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Fingerprinting groundwater pollution in catchments with contrasting contaminant sources using microorganic compounds

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HIGHLIGHTS

- Organic contaminants were measured at two contrasting groundwater study sites.
- Cocktails of compounds make good tracers of water type.
- Plasticisers, solvents, DEET and drugs were found at a peri-urban site.
- Pesticides, solvents, caffeine, parabens and food additives were found at a rural site.

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ABSTRACT

Evaluating the occurrence of microorganics helps to understand sources and processes which may be controlling the transport and fate of emerging contaminants (ECs). A study was carried out at the contrasting instrumented environmental observatory sites at Oxford, on the peri-urban floodplain gravel aquifer of the River Thames and Boxford, in the rural valley of the River Lambourn on the chalk aquifer, in Southern England to explore the use of ECs to fingerprint contaminant sources and flow pathways in groundwater. At Oxford compounds were typical of a local waste tip plume (not only plasticisers and solvents but also barbiturates and N,N-diethyl-m-toluamide (DEET)) and of the urban area (plasticisers and mood-enhancing drugs such as carbamazepine). At Boxford the results were different with widespread occurrence of agricultural pesticides, their metabolites and the solvent trichloroethene, as well as plasticisers, caffeine, butylated food additives, DEET, parabens and trace polyaromatic hydrocarbons (PAHs). Groups of compounds used in pharmaceuticals and personal care products of different provenance in the environment could be distinguished, i) historical household and medical waste, ii) long-term household usage persistent in groundwater and iii) current usage and contamination from surface water. Co-contaminant and degradation products can also indicate the likely source of contaminants. A cocktail of contaminants can be used as tracers to provide information on catchment pathways and groundwater/surface water interactions. A prominent feature in this study is the attenuation of many EC compounds in the hyporheic zone.

1. Introduction

A diverse array of synthetic organic compounds is used worldwide in large quantities for the production and preservation of food, for industrial manufacturing processes and for human and animal healthcare. In the last few decades there has been a growing interest in the occurrence, fate and potential toxicity of these contaminants in the terrestrial and aquatic environment (Daughton and Ternes, 2000; Halling-Sørensen et al., 1998; Kümmerer, 2009; Schwarzenbach et al., 2006; Stan et al., 1994; Stan and Linkerhägner, 1992). The contamination of groundwater is relatively poorly understood compared to other freshwater resources (Pal et al., 2010).

Included in this concern are so called "emerging contaminants", microorganics previously not considered or known to be significant in groundwater, which are now being detected as analytical techniques improve and which have the potential to cause adverse ecological or human health effects (Lindsey et al., 2001; Petrović et al., 2006). These include substances that have probably long been present in the environment but whose presence is only now being elucidated (Daughton, 2004). Richardson and Ternes (2011) reviewed recent analytical developments in the emerging contaminant context.

Microorganics encompass a wide array of compounds (as well as their metabolites and transformation products): pharmaceuticals and personal care products (PCPs), pesticides, veterinary products,

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industrial compounds/by-products and food additives. Because of the vast number of compounds, many studies have selected determinands according to priority lists taking into account consumption and predicted environmental concentrations as well as ecotoxicological, pharmacological and physicochemical data (Besse and Garric, 2008; Celiz et al., 2009; Crane et al., 2008; Fent et al., 2006; Hilton et al., 2003; Huschek et al., 2004). A systematic review of emerging contaminants in groundwater, by Lapworth et al. (2012) highlighted the widespread contamination of resources worldwide. Stuart and Lapworth (2013) also highlight the occurrence of transformation products of these compounds in groundwater.

It has been recognised that the range of contaminants present in groundwater is driven by activity at the surface. Wastewaters are the main sources of organics in the environment and surface waters therefore contain the greatest loads. There have been a large number of studies investigating the fate of microorganics in groundwater following the infiltration of wastewater to the ground (Clara et al., 2004; Drewes et al., 2003; Gasser et al., 2010; Glassmeyer et al., 2008; Grünheid et al., 2005; Heberer and Adam, 2004; Heberer et al., 1997; Katz et al., 2009; Rabiet et al., 2006; Sacher et al., 2001; Snyder et al., 2004).

In urban areas groundwater is likely to be impacted by pollutants from sewage, industrial activities as well as historical waste management practices. Diffuse leakage from reticulated sewerage systems poses a significant pollution risk as it bypasses natural attenuation mechanisms in the subsurface (Ellis, 2006). Wastewater may contain pharmaceuticals, household detergents, fragrances and flavourings and plant and animal steroids. Hospital wastewater forms an important source of contaminants including a wide range of pharmaceuticals (Verlicchi et al., 2010; Watkinson et al., 2009). Industrial compounds include solvents, detergents, flame retardants and polyaromatic hydrocarbons (PAHs).

In rural areas we might anticipate pesticides and veterinary medicines related to agriculture and animal waste. Boxall et al. (2004) discuss the risks to the environment from a range of veterinary medicines. Pesticides have been detected at trace concentrations in groundwater worldwide since the 1980s and remain important contaminants (Arias-Estévez et al., 2008; Baran et al., 2008; Close, 1996; Gilliom, 2007; Kolpin et al., 2000; Tappe et al., 2002; Walls et al., 1996; Zeng et al., 2011). The problem of persistent transformation products produced from partial degradation of pesticides in groundwater has also been recognised (Galassi et al., 1996; Somasundaram and Coats, 1991) and a wide range of such products have been identified in groundwater (e.g. Jacobsen et al., 2005; Kjaer et al., 2005; Kolpin et al., 2004). Risk assessment of pesticide transformation products in groundwater has been reviewed by Stuart et al. (2012).

Municipal solid waste leachate contains a wide range of organic compounds (Christensen et al., 2001; Sabel and Clark, 1984). Slack et al. (2007) reviewed the detections of xenobiotic compounds in leachate including halogenated and aromatic hydrocarbons, phenols (including bisphenol A), alkyl phenols (including nonyl phenol), pesticides, phthalates, pharmaceuticals, sulfonates, sulfones and sulfonamides (including n-butylbenzenesulfonamide (BBSA)), pyridines (including nicotine), carboxylic acids, alcohols, ethers and ketones, as well as caffeine, benzothiazoles and anilines. Barnes et al. (2004) and Buszka et al. (2009) found a range of microorganics in groundwater downgradient of landfills including detergents, antioxidants, fire retardants, plasticisers, antibiotics, ant-inflammatories, barbiturates, caffeine and cotinine.

Zheng et al. (2013) describe the use of organic water pollutant fingerprints to track the movement of industrial materials. Key target compounds were plasticisers, PCBs, PBDEs and steroids from the electronics, plastics, and biomedical industries.

Building on the documented contamination from different contaminant sources, the aims of the work described here were to investigate the use of screening for microorganic compounds in groundwater as a novel tool for understanding groundwater movement and transport processes in complex hydrogeological settings. This was addressed by screening for a very broad range of microorganics present from a range of sources at two UK sites with contrasting sources of contamination and showing how the microorganic fingerprint can help in understanding site hydrological settings. Importantly, this work was carried out at two sites where previous work had characterised the hydrogeology of the sites, and suitable borehole arrays were available for microorganic sampling (Gooddy et al., 2006; Allen et al., 2010; Macdonald et al., 2012). The study selected sampling points within each observatory: i) to collect samples from different depths, ii) to characterise microorganic pollution from a range of different potential sources, typical of lowland UK catchments, iii) to investigate the evolution of microorganic pollution along flow lines and with depth within the observatories, iv) to investigate the role of the hyporheic zone in attenuating microorganic contaminants and v) to explore the benefits of using broad screening GCMS methods for fingerprinting microorganic contamination in groundwater.

2. Study sites

2.1. Oxford Observatory

The peri-urban Oxford Observatory is found on the Port Meadow, an ancient grassland still used for communal grazing in the floodplain of the River Thames to the northwest of Oxford. This meadow is bounded on the west by the Thames and to the east by the Oxford Canal (Fig. 1a). The River Thames flows from northwest to southeast, regularly flooding areas of the Port Meadow. To the west of the Thames is an area of artificially-drained agricultural land. The study area also includes the former Burgess Field waste tip located to the east of Port Meadow and the urbanised higher ground to the east of the floodplain (Macdonald et al., 2012). Burgess Field was used as a domestic waste dump from 1937 to 1980 and is now covered by grassland and woodland. At the southern end of Burgess Field lies an allotment site which was once a Victorian waste tip.

The superficial deposits of the floodplain comprise alluvium underlain by 4 to 5 m of river terrace gravels (the Northmoor Sand and Gravel Member) which form the shallow aquifer (Fig. 1b). To the east of the canal the ground surface is a few metres higher and older terrace gravels are present (the Summertown–Radley Sand and Gravel Member). To the west of the Seacourt Stream the ground rises steeply. The bedrock beneath the entire area is the poorly-permeable Oxford Clay Formation.

Groundwater flow in the superficial deposits is from northeast to southwest (Fig. 1a). Gradients to the east of the Thames are relatively shallow, contrasting with the west where gradients are steep especially adjacent to the river. The Thames is not strongly hydraulically connected to the aquifer. In dry periods, as in Fig. 1a, the controlled river levels are higher than the surrounding groundwater in the south of the area and there may be some flow eastwards from the river. There is potential for groundwater to flow from east to west beneath the river through the gravels (Macdonald et al., 2012).

The Observatory has a comprehensive monitoring network including two transections of multi-level piezometers in the superficial deposits down gradient of the waste tip and boreholes across the site area and in the periphery of the waste tip. Table 1 gives the details of the sites used in this study. Macdonald et al. (2012) divide the study area into zones depending on geographical, hydrogeological and hydrochemical settings:

- *PUFP* — peri-urban flood plain east of the Thames and upgradient of the waste tip
- *PUFP2* — peri-urban flood plain east of the Thames and influenced by the waste tip plume
- *PUFP2 tip* — sites in PUFP2 within the waste tip boundary