

Hydrochemical profiles in urban groundwater systems: new insights into contaminant sources and pathways in the subsurface from legacy and emerging contaminants

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Abstract

It has long been known that groundwaters beneath urban areas carry a fingerprint from urban activities but finding a consistent tracer for anthropogenic influence has proved elusive. The varied sources of urban contaminants means that a single consistent and inexpensive means of tracing the fate of urban contaminants is not generally possible and multiple tracers are often required to understand the contaminant sources and pathways in these complex systems. This study has utilized a combination of micro-organic (MO) contaminants and inorganic hydrochemistry to trace recharge pathways and quantify the variability of groundwater quality in multi-level piezometers in the city of Doncaster, UK. A total of 23 MO's were detected during this study, with more compounds consistently detected during higher groundwater table conditions highlighting the importance of sampling under different hydrological conditions. Four of the compounds detected are EU Water Framework Directive priority substances; atrazine, simazine, naphthalene and DEHP, with a maximum concentration of 0.18, 0.03, 0.2, 16 µg/l respectively. Our study shows that the burden of the banned pesticide atrazine persisting in the Sherwood sandstone is detected at two of the three study sites. Emerging contaminants' are seen throughout the borehole profiles and provide insights into transient pathways for contaminant migration in the sub-surface. Long term changes in inorganic hydrochemistry show possible changes in contaminant input or the dissolution of minerals. Nitrate was detected above 50 mg/L but on the whole nitrate concentrations have declined in the intervening years either due to a reduction of nitrate application at the surface or a migration of peak nitrate concentrations laterally or to greater depth. This study shows that multiple tracers together with multi-level piezometers can give a better resolution of contaminant pathways and variable flow regimes within the relatively uncomplicated aquifer of the Sherwood Sandstone compared with single long screened wells.

Keywords: Micro-organic contaminants; Multi level piezometer; Pesticides; Tracers; Inorganic hydrochemistry

1 Introduction

Recharge to groundwater is usually dominated by local meteoric sources in temperate climates, but in an urban context urban leakage from mains and waste water can be a significant component (Lerner, 1990). In urban settings groundwater recharge processes are complex, spatially and temporally variable and significantly affected in terms of quantity and

quality by an overlying urban environment, especially if the aquifer is unconfined and covered by permeable or thin strata. Appleyard et al. (1999) highlighted the increased occurrence of contamination of the unconfined sandy aquifer below Perth, Australia, and discussed the problems of increased water levels due to imported water recharge. Lerner (2002) reviewed the issues involved with quantifying the urban water budget including the issues of increased recharge from imported water and leaking pipe networks and the changed runoff/recharge from land cover. The problems of finding a universally applicable tracer for identifying recharge sources are well established as many environmental tracers have several potential sources producing results that are difficult to untangle (Lerner, 2002). Barrett et al. (1999) were unable to find marker tracers for the three main sources of urban recharge (precipitation, mains leakage and sewer leakage) that could be applied to groundwaters in any urban area regardless of geology. They looked at isotopic, microbial and potential markers derived from human waste and detergents but concluded that no one marker could be used on its own.

Conventional age tracers that are used in hydrogeological studies (e.g. CFCs and tritium) are by definition better suited for characterising the bulk age of groundwater rather than more transient and rapid pathways. Stuart et al. (2014), Sorensen et al. (2015) and Lapworth et al. (2015) have all recently demonstrated the use of emerging organic contaminants to assess rapid recharge pathways in vulnerable hydrogeological settings. Compounds such as artificial sweeteners and pharmaceuticals are starting to be used as tracers (Van Stempvoort et al., 2011; Wolf et al., 2012)

It has been suggested that the anthropogenic influence on an aquifer can be seen by the quantity, concentration and type of synthetic organic compounds found in groundwater samples (Glassmeyer et al., 2005). Society uses a vast array of compounds for a range of uses including personal care, food preparation and preservation, medication (human and animal), industrial manufacturing processes and agriculture. A growing number of micro-organic contaminants have been found in groundwater resources over the last few decades as analytical techniques have become more affordable and advanced and as awareness of different sources of contaminants has grown (Farré et al., 2012; Lapworth et al., 2012). Many of these are now being detected in urban groundwater across the world (Duong et al., 2015; Jurado et al., 2014; Jurado et al., 2012; Lin et al., 2015; López-Serna et al., 2013; Osenbrück et al., 2007)

The sources and pathways for organic micro-pollutants to reach the groundwater include point and diffuse sources and are summarised for an urban settings in Stuart et al. (2012). A large number of different sources and pathways have the potential to pollute the partially unconfined Sherwood Sandstone aquifer. These include pesticides from amenity use as well as compounds from industrial and domestic waste. Sewerage pipe leakage rates from the foul sewerage system are high in Doncaster, for example up to 10% of flow per annum and 30-40% of urban recharge have been estimated for Doncaster (Rueedi et al., 2009).

The Permo-Triassic Sherwood Sandstone is the second most important aquifer in the UK used for public supply, agricultural and industrial use. Shallow groundwater levels and thin or absent overlying deposits make it vulnerable to contamination from a range of anthropogenic sources (Lapworth et al., 2006; Tait et al., 2004). Low permeability marl bands can focus recharge making the groundwater vulnerable to rapid migration of

contaminants to depth via rapid pathways with limited attenuation potential, in some cases this is greatly enhanced by the dip of the lithology allowing rapid migration of faecal contamination to depth (Cronin et al., 2003; Taylor et al., 2006).

Multilevel piezometers allow a unique three dimensional conceptual model of water and contaminant movement to be developed, which unlike fully or partly penetrating wells provide adequate vertical resolution (Stuart et al., 2004). Combined these two approaches provide a powerful technique for addressing contaminant sources and pathways in the urban subsurface.

This paper investigates the use of micro-organic pollutants (MOs), and inorganic chemistry from two sampling campaigns in contrasting hydrological conditions within a well-characterised, vulnerable urban Sandstone aquifer system. The specific purpose of this study was to: i) profile vertical changes in a range of tracers, MOs, and hydrochemistry, ii) to understand temporal change in groundwater chemistry in response to contrasting hydrological regimes, as well as long-term (10 years) changes in inorganic chemistry profiles and iii) to investigate use of MOs for assessing rapid groundwater recharge pathways in the subsurface.

2 Methodology

2.1 Study area

Doncaster is a town in South Yorkshire, UK, with a population of about 200,000 and is dependent on groundwater for public and industrial supply taking its water from the Sherwood Sandstone aquifer (Figure 1). Doncaster has a history of mining and industry as it was an important coal mining area in the UK in the 19th and 20th centuries and industries such as steel foundries, rolling mills, wire mills and glass works followed due to coal supplies and transport links.

2.2 Geology & Hydrogeology

The Bessacarr-Cantley area of Doncaster (Figure 1) is underlain either directly by the Permo-Triassic Sherwood Sandstone Group, or by up to 8 m of intervening permeable Quaternary superficial sands and gravels. The Sherwood Sandstone is a dual porosity aquifer which is highly anisotropic. In this area, it consists of friable to moderately cemented, well to poorly sorted and fine to medium grained sandstones with some thin lenses of mudstones, which can lead to some stratification. Fractures, which occur widely in the Sherwood Sandstone, make a significant contribution to groundwater flow but are thought to be only important on scales of 10's to 100's of metres due to the dominant matrix permeability of the aquifer (Shand et al 2002). The local groundwater flow in the area is W – E down geological dip. The fractures and marl bands within the Sherwood Sandstone give varying transmissivities of between 76 and 92 m²/d (Morris et al., 2006). The geology, hydrogeology and setting is further described in Morris et al. (2006).

2.3 Multi-level borehole design and sampling

The multi-level boreholes used during this study were installed for the Assessing and Improving Sustainability of Urban Water Resources and Systems (AISUWRS) project in 2003 to characterise the vertical changes in water quality below Doncaster (Morris et al., 2006). Study sites were selected within green spaces (parks and playing fields) to act as a buffer zone from direct contaminant sources such as small works or garages, and hopefully normalize the samples. Multi-level sampling arrays were constructed as a bundle of 7 different length small-diameter piezometers inserted into a drilled borehole the shallowest and deepest being constructed of polyvinyl chloride (PVC) and the other 5 of high-density polyethylene (HDPE) tubing. Each piezometer has a 30 cm screened section and a cap at the bottom. All piezometer completions are hydraulically separated (Morris et al 2006). The drillers' logs for each of the boreholes (Figure 2) give an indication of weathered zones within the sandstone. It is noted that the boreholes had alternating thin bands of 'soft'/'hard' lithology until the lithology becomes 'hard' with no 'soft' layers. This junction occurred at about 22 m below ground level (bgl) for both Bolton Hill (BH) and Haslam Park (HP) and 7 m bgl at McAuley School (MS). During February and July 2014 all piezometers (Figure 2) at HP and MS were sampled, however, at BH only depths 28, 34, 39 and 51 m bgl were sampled in February and July with the additionally of 22 m bgl in July.

During sampling for MOs, plasticiser compounds are often detected (Lapworth et al., 2015). In four of the piezometers inertial pumps had been left in-situ since the end of the AISUWRS study 10 years previously. These were in ports 34, 39 and 51 m bgl at BH and 19 m bgl at HP. We wanted to assess the difference in detected plasticisers between ports with and without in-situ pumps. Samples were collected from the inertial pumps by withdrawing them sufficiently to allow the connection of a Waterra PowerPack PP1; a petrol driven actuator. Samples taken from the other multilevels were taken using a peristaltic pump (Solinst Model 410) and PE tubing. The polyethylene (PE) tubing and peristaltic pump tubing (platinum cured silicon) was thoroughly washed with Virkon® and rinsed with ultra-pure water at the beginning of each sampling campaign. The same tubing was used in each of the three multilevels but between the piezometers it was kept as clean as possible and laid on clean plastic sheet at the surface. To reduce cross-contamination, after sampling a port as much of the sample water as possible was removed from the tubing using the peristaltic pump and then the next port was fully purged before sampling.

2.4 Sample analysis

Field parameters (specific electrical conductivity (SEC, standardized to 25 °C), dissolved oxygen, pH and Eh) were determined by running the sample water from the peristaltic pump outlet through a flow-through cell to reduce the samples contact with air. SEC and temperature were determined externally from the flow-through cell. The samples were taken and a HACH alkalinity titration performed at site (using 1.6 N or 0.16 N sulphuric acid cartridges and a bromocresol green indicator) after the field parameters had stabilised. Due to the nature of flow from the inertial pump a flow-through cell could not be used and in this case the field parameters were measured in a bucket during pumping until 3 well volumes had been purged. Alkalinity titration and sampling occurred at this point.

Inorganic samples were collected in a rinsed plastic beaker and filtered through 0.45 µm cellulose nitrate filters into clean Nalgene LDPE bottles. Analysis of inorganic parameters (anions and cations) were carried out at the BGS laboratories in Keyworth by ICP-MS and IC.

Micro-organic samples were collected into a 1-litre glass bottle provided specifically for this purpose. No external object came in contact with the inside of the bottle to reduce the risk of contamination. The use of sun-screen and personal care products was kept to a minimum and no gloves were worn. Samples were stored in the dark prior to analysis, Sorensen et al. (2015) found that refrigeration of groundwater samples for this type of analysis made no difference to sample stability. A blank was collected using laboratory grade ultrapure water collected into 1 litre glass bottles, and equipment blanks (taken using the same pump tubing) were collected for each sample round. Analysis was conducted by the UK Environment Agency National Laboratory Service (NLS) using a double liquid–liquid extraction method followed by a semi-quantitative multi-residue GC-MS method which screens for over 1000 organic compounds as fully described in Sorensen et al. (2015). The detection limits are within 0.01–0.1 µg/l for 90% of compounds, with a reporting limit of 0.01 µg/L for 75% of determinands.

Results were corrected for compounds found in the laboratory blanks by NLS and were further blank corrected for the equipment blanks run during the sampling campaign and any compounds found in the trip blanks. The results were also screened and corrected from a list of compounds provided by NLS frequently found in the laboratory blanks in low concentrations (See Table S1 in supplementary material). The remaining data was then censored at 0.01 µg/l.

3 Results and Discussion

3.1 Groundwater levels

Hydraulic heads were determined prior to sampling the multilevels. Unfortunately groundwater levels were measured to individual piezometer tops and not ground level during the February sampling round at BH but groundwater levels were consistently higher in July than in February at all three sites (see Figure S1 in supplementary information). Water levels were approximately 0.2 m higher in July than February at all depths within the HP and MS multilevels. There appeared to be a slight downward gradient in the HP multilevel. During the July sampling at BH a downward gradient was also seen as water levels in the shallowest level was 4 cm higher than water levels in the deepest level. However, MS does not show the same consistent trend. During the July sampling at the MS multilevel there was a 1 cm variation between the separate depths but it is more variable in February with a total variability of 4 cm over the entire length of the multilevel. Due to the small variability in the measured water level during each round of sampling these profiles are likely to be affected by measurement error with no significant changes in piezometric head detected down the profile at MS and BH.

3.2 Temporal changes in hydrochemical profiles: 2004-2014

Morris et al. (2005) and Morris et al. (2006) only provide flow regime and mean concentrations for a range of inorganics, however, this provides a useful comparison for this study. There was very little seasonal variation seen in the 2004 inorganic data (Morris et al., 2005). Figure 3 shows the vertical profiles for a selection of major ions (Na, Ca, Mg, K, Cl, SO₄, HCO₃, NO₃, and SEC) at HP, MS and BH. Results from this study (February and July 2014) and the averaged data from Morris et al. (2005) are shown for comparison. Groundwaters

were oxic (dissolved O_2 were between 3 mg/l and 11 mg/l), pH values were between 6.4 and 8.5 with low Fe and Mn concentrations.

Figure 4 shows current and historical profiles for boron. Boron (B) is a constituent of a bleaching agent in washing powders (borax, sodium perborate monohydrate, disodium tetraborate) and was of interest to the historical study during 2003-4 as a possible wastewater tracer in the aquifer. Boron concentrations in washing powders have decreased over time hence Neal et al. (2010) was able to show falling boron concentrations in river waters due to falling concentrations in wastewaters. Comparing the historical average concentrations (Morris et al., 2006) with concentrations found in February and July 2014 there is an overall decrease in concentration over time.

Both the high dissolved oxygen concentrations, and the low Fe concentration indicate oxic conditions within the aquifer at each of the multilevels during both sampling campaigns in 2014. The concentrations of specific electrical conductivity (SEC) and HCO_3 (Figure 3) are, on the whole, variable with depth at each multilevel but comparable between both sampling events. However, during the July sampling round the SEC was slightly lower in the top ports of both BH and MS and higher at 60 m bgl at HP. The average historical (Morris et al. 2005) HCO_3 concentrations at HP are also comparable with the more recent concentrations, however, BH shows a distinct change over time and HCO_3 concentration are now higher than ten years ago.

Concentrations of NO_3 and Cl within the 3 multilevels were comparable between the 2014 sampling rounds in the mid to lower ports/ depths but there was variability between the winter and summer concentrations in the shallower ports (MS 9-21; HP 10- 28). The upper ports at BH could not be sampled, only 28 m bgl and below were consistently sampled, hence a comparison cannot be made with the shallower ports at this site. The averaged historical Cl data shows variation with the 2014 data, BH data shows the greatest variation with time. BH exhibits higher SEC and higher concentrations of HCO_3 , Cl, Ca, K, Mg, over much if not all of its depth compared to the other two boreholes.

Concentrations of NO_3 are above the EU drinking water standard of 50 mg/l NO_3 at several depths within the multilevels. Variation between the data sets can be seen and is marked at both HP and MS with lesser variation at BH. The 2014 concentrations of NO_3 at HP show a marked decrease in comparison to the earlier data. This may be due to greater dilution or a change in concentration of the source(s). The greater variation in concentration between the two sampling campaigns is seen at MS; concentrations are seen to roughly halve over the intervening 10 years at 45 m bgl and more than halve at 28 m bgl but to increase at 60 m bgl. This shows variability of sources within the different level of the aquifer or the migration of a source/peak.

Variation with depth is seen in the SO_4 and Ca concentrations with the greatest variability at the 28 and 35 m bgl ports below MS. The 2014 data are comparable but the historical average is considerably greater. There is also a significant variation in the Na concentrations above 30 m bgl at MS with time, the averaged historical data is a significantly higher and more variable than the 2014 results. This is just above the marl band found in the Sherwood Sandstone at this site. Concentrations of Na at MS above 30 m bgl during 2014 and throughout the HP borehole are below 10 mg/l.

The decrease of Ca, Mg, NO₃ and SO₄ within the central area of the MS borehole since the 2004 study is noteworthy (Figure 3). The original high concentrations are not attributable to just sewage input of SO₄ as the concentration of SO₄ within sewage was found to be at 60 – 100 mg/l (Morris et al., 2006) whereas the concentration of SO₄ at MS28 is in excess of this. The additional source of Ca, Mg and SO₄ may have been anhydrite in the sandstone or some other source such as landfill or mine spoil heaps as suggested by Morris et al. (2006) for Cl and NO₃, but it appears that by 2014 this source was much depleted. There is also a large variation and reduction in the concentration of Na between the historical data and the 2014 data at the upper ports. This indicates different sources and/ or conditions at MS between the two sampling campaigns. However, B used as a foul sewer indicator, is seen to be elevated above the 30 m bgl port during the two sampling campaigns indicating possible foul sewer influence. The decrease between the two sampling campaigns could be explained by the decrease in the use of B as an optical brightener in detergents (Neal et al. 2010). The evidence from changes in concentration of inorganic ions suggests multiple sources at this site and changes in these sources over time.

The BH borehole is sited in a park, part of which overlies a sand and gravel quarry, shown on historical maps up to 1948 as a “sand pit”. It has consistently had higher SEC, Ca, Mg, K, Cl and SO₄. Originally the high Cl and SO₄ at the mid-level in the borehole was attributed to an additional source than just sewage and possibly thought to be road salt run-off (Stuart et al., 2004). The HP Borehole has been the most consistent, with little change in inorganic ion concentration over time or even much variation with depth compared to the other two boreholes. It should be noted the greatest variation in inorganic ions have been seen just above the marl layer in the MS borehole and in the upper ports of all of the boreholes. This corresponds to a change in the hardness/ competency of the rock and therefore the transmissivity. The upper, more weathered area of sandstone is likely to see greater variability and mixing of waters.

3.3 Vertical and temporal changes in micro-organic profiles

A total of 23 different compounds were detected in groundwater samples from the multilevels during the study. Three of the compounds found in July were identified as ‘other’ compounds using the database library as NLS do not run a reference standard for all compounds (Table 1).

The frequency of detects and concentrations of the compounds were variable between the two sampling rounds. The compound detected most frequently was n-propylbenzene (solvent), it was detected in 18 out of the 19 ports in July with a maximum concentration of 0.02 µg/l, but was not detected in February.

Four of the compounds detected are WFD priority substances (EU, 2008b); atrazine, simazine, naphthalene and bis (2-ethylhexyl)phthalate (DEHP). DEHP (a plasticizer) was detected in 7 of the ports in February and 6 of the ports in July at a maximum concentration of 16 µg/l and 13 µg/l respectively. DEHP was found at different depths within all the multilevels during the repeat sampling and was the contaminant found at the highest concentration during the study (Table 1). Naphthalene (an industrial compound) was detected only once in February at a concentration of 0.2 µg/l; it was not detected in July.

Other compounds are regulated in drinking water, two of the compounds detected are herbicide breakdown products (desethyl atrazine and 2,6-dichlorobenzamide (BAM)) (EC, 1998).

Stacked bar charts showing the concentrations of selected MO compounds with depth is shown for each borehole in Figure 5. Only those compounds which were detected above 0.05 µg/l are plotted for clarity. This highlights the difference between sampling depths and the differences seen between the February and July sampling events. Of the 23 micropollutants found in this study 2 were pesticides and a further 2 were pesticide metabolites, these are discussed as a separate group within the MOs but are still included in Figure 5 for completeness.

Pesticides and their degradation products were found during both sampling rounds in the HP and MS multilevels (Figure 6) but were absent from the BH multilevel. Atrazine desethyl and 2,6-dichlorobenzamide are degradation products of atrazine and dichlobenil respectively. Pesticides or their metabolites were found only in MS21, MS28 and MS36; HP14, HP19 and HP27 during both sampling rounds and HP60 during July round only. Atrazine is detected above the EU prescribed concentration value in the MS multilevel at 28 m bgl during both sampling rounds; atrazine desethyl is also detected in this port at higher concentrations.

Generally, fewer MOs were detected during the Feb 2014 sample round compared to the greater concentrations and variety of compounds detected during July 2014 (Table 1). However, most of the mid-depths at BH and MS exhibit higher total concentrations in February than July. (BH 28 m bgl (Figure 5a), and MS 14, 21, 28 m bgl, figure 5c) There were few MOs detected in either Feb or July at 19 m bgl at HP (Figure 5b) and higher total concentrations in February than July at HP10, 14, 27 and 35 m bgl.

Results for the pesticides and metabolites from HP (Figure 6) show the exact opposite for the central zone; concentrations are higher in July than February and no pesticides or metabolites are seen in the other ports. This leads to the conclusion that the pesticides probably have a separate source from the other micro-organics or behave differently in the aquifer. It may be that a significant rainfall event after a period of dry weather before the July sampling has flushed micropollutants into the aquifer and increased the concentration in selected ports and that as the flow rates are slower in the central zone the signature of the pesticides have not been diluted yet by the recharge event and the pulse of other micropollutants has not yet appeared. This also confirms that the groundwater flow, and hence the residence time, in the central zone is greater and that dilution is less as has been found previously at this site (Morris et al 2006).

At MS (Figure 6) a similar number of total compounds are detected in February and July but at low concentrations, and the greatest number (and concentration) of pesticides and metabolites are found just above the marl band at the 28 m bgl port. Half of the MOs (50% Feb, 43% July) are accounted for by pesticides and their metabolites. Below the marl band seasonal variation is again seen in the MOs with concentrations and amount of compounds detected higher in July than in February. A marl band within the Sherwood Sandstone will impede the downward movement of water and compounds and influence the direction of flow – more horizontal than vertical. Again, this is consistent with previous finding of areas of different flow velocity throughout the borehole (Morris et al 2006).

Morris et al. (2006) reported above modern concentrations of CFC in these multilevels above 30 m bgl signifying enrichment from local sources. Below 30 m bgl they found much lower CFC concentrations and a rise in concentration at the deepest level in each borehole. They concluded that this again supported preferential flow at the upper and deepest level with slower flow in the central zone.

There are no pesticides or metabolites detected at BH during either sampling round. During February 2014 the concentration and the number of compounds found at BH, as at MS, was very low. During July a greater number and total concentration of MOs were found with higher concentrations at BH34, 39 and 51 m bgl. The highest total concentration of contaminants of all the boreholes was found at 34 m bgl which coincides with the highest SEC, Cl, Mg, SO₄, (Fe, Al) and B concentrations. Bromide concentrations are also an order of magnitude higher at BH than MS and HP. This could be evidence of wastewater ingress (Katz et al., 2011).

Using fluorescence spectroscopy Lapworth et al. (2008) concluded that at 35-45 m bgl at both HP and BH there is a different source of dissolved organic matter (DOM) than waste water sources, possibly groundwater with a smaller component of rapid fracture flow and larger component of slower intergranular flow. Morris et al., (2006) and Lapworth et al., (2008) both conclude that although there is an urban waste water signature seen the aquifer is not grossly polluted from this source. Lapworth et al., (2008) suggest that DOM is probably a mixture of both natural terrestrial and a minor component from urban sewage system leakage.

Overall more compounds were detected in the 3 boreholes in July than in February 2014. Groundwater levels are consistently higher within the 3 boreholes in July and therefore the higher concentrations could have been due to localised recharge processes. Cumulative rainfall was noticeably high during May-July in the Doncaster area and nationally in 2014 compared to recent years, resulting in higher groundwater levels in the Sherwood Sandstone during this period. Groundwater levels were also above normal during February 2014. Published data shows a wet summer in Doncaster compared to a dryer winter (Hydrological Outlook 2014). Prior to the July 2014 sampling there was increased precipitation, including high volume events with rainfall 120% of average in the preceding 3 months (Parry et al., 2014) compared to the more constant but drier weather prior to the February sampling.

Bis(2-ethylhexyl)phthalate (DEHP) (plasticiser) is the compound with the highest concentration detected at all three of the sites (see Figures 5a-c. N-propylbenzene (solvent) was detected at every port except one (BH 34) during July 2014 but none of the ports during February 2014 (Figure 5).

While careful sampling protocols were used to minimise the introduction of contamination during sampling, contamination from the plastic piezometers cannot be ruled out. As HDPE plastic tubing was used to sample the ports and the multilevels themselves are made from plastics it is impossible to know if the plasticisers detected during the study were those found in the groundwater or due to the sampling equipment or multilevel. It is at least possible to say that n-propylbenzene was not an artefact of the sampling event due to the high frequency of detection for only one of the events. However, as two sampling methods were used for both campaigns it is unlikely that these compounds were an artefact of the

new HDPE tubing used with the peristaltic pump or the HDPE tubing of the in-situ inertial pumps. The plasticizer DEHP is intermittently detected in the multilevels making it unlikely to be an artefact of the sampling. No single compound was detected in every sample. It is interesting to note that no patterns in contaminants detected were seen between samples collected using the installed inertial pumps and the peristaltic pump.

Octocrylene, a UV blocker, is only detected at a low concentration in one of the samples (34 m bgl at Bolton Hill) and although unlikely cannot be ruled out as an introduced contaminant. Similarly, if DEET (see Figure 5) were to have been an introduced contaminant it would have been expected to have been detected in the summer and not the winter sampling as is reported in the data. DEET was not used by the sampling team but it was detected in several ports in the winter sampling event confirming other recent studies which suggest that this is a commonly detected urban waste water tracer (e.g. Sorensen et al., 2015). Overall, there were few pharmaceuticals found in the groundwater samples, and only a few personal care compounds were detected. This was perhaps surprising as there was evidence of sewage influence to the groundwaters at these multilevels during previous studies using faecal contamination indicators, however the detects were low (Morris et al., 2006). Morris et al. (2006) report faecal indicator counts (faecal streptococci and sulphite-reducing clostridia) for the same HP multilevel as used in this study. It is interesting to note that, increased counts were on average seen at the shallowest and deepest ports (10 m bgl and 60 m bgl) where groundwater flow is thought to be greater and little was detected in the intervening levels which correspond to slower groundwater flows.

3.4 Micro-organic tracers: evidence of multiple pathways in the subsurface

Overall the MO pollutants demonstrate contamination down to the deepest ports within each borehole and temporal variability with higher net concentrations in the July sampling event than February. As discussed above, MO individual compound and concentration change significantly between the February and July sampling rounds and between boreholes. For instance DEHP, the compound detected at highest concentrations, is not consistently detected at high concentration in certain ports, or during one sampling event. In a single port (e.g. BH34) it is often detected at high concentrations in one of the rounds and not detected at all in the other. This points to variable sources of MO's and mixing of these sources within the groundwater system.

Atrazine and simazine were finally banned from use and storage in the EU in 2004 with dichlobenil similarly banned in 2008 (EU, 2004; EU, 2008a). Concentrations of atrazine in this study were found above 0.1 µg/L, the UK drinking water limit for individual pesticides, as set out in the Drinking Water Regulations (HMSO, 2000), which were transposed from the Drinking Water Directive (EC, 1998).

Lapworth et al. (2006) detail the concentrations of pesticides (no metabolites in the analytical suites used) in 14 wells < 30 m bgl over the period January 2002 to November 2003 (prior to the ban) in the Sherwood Sandstone aquifer underlying Doncaster and the area to the east. The study found atrazine and simazine in 4 of the study sites, maximum and average concentrations found for atrazine were 4.2 µg/L and 0.585 µg/L; and simazine 0.062 µg/L and 0.030 µg/L respectively. The current study detected banned pesticides or their metabolites at 3 of the same depths in both the HP and MS multilevels during both of the sampling periods (Figure 6). The repeatability of the depths and concentrations implies a

consistent source/ pathway at each site. As discussed above, evidence from previous studies and other analytes within this study point at an area of slower groundwater flow and greater residence time at these central depths within the sandstone beneath HP and MS. Atrazine was used extensively for amenity use in the UK prior to its registration being withdrawn for non-crop uses in 1992 due to its persistence in groundwater, and this is a likely source of atrazine contamination within this urban Sandstone aquifer (Knapp, 2005; Lapworth et al., 2006). The atrazine peaks at these two sites suggests multi-point contamination within the Sandstone matrix, and if the ban on non-crop use is taken as the last usage date this corresponds to contamination from at least 22 years ago.

Work on the Brusselian aquifer (Leterme et al., 2006) an unconsolidated sedimentary aquifer in Belgium, concluded that even after the ban on use of atrazine the concentrations in the aquifer would stay above the detection limit for many years based on the mean transfer time of nitrate between the surface and the water table of between 4 and 12 years (Vanclooster et al., 2004). The transport, leaching and degradation of pesticides in the soil zone has been studied by many authors, and a review of these can be found in Beulke et al. (2000). Arias-Estévez et al. (2008) and Köhne et al. (2009) have tried to bring the studies of specific aspects of the problem together. Overall, the level of groundwater contamination by pesticides depends on many variables not least soil depth, moisture content, chemical constituents, physical make-up, preferential pathways; pesticide half-life, chemical properties, sorption potential, usage; aquifer water levels, groundwater flow type to name but a few. Another possibility is that quantities of the pesticides may have been still used on a small scale in agricultural environments using up old stocks, but this is less likely for urban amenity use.

The previous study using these multilevels with anthropogenic tracers found a more rapid flow in the higher and lower parts of these multilevels and a lower flow in the central section due to the geology of the aquifer (Morris et al., 2006) as well as large scale mixing. They surmised that the stratification seen is not the result of contaminants moving downwards but a product of mixing between various water 'cells' and water moving generally down-dip and occasionally cross-dip along discontinuities deeper into the aquifer. Intergranular flow dominates the top 30 m of the saturated aquifer with fracture horizons allowing penetration of contaminants to deeper horizons. The top 30 m is dominated by poorly cemented sandy strata interspersed with harder fractured horizons. Below 30 m more competent strata with fracture systems brings water down for mixing. This is consistent with the behaviour of atrazine in this study.

The depths of detection of pesticides and their metabolites in the HP borehole (14, 19 and 27 mbgl) corresponds to above modern concentrations of CFC-11 and CFC-12 found by Morris et al (2006) although atrazine was also detected in Jul 2014 at 60 m bgl. They concluded that the correlation between the two CFCs in the HP borehole indicated mixing (depths 14, 19, 27 m bgl) or dilution (depths 10, 35, 45, 60 m bgl) occurring. However, the MS and BH multilevels did not show the same correlation between CFCs so Morris et al. (2006) proposed that 'additional sources have appeared over time or the catchments are much more heterogeneous in terms of additional sources'.

The pattern of pesticide contamination at HP and MS suggest rapid flow through the upper and lower levels and slower flow through the middle portion of the saturated zone (14-27 m

bgl HP and 21-36 m bgl at MS). The field conductivity shows a slight decrease in the upper ports at HP and MS during the July sampling period possibly indicating dilution in these areas of the sandstone.

3.5 Application of MO tracers in urban settings

The previous studies using the Doncaster multilevels suggest the aquifer was influenced by waste waters and as such it was assumed that artificial sweeteners and prescription drugs may be detected as these are often found in urban waters impacted by sewers (Jurado et al., 2012; Wolf et al., 2012; Van Stempvoort et al., 2011). In this study these compounds were not detected by the GCMS scans. It could be that the screening GCMS method used was not able to detect the very low concentration of these urban contaminants and a more-sensitive technique or an LCMS method targeted towards more-polar compounds would be needed. This is a common issue for research into MOs in the environment and a particular issue when we are trying to detect them in groundwaters as they are commonly at concentrations close to detection limits. Alternatively these non detections could perhaps be attributed to dilution from the increased precipitation, including high volume events, which occurred in the 3 months prior to the July sampling, or the dilute nature of wastewater sources in Doncaster. This is evident by the higher groundwater levels in the piezometers during the July sampling event than the February sampling round. Doncaster, similar to other UK cities, has combined sewers which means that increased rainfall leads to increased dilution within the sewerage network. If it had been possible to sample the multilevels more frequently, a more detailed picture may have emerged regarding the dynamic nature of MO contamination and changes due to a component of rapid recharge (Manamsa et al., 2016). The use of a multi-tracer techniques to characterise the anthropogenic influence on an aquifer and multiple contaminant pathways has been shown to be relevant to other urban areas around the world (e.g. Hillebrand et al., 2015; Sorensen et al., 2015). MOs, detected using multi residue scans are able to trace urban anthropogenic contamination from a broad spectrum of sources, making it suitable for multiple settings, and are able to provide new insights into the hydrological processes including recharge pathways and recharge sources.

4 Conclusions

The use of multi-levels piezometers has highlighted the heterogeneous nature of the Sherwood Sandstone in terms of hydraulic conductivity and sources of recharge (and hence contaminants). Mixing is seen within the aquifer system which comprises longer residence time matrix flow and more rapid flow paths that are often focussed along marl bands. This study corroborates previous findings at these sites and highlights the use of multi-levels to capture the flow of contaminants through an aquifer system. This study also emphasises the benefits of using multilevel piezometers to understand processes within the subsurface, and the caution needed when interpreting results from boreholes screened over large intervals. This study used a range of micro-organic compounds to indicate anthropogenic influence and highlights the need for multiple tracers to understand differing flow regimes, contaminant sources and pathways within an aquifer.

The study showed widespread anthropogenic influence at these sites with the persistence of banned triazine herbicides in groundwater, nitrate concentrations still above the drinking water standard at some of the depths and organic micro-pollutants found at every port sampled.

The pattern of occurrence of pesticides and their metabolites with depth differs to that seen with other organic micro-pollutants especially in areas of differing flow regimes. This leads to the conclusion that the pesticides are likely to have a different source from the other micro-organics.

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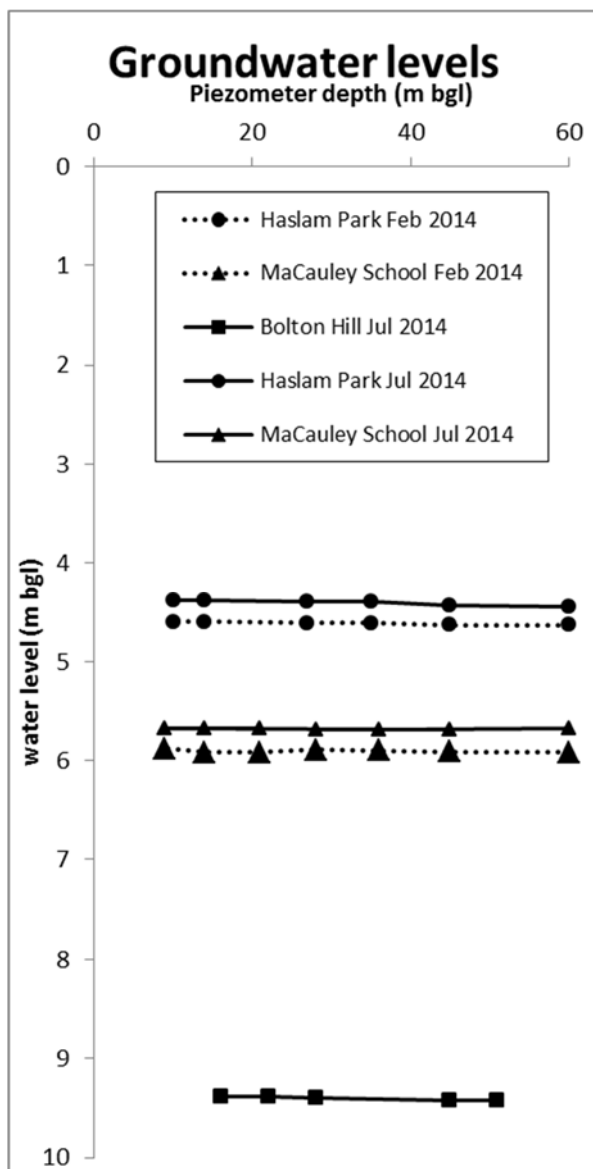


Figure S1. Graphical representation of groundwater levels at the piezometers before each sampling round.

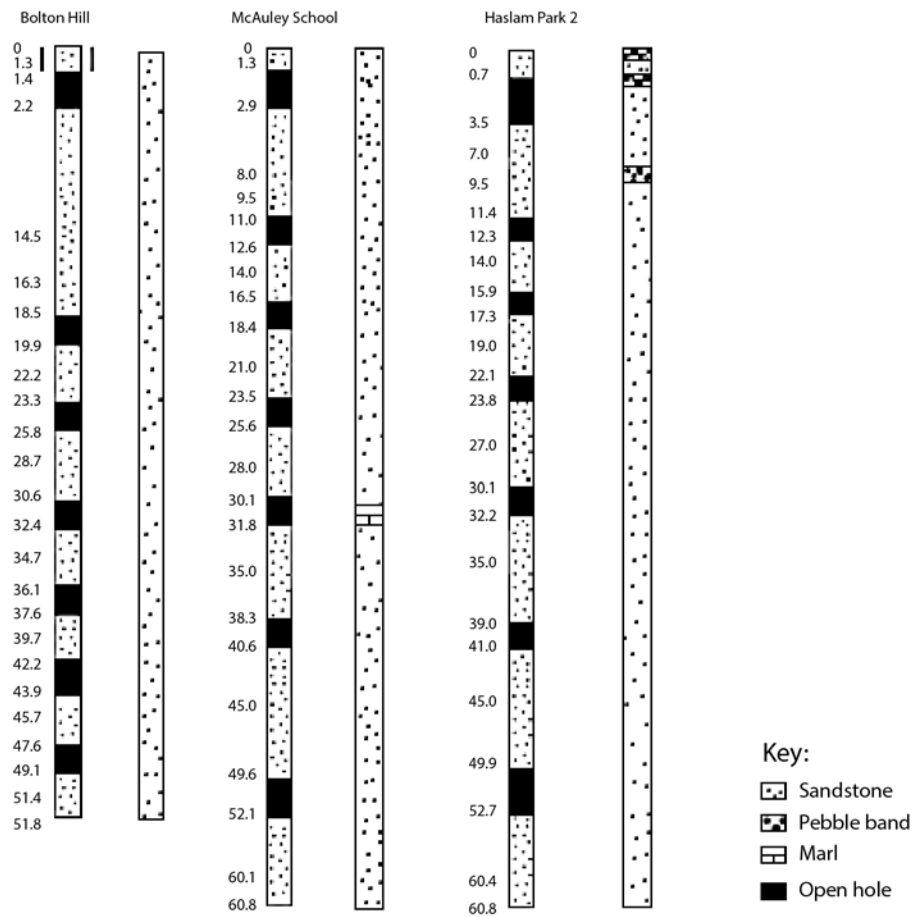


Figure 2. Multi-level construction and lithology. Depths (in metres below ground level) of the seal locations and sampling intervals of each of the three multilevels at Bolton Hill (BH), McAuley School (MS) and Haslam Park (HP). Dark areas denote open section of multilevel (After Morris et al 2006).

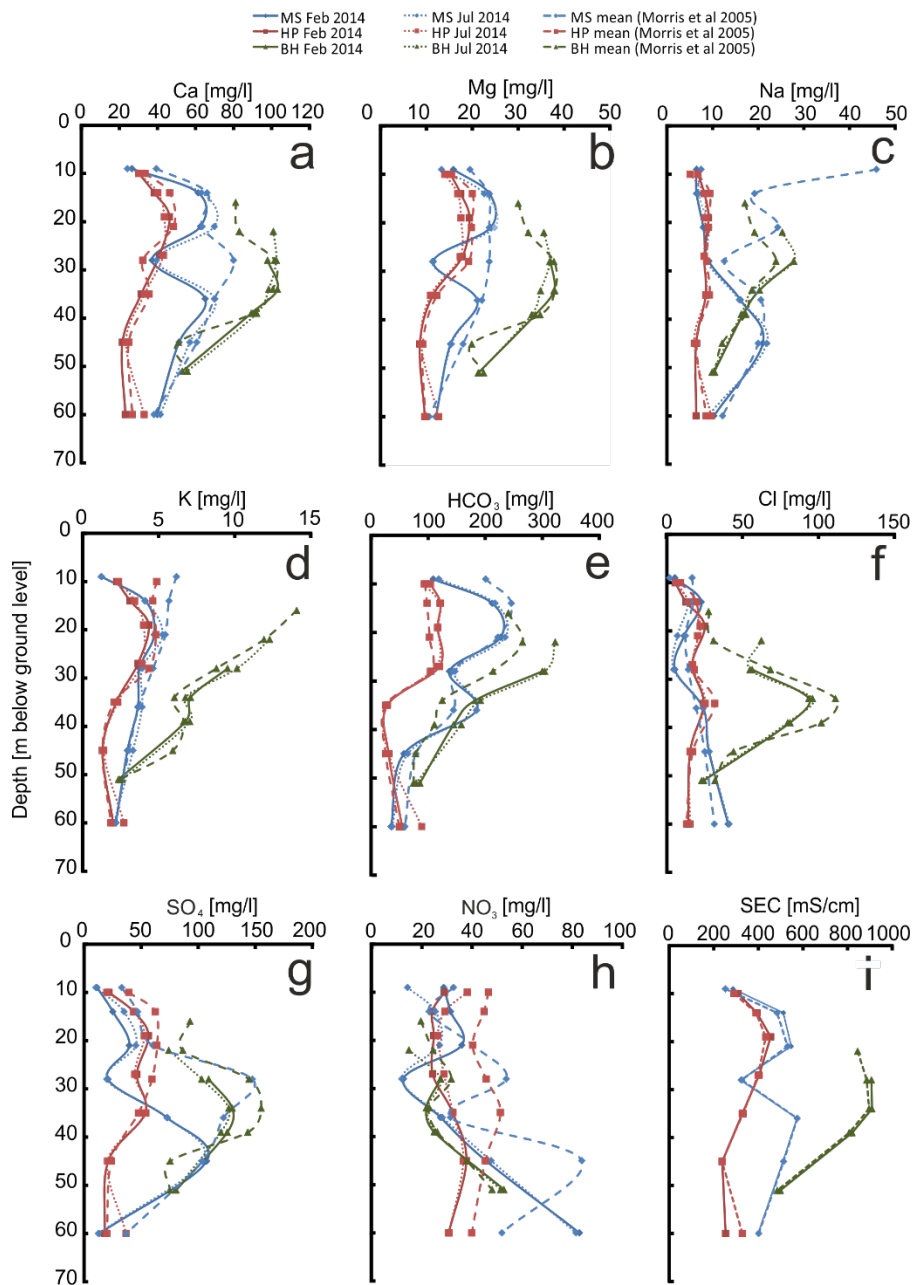


Figure 3. Vertical profiles for hydrochemistry showing historical and recent trends. Average values used for historical data from Morris et al (2005): a) Ca (mg/l), b) Mg (mg/l), c) Na (mg/l), d) K (mg/l), e) HCO_3 (mg/l), f) Cl (mg/l), g) SO_4 (mg/l), h) NO_3 (mg/l), i) field conductivity ($\mu\text{S}/\text{cm}$) for MS (McAuley School), HP (Haslam Park) and BH (Bolton Hill). No historical data is available from Morris et al. (2005) for field conductivity.

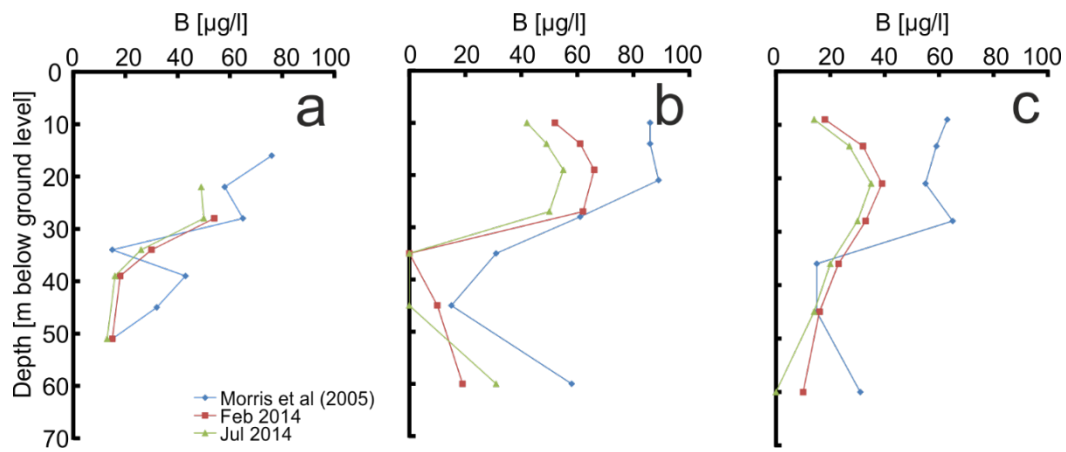


Figure 4. Boron depth profiles. Morris et al. (2005) is averaged data. Concentrations of B for a. BH (Bolton Hill), b. HP (Haslam Park) and c) MS (McAuley School).

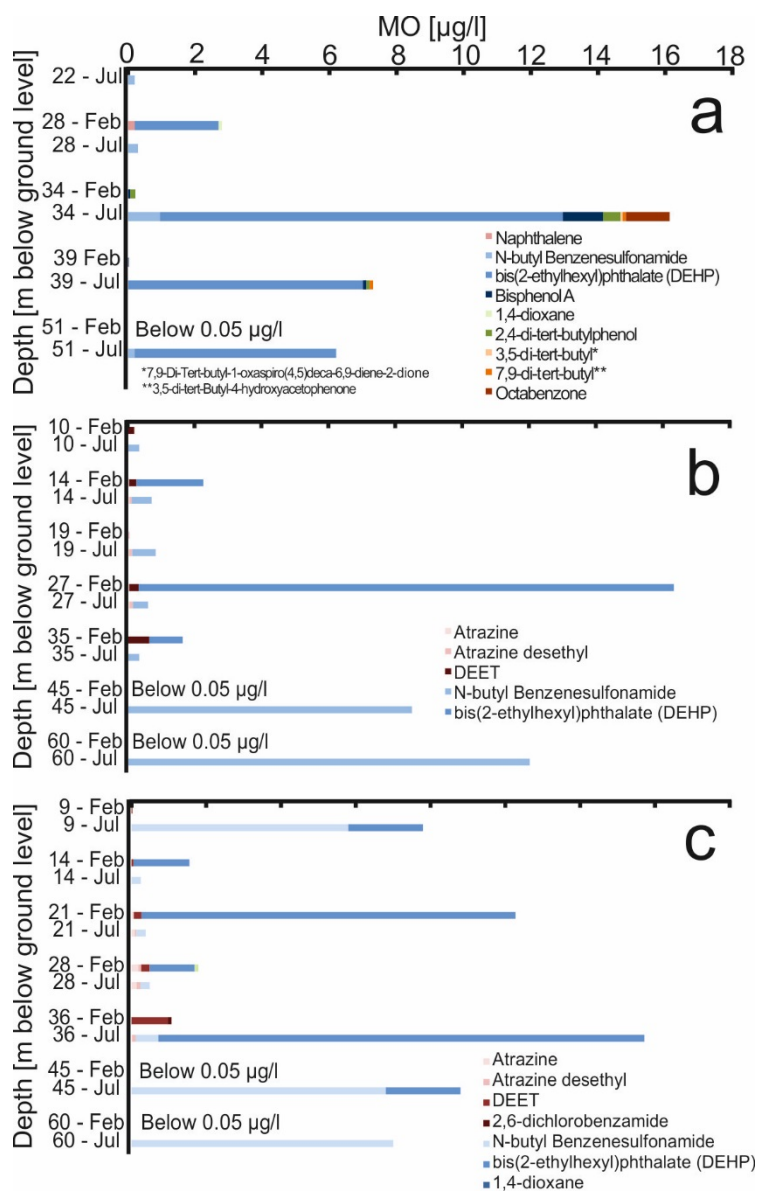


Figure 5. Stacked bar chart of MO's with concentrations above 0.05 µg/l for: a) at BH (Bolton Hill) (22 m bgl piezometer not sampled in February 2014), b) HP (Haslam Park), c) MS (McAuley School).

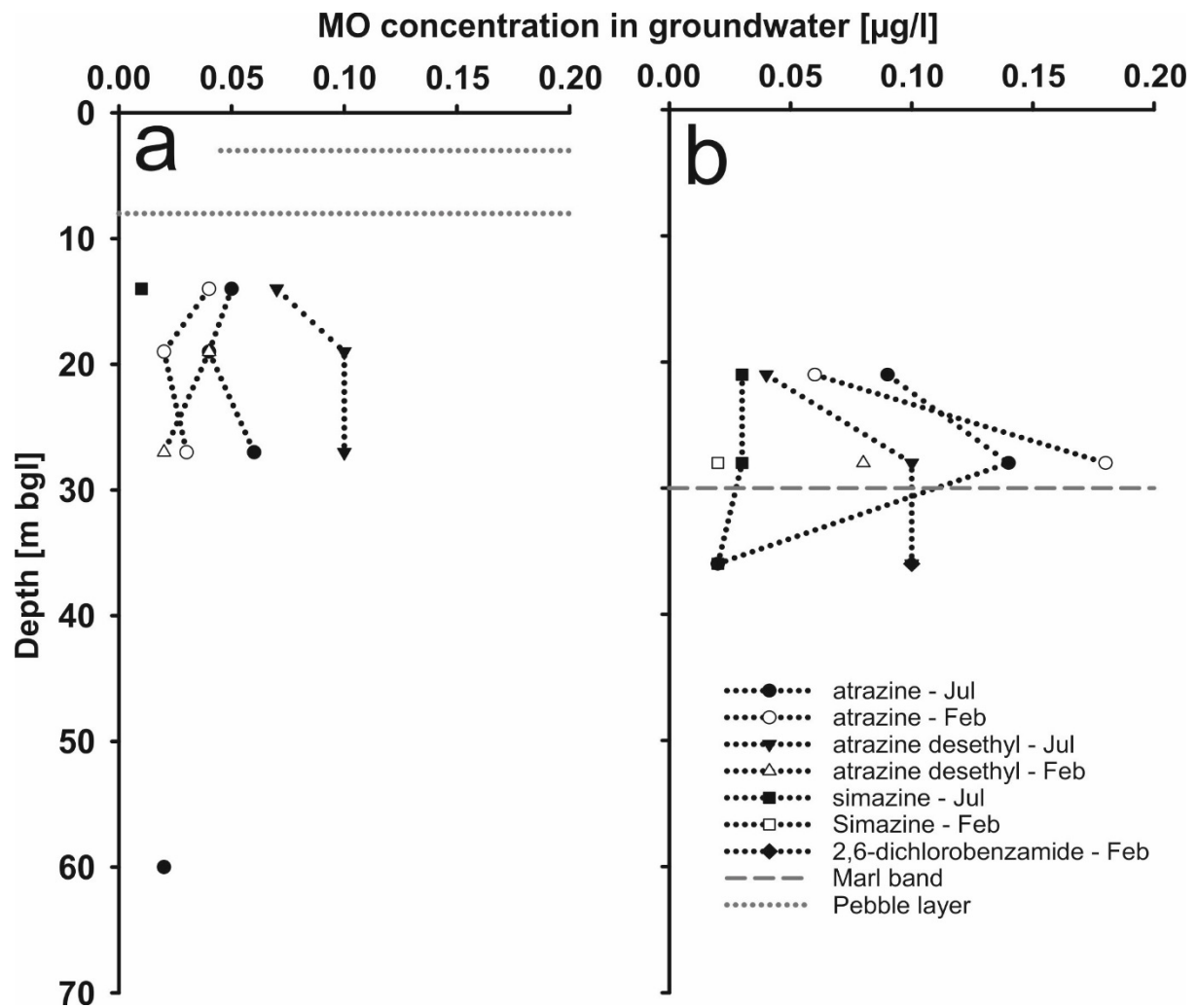


Figure 6. Pesticide profiles at the a) HP (Haslam Park) and b) MS (McAuley School) multilevels. Geology is sandstone unless otherwise indicated.

Table 1. Detection frequency and maximum concentration for compounds detected in the Doncaster multilevels during the study. Compounds in bold are WFD priority substances and/ or covered by the Drinking water directive (EC 1998). Table S2 in supplementary materials details the compounds' usage.

Compound	CAS number	Number of detects		total detects	Max concentration (µg/l)	
		Feb-14	Jul-14		Feb-14	Jul-14
1,4-dioxane	123911	2		2	0.1	0.1
2,4-dimethylphenol	105679		2	2	<DL	0.04
2,4-Di-tert-butylphenol	96764	1	2	3	0.15	0.52
2,6-dichlorobenzamide (BAM)	2008584	1		1	0.1	<DL
2,6-di-tert-butylphenol	128392		1	1	<DL	0.01
3,5-dimethylphenol	108689		1	1	<DL	0.02
Atrazine	1912249	5	7	12	0.18	0.14
Atrazine desethyl	6190654	3	6	9	0.08	0.1
bis(2-ethylhexyl)phthalate (DEHP)	117817	7	6	13	16	13
Bisphenol A	80057	2	2	4	0.7	1.2
Dibromomethane	74953		1	1	<DL	0.01
Indane	496117		15	15	<DL	0.02
Indene	95136		2	2	<DL	0.01
Isopropylbenzene	98828		3	3	<DL	0.01
N,N-diethyl-m-toluamide (DEET)	134623	10		10	0.97	<DL
Naphthalene	91203	1		1	0.2	<DL
<i>Non-regulated compounds</i>						
n-propylbenzene	103651		18	18	<DL	0.02
Octocrylene	6197304		1	1	<DL	0.01
o-phenylphenol	90437		9	9	<DL	0.03
other Octabenzone	1843056		1	1	<DL	1.3
other 3,5-di-tert-butyl-4-hydroxyacetophenone	no number		1	1	<DL	0.06
other 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-	82304663		2	2	<DL	0.1

2,8-dione						
Simazine	122349	3	4	7	0.02	0.03
total ports sampled		18	19			

Supplementary Information

Table S1. Blank correction data. a) Compounds removed from results after consultation with NLS, b) Compounds and concentration found in equipment blanks and trip blanks.

a)

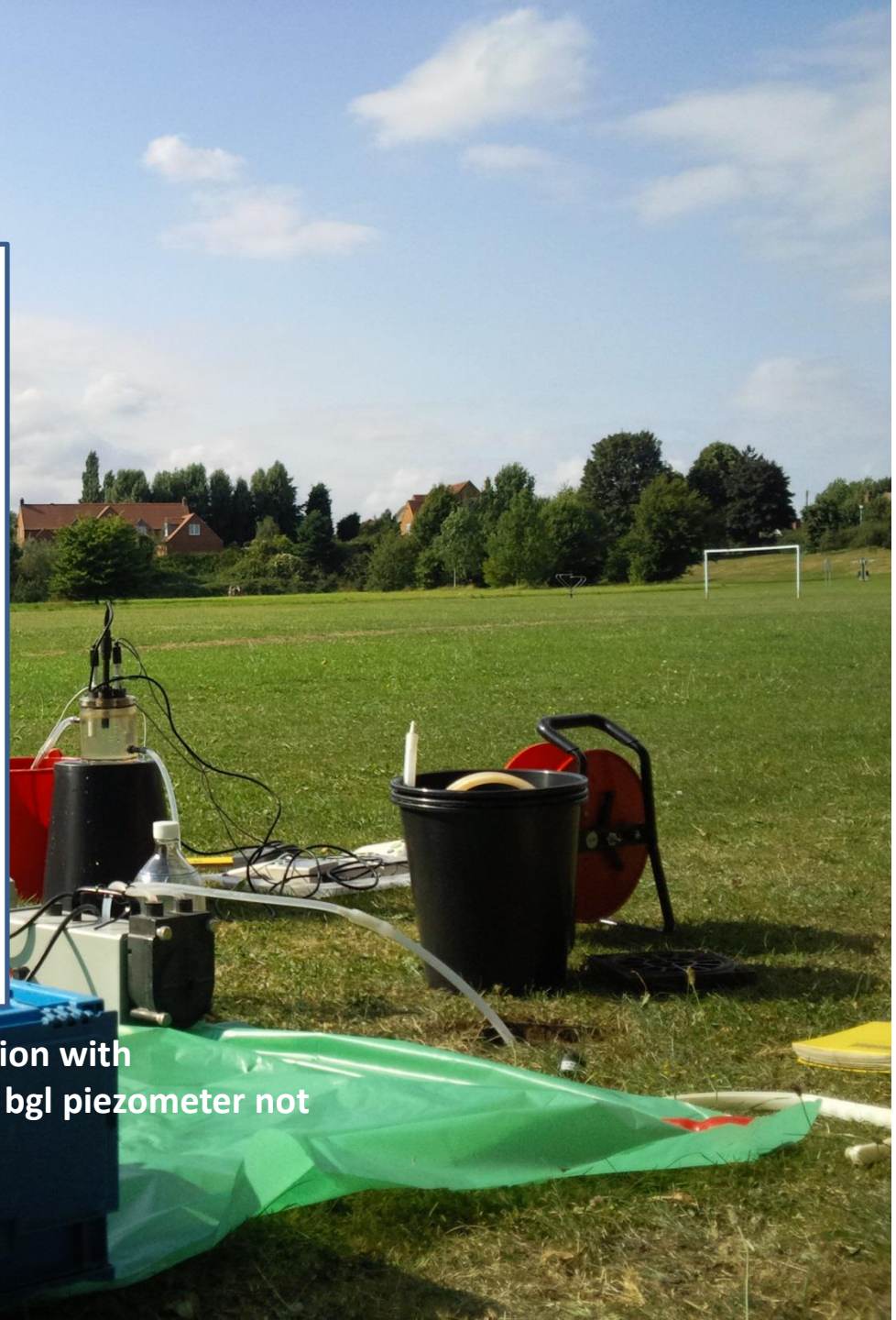
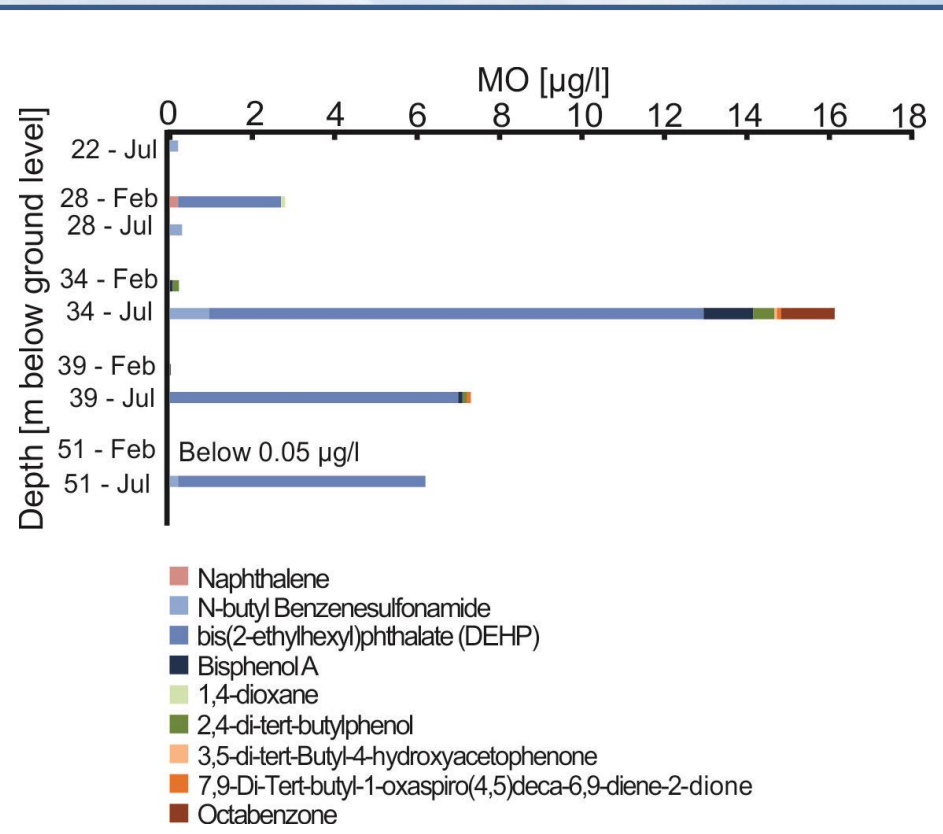
Compound	Rule
1,3-dichlorobenzene	Detection limit of 0.05 µg/l
2,4-Di-tert-butylphenol	Detection limit of 0.05 µg/l
naphthalene	Detection limit of 0.05 µg/l

b)

Compound	equipment or trip blank	concentration (µg/l)	date
Triacetin	Trip blank	0.05	Feb 2014
DEET	Trip blank	0.13	Feb 2014
Benzophenone	Trip blank	0.05	Feb 2014
N-butyl-benzene sulfonamide	Trip blank	3.9	Feb 2014
Octocrylene	Trip blank	0.03	Feb 2014
Dimethylphthalate	Trip blank	2.2	Feb 2014
Dibromomethane	Trip blank	0.03	Feb 2014
Diethylphthalate	Trip blank	2.0	Feb 2014
Furfural	equipment blank	0.01	Jul 2014
Isopropylbenzene	equipment blank	0.01	Jul 2014
n-propylbenzene	equipment blank	0.02	Jul 2014
N-butyl Benzenesulfonamide	equipment blank	0.7	Jul 2014
Indane	equipment blank	0.02	Jul 2014
o-Phenylphenol	equipment blank	0.02	Jul 2014
1(3H)-Isobenzofuranone	equipment blank	0.01	Jul 2014
Octocrylene	equipment blank	0.01	Jul 2014
Bis(2-ethylhexyl) adipate	equipment blank	0.02	Jul 2014
other Cas# 95169	equipment blank	0.01	Jul 2014
Benzothiazole			
other Cas# 4228108	equipment blank	0.02	Jul 2014
Ethanone, 1-(2,3-dihydro-1H-inden-5-yl)			
no compounds found	trip blank		Jul 2014

Table S2. Detected compounds and their common usage.

Compound	Usage	Cas number
<i>Solvents</i>		
n-propylbenzene	Volatile Solvent	103651
Isopropylbenzene	Volatile Solvent	98828
Dibromomethane	Volatile Solvent	74953
Indene	Used as a solvent and raw material for making other organic compounds.	95136
<i>plastic additives</i>		
bis(2-ethylhexyl)phthalate (DEHP)	Additives for phthalates (plastics)	117817
N-butyl benzenesulfonamide	Neurotoxic plasticiser	3622842
Bisphenol A	In the manufacture of epoxy resins and polycarbonates for food packaging	80057
<i>Pesticides and their metabolites</i>		
Atrazine	Herbicide	1912249
Simazine	Herbicide	122349
naphthalene	PAH/Insecticide	91203
N,N-diethyl-m-toluamide (DEET)	insect repellent	134623
Atrazine desethyl	Metabolite of Atrazine	6190654
2,6-dichlorobenzamide	Metabolite of Dichlobenil & Fluopicolide	2008584
2,4-dimethylphenol	Used as pesticides and in the manufacture of antioxidants	105679
3,5-dimethylphenol	Used as pesticides and in the manufacture of disinfectants	108689
<i>everything else</i>		
Indane	Petrochemical compound	496117
o-phenylphenol	Household disinfectants	90437
2,4-Di-tert-butylphenol	Used in phosphile anti-oxidants, UV stabilizers, pharmaceuticals & fragrances.	96764
1,4-dioxane	Personal Care Products, Stabilizer in chlorinated solvents	123911
2,6-di-tert-butylphenol	Used industrially as a UV stabilizer, antioxidant for hydrocarbon based products, prevents gumming in aviation fuels.	128392
Octocrylene	UV-filter	6197304
other 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione		82304663
other 3,5-di-tert-butyl-4-hydroxyacetophenone		no number
other Octabenzene		1843056



Stacked bar chart of micro-organic (MO) contamination with concentrations above 0.05 $\mu\text{g/l}$ for Bolton Hill (22 m bgl piezometer not sampled in February 2014)