibility with the chromatographic method. For solid environmental samples, 5.0 g dry weight of sediment was homogenised in a mortar and pestle with Chem tube-Hydromatrix and packed into a 66 mL cell. For the extraction of phthalates, a 1:1 % v/v dichloromethane: acetone mix at 110 ^{0}C was used and a 1:1 % v/v acetone: methanol at 100 ^{0}C was used for nonylphenol. Each enrichment procedure was underwritten by recovery experiments, which culminated in the realisation of recovery factors necessary for accurate quantification of analytes.

3.0 Results and discussion

3.1 Development and validation of analytical methods

Linearity studies in the range 1 - 50 μg ml^{-1} and 0 - 1 μg ml^{-1} yielded multiple regression coefficient values of 0.99 (see **Table 1**). Limits of quantitation less than or equal to 40 ng l^{-1} were established for some analytes whilst limits of detection of 22 ng l^{-1} were reached with the combined enrichment techniques. Such ultra-trace quantitation is timely as the reported oestrogenic potencies of the test chemicals vary, e.g. alkylphenols are weaker than the natural endogenous hormones (μg l^{-1} concentrations are required before effects are observed) and phthalates are less potent than alkylphenols [4]. To date, however, no adverse effects on wildlife in terms of reproduction have been noted in the Shannon catchment region, although it was reported by verbal communication with a member of the Shannon Fisheries Board that 80 % of some game fish sexed in the region were female.

[insert table 1 about here]

In unpublished work all possible laboratory contaminants were identified and the uses of plastic apparatus or equipment shown to contain phthalates were avoided. Contamination from SPE syringe barrels was also identified, leading to the preferred usage of disks. Significant quantities of phthalates were found to leach from various components commonly found in the environmental analytical laboratory, such as plastic syringes, pipette tips, filters and Parafilm® which were thus completely avoided with glass being used instead. Nylon filters used in the filtration of mobile phase were shown to be contamination free. For drying down samples under nitrogen, rubber tubing was eliminated due to significant levels of DBP and DEHP leaching and Teflon tubing was used in its place.

[insert table 2 about here]

The temperature of the River Al at Ballydonagh is lower than that of the Shannon at Burgess Park because it is concealed by overgrowth and is shaded. Similar pH values are observed for both and dissolved solids are higher in the River Al because it is quite fast flowing.

[insert table 3 about here]

Somewhat surprisingly, the landfilled facility (Ballydonagh) displays levels comparable (**Table 3**) to Burgess Park. However, the River Al at Ballydonagh is less than two metres in width and fast flowing whereas the River Shannon adjacent to Burgess Park, is 199 metres wide, and is situated below a weir wall with a much greater depth by comparison, so analytes will undoubtedly be more dilute at this location.

[insert tables 4 & 5 about here]

Leachate sediments from the same locations were similarly characterised and analysed for phthalates and NP. The underlying physicochemical parameters are given in **Table 4** and the levels quantified are given

in **Table 5**. DBP and DEHP seem to be the most predominant analytes present in these two locations and this may be explained due to DBP being the most soluble whilst DEHP is the most frequently used. The results also correlate with the temperature changes and levels of dissolved solids.

The pH of the leachate sediment (**Table 3**) indicates an alkaline nature resulting from carbonate contents between 18.0-24.1 % for Burgess Park and 22.0-24.7 % for Ballydonagh due to the limestone in the area. Limestone, because of its porosity can allow certain substances to permeate through, permitting penetration into groundwater. The organic content varied between 2.67-12.2 % and 2.34-7.33 % for Burgess Park and Ballydonagh respectively. This would indicate that Burgess Park should leach more than Ballydonagh. Adsorption of chemicals to organic residues may occur hence accumulating the levels found present in sediment. The results, however, do not reflect a fair comparison as the dilution factor at Burgess Park is so immense.

It can be observed from **Table 4** that the overall properties of the sediments are quite similar. The only difference observed is that Burgess Park contains a higher percentage of organic residues. On examining sediment, DEHP was found at both locations. NP was found at Burgess Park but not at Ballydonagh and both DBP and DIDP were found at the latter. Much greater quantities were found in sediment compared with the liquid leachate.

[insert table 6 about here]

Table 6 also includes data from a sample of concentrated leachate taken from the landfill facility at Derryclure in Tullamore, which is located near the Silver/Tullamore River, which also flows into the River Shannon. On looking at the levels of DEHP, which is found most often and in the greatest quantities it can be seen that concentrated leachate (Tullamore) contains the highest levels and the leachate from an unlined dump (Burgess Park) was greater than that from a lined landfill (Ballydonagh). The leachate accumulated in silt from the Tullamore landfill contained roughly ten times less than the sediment from the other landfills. This may be due to the silicaceous nature of the sediment combined with the fact that the pH of the silt was slightly lower (7.01) and competition with other molecules sorbing onto the silt, although a further battery of tests would be needed to confirm this. In comparing

these results with our European counterparts, we see that levels found in the Irish midlands are approximately in the same range. Jonsson *et al*., 2003, (Sweden) [18, 19, 20] carried out an investigation of the levels of phthalates present in landfill leachate and found concentrations between 2 – 880 μg l^{-1}. DBP was found in the concentration range 1 – 23 μg l^{-1}, and DEHP from 3 – 460 μg l^{-1}. Martinnen *et al*., 2003, (Finland) [32] found DEHP to be the most abundant occurring pollutant in landfill leachate, with levels of up to 122 μg l^{-1} DEHP being found and concentrations of other phthalates below 17 μg l^{-1}. In this study, levels of DBP, DEHP, DINP and DIDP were found in all three types of landfill studied, ranging from 0.05 – 226 μg l^{-1} in leachates (the highest value being found in concentrated leachate) and 0.08 – 49.8 mg kg^{-1} in sediments. Levels of NP between 0.03 – 6.16 μg l^{-1} in leachate and 0.08 – 1.14 mg kg^{-1} in sediment were determined. Blackburn and Waldock [33] in the UK quantified levels of 330 μg/l NP in one particular area releasing wastewater into the River Aire, and levels of up to 180 μg/l was detected in river water downstream of this although concentrations in the range of 0.2 – 12 μg/l NP were detected in other UK river waters. Valsecchi et al., 2001 [34], found levels of around 2.9 mg kg^{-1} in ordinary river sediment. The Environment Agency (UK) report that some EDCs present even in ng l^{-1} range may provoke reproductive disturbances in riverine fish [35].

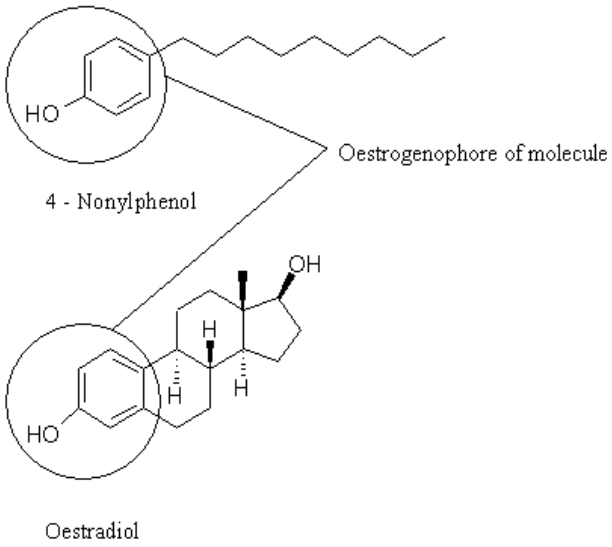
3.0 Conclusion

The four phthalates and 4-nonylphenol, analysed for were quantified at the three landfill types tested in this study so both stages were manifest. In terms of regulations on theses chemicals, the US EPA has established a maximum admissible concentration (MAC) in drinking water of 6 μg l^{-1} for DEHP [36] and for NP, the MAC for freshwaters for the UK is 3.5 μg l^{-1} [31]. As of yet there does not appear to be a maximum admissible concentration value for Irish waterways. Leachate from Burgess Park and Ballydonagh entered into river water and at first glance the results appear comparable but the vastly increased dilution at the former must be considered. The sediment near Ballydonagh, however, contained three main phthalates whereas Burgess Park contained only DEHP and NP for the most part. Much greater quantities were observed in solid compared to liquid matrices (concentrated leachate excepted) as expected. To get a better picture of the environmental situation in relation to the levels of these chemicals in the environment, more continuous monitoring at strategic intervals needs to be carried out to identify

297 situations where increased levels may occur. The levels observed in concentrated leachate indicate the
298 importance of subsequent treatment. The levels that we found were otherwise comparable with
299 international levels.
300
301 **4.0 Acknowledgements**
302 Council of Directors/Department of Education and Science, Strand III, Core Research Strengths
303 Enhancement Programme.
304
305 **5.0 References**
306 [1] U. Bolz, H. Hagenmaier, W. Korner. Environmental Pollution 115 291 – 301 (2001).
307 [2] S.Dempsey, M.Costello. EPA Report (1998).
308 [3] C. Desbrow, E. Routledge, P. Sheehan, M. Waldock, J. Sumpter. Environmental Agency 32 (11)
309 1 – 55 (1998).
310 [4] J. Sumpter. Toxicology Letters 102 – 103: 337 – 342 (1998).
311 [5] T. Ternes, M. Stumpf, J. Mueller, K. Haberer, R. Wilken, M. Servos. The Science of The Total
312 Environment 225 81 – 90 (1999).
313 [6] S. Choe, S. Kim, H. Kim, J. Lee, Y.Choi, H. Lee, Y. Kim. The Science of the Total
314 Environment 312: 15 – 21 (2003).
315 [7] M. Martin, R. Reiter, T. Pham, Y. Avellanet, J. Camera, M. Lahm, E. Pentecost, K. Pratap, B.
316 Gilmore, S. Divekar, R. Dagata, J. Bull, A. Stoica. Endocrinology 144 (6) 2425 – 2436 (2003).
317 [8] L. Archand-Hoy, A. Nimrod, W. Benson. International Journal of Toxicology 17 139 – 158
318 (1998).
319 [9] I. Nascimento Filho, C. von Muhlen, P. Schossler, E. Bastos Caramao. Chemosphere; 50 657 –
320 663 (2003).
321 [10] M. Petrovic, E. Eljarrat, M. Lopez de Alda, D. Barcelo. Trends in Analytical Chemistry; 20 (11)
322 637 – 648 (2001).
323 [11] K. van den Belt, R. Verheyen, H. Witters. Ecotoxicology and Environmental Safety 56 271 –
324 281 (2003).
325 [12] K. van den Belt, P. Berckmans, C. Vangenechten, R. Verheyen, H. Witters. Aquatic Toxicology
326 66 183 – 195 (2004).

[13] G. Prokupkova, K. Holadova, J. Poustka, J. Hajslova. Analytica Chimica Acta 1 – 13 (2002).
[14] M. Polo, M. Llompart, C. Garcia-Jares, R. Cela. Journal of Chromatography A 1072 63 – 72 (2005).
[15] A. Penalver, E. Pocurull, F. Borrull, R. Marce. Journal of Chromatography A 872 191 – 201 (2002).
[16] T. Niino, T. Ishibashi, T. Itho, S. Sakai, H. Ishiwata, T. Yamada, S. Onodera. Journal of Chromatography B 780 35 – 44 (2002).
[17] B. Tienpont, F. David, F. Vanwalleghem, P. Sandra. Journal of Chromatography A 911 235 – 247 (2001).
[18] S. Jonsson, J. Ejlertsson, B. Svensson. Waste Management 23 641 – 651 (2003).
[19] S. Jonsson, J. Ejlertsson, B. Svensson. Advances in Environmental Research 7 429 – 440 (2003).
[20] S. Jonsson, J. Ejlertsson, B. Svensson. Water Research 37 609 – 617 (2003).
[21] J. Kang, F. Kondo. Research in Veterinary Science 73 177 – 182 (2002).
[22] A. Zafra, M. Olmo, B. Suarez, E. Hontoria, A. Navalon, J. Vilchez, Water Research 37 735 – 742 (2003).
[23] S. Valsecchi, S. Polesello, S.Cavalli. Journal of Chromatography A 925 297 – 301 (2001).
[24] W. Ding, and J. Fann. Journal of Chromatography A 866 79 – 85 (2000).
[25] C. Staples, C. Naylor, J. Williams, W. Gledhill. Environmental Toxicology and Chemistry 20 (11) 2450 – 2455 (2001).
[26] A. Johnson, A. Belfroid, A. Di Corcia. The Science of The Total Environment 256 163 – 173 (2000).
[27] H. Fromme, T. Kuchler, T. Otto, K. Pilz, J. Muller, A. Wenzel. Water Research 36 1429 – 1438 (2002).
[28] Meesters, R., Schroder, H. Analytical Chemistry 74 3566 – 3574 (2002).
[29] J. Vikelsoe, M. Thomsen, L. Carlsen., The Science of The Total Environment 296 105 – 116 (2002).
[30] McClure Morton Lough Derg Lough Ree Catchment Monitoring Group – Final Report, Belfast (2001).
[31] P. Behnisch, K. Fujii, K. Shiozaki, I. Kawakami, S. Sakai. Chemosphere 43 977 – 984 (2001).
[32] S. Marttinen, R. Kettunen, J. Rintala. The Science of the Total Environment 301 1 – 12 (2003).
[33] M. Blackburn, M. Waldock. Water Research 29 (7) 1623 – 1629 (1995).
[34] S. Valsecchi, S. Polesello, S. Cavalli. Journal of Chromatography A 925 297 – 301 (2001).
[35] M. Kimber. Chemistry in Britain, May; 39 (5) 26- 30 (2003).
[36] K. Luks – Betlej, P. Poop, B. Janoszka, H. Paschke. Journal of Chromatography A 938 93 – 101 (2001).

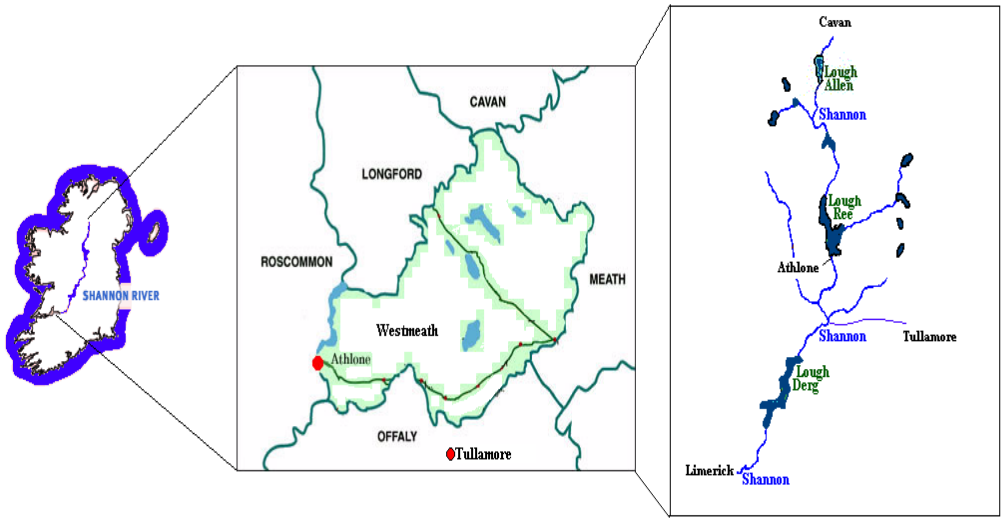
Word count : 5,161



364

365 **Fig. 1** Structure of an analyte with endocrine disrupting potential.

366



367
368 **Fig. 2** Map of the River Shannon Catchment and the Irish Midlands, identifying both Athlone and
369 Tullamore from where samples were taken.
370
371
372
373
374
375
376
377
378
379
380

Table 1 Validation Parameters

Analyte	Limit of detection		Limit of quantitation	Linearity multiple regression coefficient (r^2)		Enrichment recovery
	μg l^{-1}	mg kg^{-1}	μg l^{-1}	0 – 1 μg ml^{-1}	0 – 50 μg ml^{-1}	(leachate)
DBP	0.022	0.011	0.040	0.99	0.99	73.0
DEHP	0.028	0.014	0.040	0.99	0.99	83.6
DINP	0.053	0.026	0.400	0.99	0.99	114.9
DIDP	0.051	0.026	0.800	0.99	0.99	84.0
NP	0.031	0.015	0.040	0.99	0.99	97.0

Table 2 Some physical characteristics of the sampled leachates from rivers adjacent to landfill in 2004.

Burgess Park	Master Variable	Jun	Jul	Aug	Sept	Oct	Dec
	Temperature (^0C)	17.9	16.5	19.1	16.0	12.1	11.1
	Dissolved Solids (g/L)	0.303	0.364	0.341	0.309	0.341	0.198
	Suspended Solids (g/L)	0.007	0.005	0.009	0.007	0.009	0.002
	pH	7.94	8.35	7.46	7.40	7.83	7.94
	Rainfall (mm)*	111.2	68.4	9.9	45.2	39.1	70.0
Ballydonagh	**Master Variable**	**Jun**	**Jul**	**Aug**	**Sept**	**Oct**	**Dec**
	Temperature (^0C)	15.2	13.4	15.0	14.6	9.8	8.4
	Dissolved Solids (g/L)	0.490	0.497	0.432	0.440	0.516	0.283
	Suspended Solids (g/L)	0.005	0.005	0.007	0.005	0.007	0.008
	pH	8.12	8.25	8.00	7.98	8.10	7.96
	Rainfall (mm)*	111.2	68.4	9.9	45.2	39.1	70.0

* Athlone weather station

Table 3 Concentrations of oestrogenic compounds in the sampled leachates (μg l^{-1}) in 2004.

Burgess Park	**Jun**	**Jul**	**Aug**	**Sept**	**Oct**	**Dec**
DBP	1.71	1.85	4.27	0.22	6.49	3.92
DEHP	2.59	2.29	7.37	1.75	1.47	3.72
DINP	<LOD	0.61	5.56	0.06	0.18	0.20
DIDP	0.08	≤LOD	0.90	0.07	0.56	0.56
NP	≤LOD	≤LOD	1.74	1.02	0.36	0.51
Ballydonagh	**Jun**	**Jul**	**Aug**	**Sept**	**Oct**	**Dec**
DBP	1.41	2.08	7.05	5.62	4.79	2.56
DEHP	2.26	2.63	2.93	1.83	3.86	3.88
DINP	0.06	1.23	2.04	0.81	0.32	0.27
DIDP	≤LOD	≤LOD	0.23	1.19	0.17	0.68
NP	<LOD	<LOD	6.16	1.99	2.16	0.36

Table 4 Some physical characteristics of the sampled leachate sediments from November 2004 to April 2005.

Burgess Park	**Master Variable**	Nov	Dec	Jan	Feb	Mar	Apr
	Organic Residue (%)	2.67	12.2	4.04	6.84	6.00	5.47
	Carbonate Content (%)	24.1	23.9	23.9	18.0	22.1	22.8
	pH	7.89	7.63	7.85	7.51	7.68	7.91
Ballydonagh	**Master Variable**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**

	Organic Residue (%)	7.33	2.55	2.34	2.71	5.46	4.11
	Carbonate Content (%)	24.7	24.5	24.3	22.0	23.1	24.5
	pH	8.12	8.19	8.17	8.38	8.12	8.08

Table 5 Concentrations of oestrogenic compounds in the sampled leachate sediments (mg kg^{-1}) based on dry weight, from November 2004 to April 2005.

Burgess Park	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**
DBP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DEHP	12.7	<LOD	22.2	42.2	40.9	40.9
DINP	<LOD	<LOD	36.2	<LOD	<LOD	<LOD
DIDP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NP	0.93	1.14	0.21	0.08	0.16	0.14
Ballydonagh	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**
DBP	5.26	<LOD	42.3	1.29	22.3	11.2
DEHP	29.7	42.9	25.7	5.06	49.8	38.9
DINP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DIDP	12.0	19.6	0.57	0.55	20.0	14.3
NP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table 6 Summary of overall concentrations found in matrices for the month of April 2005.

	Liquid matrices - Results expressed in µg/l					**Solid matrices in contact with liquid leachate (mg/kg), based on dry weight**		
Analyte	**Leachate Burgess Park (unlined)**	**Leachate Ballydonagh (lined)**	**Leachate Tullamore (surface water) #1**	**Leachate Tullamore (ground water) #2**	**Conc. Leachate Tullamore (leachate in silt trap) #3**	**Leachate Sediment (Burgess Park) #A**	**Leachate Sediment (Ballydonagh) #B**	**Conc. Leachate in Silt (Tullamore) #C**
DBP	1.77	2.03	<LOD	<LOD	<LOD	<LOD	11.2	8.62
DEHP	30.4	6.59	39.7	202	226	40.9	38.9	4.16
DINP	6.75	2.74	<LOD	<LOD	<LOD	<LOD	<LOD	2.07
DIDP	35.4	10.6	8.56	<LOD	0.23	<LOD	14.3	1.62
NP	10.6	2.84	<LOD	<LOD	<LOD	0.14	<LOD	0.15

Note: #A = clay, #B = semi-sand, and #C = sand.

Toxicological & Environmental Chemistry, Oct.–Dec. 2007; 89(4): 697

Erratum

The following article published in *Toxicological and Environmental Chemistry*, July 2007; 89(3): 399–410 contained a number of errors:

'Isocratic LC methods for the trace analysis of phthalates and 4-nonylphenol in varying types of landfill and adjacent run-offs'.

Reference [35] in the first paragraph of p. 409 should read: [34]. Reference [36] in the second paragraph of p. 409 should read: [35]. The final entry in the reference section should read as follows: 36. Braun P, Moeder M, Schrader St, Popp P, Kuschk P, Engewald W. J. Chromatogr. A. 2003;988:41–51.

Taylor and Francis apologise for these errors.

ISSN 0277-2248 print/ISSN 1029-0486 online © 2007 Taylor & Francis
DOI: 10.1080/02772240701646972