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Nitrogen sources, transport and processing in peri-urban floodplains

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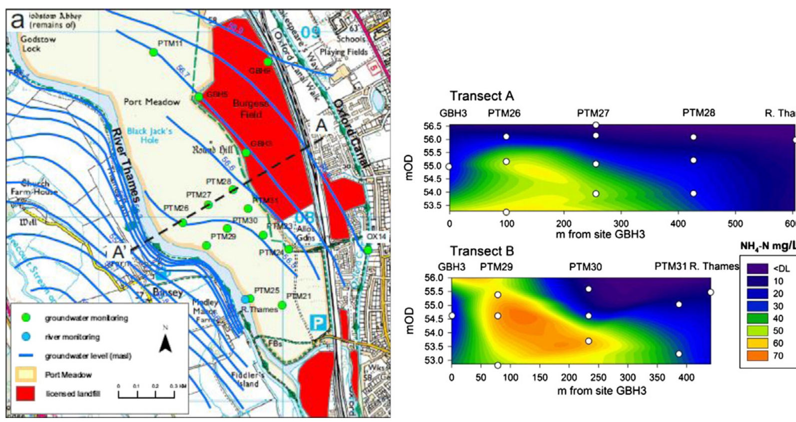
HIGHLIGHTS

- Peri-urban floodplains have been found to be populated with legacy landfills.
- Very high concentrations of nitrogen as ammonium are found.
- Isotopic methods identify legacy landfill as the ammonium source.
- Ammonium is not attenuated and is reaching the river.
- It is estimated that 27.5 tonnes of ammonium may be delivered to the river annually.

GRAPHICAL ABSTRACT



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ABSTRACT

Peri-urban floodplains are an important interface between developed land and the aquatic environment and may act as a source or sink for contaminants moving from urban areas towards surface water courses. With increasing pressure from urban development the functioning of floodplains is coming under greater scrutiny. A number of peri-urban sites have been found to be populated with legacy landfills which could potentially cause pollution of adjacent river bodies. Here, a peri-urban floodplain adjoining the city of Oxford, UK, with the River Thames has been investigated over a period of three years through repeated sampling of groundwaters from existing and specially constructed piezometers. A nearby landfill has been found to have imprinted a strong signal on the groundwater with particularly high concentrations of ammonium and generally low concentrations of nitrate and dissolved oxygen. An intensive study of nitrogen dynamics through the use of N-species chemistry, nitrogen isotopes and dissolved nitrous oxide reveals that there is little or no denitrification in the majority of the main landfill plume, and neither is the ammonium significantly retarded by sorption to the aquifer sediments. A simple model has determined the flux of total nitrogen and ammonium from the landfill, through the floodplain and into the river. Over an 8 km reach of the river, which has a number of other legacy landfills, it is estimated that 27.5 tonnes of ammonium may be delivered to the river annually. Although this is a relatively small contribution to the total river nitrogen, it may represent up to 15% of the ammonium loading at the study site and over the length of the reach could increase in-stream concentrations by nearly 40%. Catchment management plans that encompass floodplains in the peri-urban environment need to take into account the likely risk to groundwater and surface water quality that these environments pose.

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1. Introduction

In recent decades anthropogenic inputs of N, for food production by intensive agriculture and urbanisation, have caused increases in macronutrient fluxes, and have led to widespread N pollution of aquatic systems (Foster et al., 1982; Burt et al., 2011; Whitehead and Crossman, 2012; Lapworth et al., 2013). This is a global issue with implications for food production and security, water quality and land management/planning (Galloway, 1999; Galloway et al., 2004). In Europe and North America there have been a series of policies and accompanying regulations which have focused on reducing point and diffuse N and P pollution and associated problems of eutrophication and ecological degradation of freshwaters. For example, the European Water Framework Directive (WFD 2000) has the aim for fresh and marine waters to reach 'good ecological status' by 2015.

The zone of transition from rural to urban land-use is often referred to as the peri-urban area. Un-lined waste sites or landfills are a common source of N and C inputs to surface and groundwaters in peri-urban floodplains (Wakida and Lerner, 2005; Corniello et al., 2007). In Europe and North America there is a legacy of historic pollution from these sites (e.g. Heaton et al., 2005; Lorah et al., 2009). As such, landfill leachate plumes may contain high dissolved organic C (DOC) and NH_4^+ concentrations as well as ferrous iron, chloride and bicarbonate relative to natural floodplain conditions (Lorah et al., 2009). These commonly develop a series of distinct redox zones (Lyngkild and Christensen, 1992). In such systems, dilution, sorption and denitrification may be effective attenuation processes within the shallow groundwater system. The attenuation of N pollution from landfills, as well as other sources within peri-urban settings, requires fluctuations in redox conditions. These may be expected in floodplain settings due to rapid changes in water levels and episodes of surface water recharge and inundation.

Nitrogen in the form of ammonium (NH_4^+) is present naturally in groundwater as a result of anaerobic degradation of organic matter, and in the form of nitrate (NO_3^-) from the microbial oxidation of NH_4^+. However, NH_4^+ and NO_3^- also occur in groundwater from anthropogenic sources. High concentrations of NH_4^+ (10–1000 mg/L) have been found in groundwaters impacted by landfill leachates and as a result of domestic and agricultural waste water disposal practices (Gooddy et al., 1998; Lawrence et al., 2000; Christensen et al., 2001; Heaton et al., 2005). High concentrations of NO_3^- are typically association with diffuse agricultural pollution from fertilisers (Oakes et al., 1981; Addiscott et al., 1991) although oxidation of anthropogenic ammonium sources also causes high NO_3^- concentrations (Gooddy et al., 2002).

Ammonium transport in the subsurface may be retarded by sorption (Ceazan et al., 1989; Buss et al., 2004). Both NH_4^+ and NO_3^- can be attenuated through microbially-induced transformations (DeSimone and Howes, 1998). Ammonium oxidation commonly occurs in conjunction with oxygen reduction and is termed nitrification. This results in the production of nitrite (NO_2^-) followed by NO_3^-.

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (2)$$

In addition to degrading groundwater quality, NO_3^- and NH_4^+ can both be substantial sources of N in surface waters receiving groundwater (Jackson et al., 2007). Therefore it is desirable that this nitrogen is completely removed from the aquatic system. This requires bacterially mediated denitrification to convert the nitrate through intermediate stages to nitrous oxide and ultimately to nitrogen gas (Eq. (3)), which is a process requiring anaerobic conditions. This process is controlled by the availability of soluble carbon, redox status, pH as well as soil/groundwater residence times and hydrology (Haycock and Burt, 1993; Thomas et al., 1994; Burt et al., 1999; Gooddy et al., 2002).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2(g) \quad (3)$$

Therefore attenuation of N pollution from organic wastes requires alternating redox conditions, from oxidising to reducing, such as generated during water table fluctuations. Alternatively, through the anammox process, NH_4^+ can be oxidised anaerobically to nitrogen gas through the reduction of (NO_2^- derived from NO_3^- (see Eq. (3) above).

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (4)$$

Despite the environmental importance of NO_3^- and NH_4^+, there are few studies documenting their transport and reaction processes in aquifers (Heaton et al., 2005). Isotopic fractionation studies can provide an excellent tool for understanding N transport and speciation (Wassenaar, 1995; Böhlke et al., 2006). Isotopic fractionations have been reported for NH_4^+ sorption to clays (Karamanos and Rennie, 1978), with the remaining NH_4^+ in solution relatively depleted in ^{15}N. By contrast, nitrification results in a substantial increase in ^{15}N for the remaining NH_4^+ (Delwiche and Steyn, 1970). Stable isotope ratios in NO_3^- have often been used to distinguish various sources of NO_3^- in groundwater, such as synthetic fertilisers and animal wastes (Gormly and Spalding, 1979; Flipse and Bonner, 1985). Denitrification causes an isotopic enrichment in the remaining nitrate (Mariotti et al., 1988). A disadvantage of the single isotope approach to denitrification studies is that process such as ammonia volatilisation can also lead to enrichment of ^{15}N in the residual NH_4^+ source material and in the NO_3^- produced during nitrification. However, by combining the $\delta^{18}O$ of the NO_3^-, a more reliable indicator of the denitrification process is achieved (Böttcher et al., 1990; Wassenaar, 1995; Kendall, 1998; Fukada et al., 2004). The opposing isotope fractionation effects make it possible to distinguish between sorption, nitrification and denitrification as major processes affecting N distribution in a field setting through evaluating variations in concentration and isotopic composition.

Riparian floodplains provide an important interface between terrestrial and aquatic systems (Harms and Grimm, 2008). Floodplain aquifers can be important sources of drinking water and sustain baseflow in surface waters, with important ecological implications (Sophocleous, 2002; Murray-Hudson et al., 2006). However, globally, floodplains are increasingly being encroached and developed due to anthropogenic pressures including urbanisation and intensive agriculture (Tockner and Stanford, 2002; Pinter, 2005; Werritty, 2006). In many parts of Europe, and elsewhere, there is a historical legacy of change in land use and associated historical pollution loading to floodplain groundwaters and surface waters (Burt et al., 2011; Stuart and Lapworth, 2011). Peri-urban floodplains are therefore complex, in terms of spatial heterogeneity in land use and topography, and temporal variability in recharge and redox processes (Burt et al., 2002; Burt and Pinay, 2005; Macdonald et al., 2012a; in press).

Due to changing redox conditions, floodplains and riparian settings are considered hot-spots for nutrient attenuation (Devito et al., 1999; McClain et al., 2003; Harms and Grimm, 2008). Groundwater levels within floodplain environments are typically shallow and responsive to recharge events. Vertical and spatial soil moisture conditions are also highly variable, and together these have important implication for attenuation of oxidised N (Burt et al., 1999). Periods of inundation may stimulate denitrification due to the mobilisation of C pools at shallow depths; during periods of low water tables denitrification may be restricted due to reduced C pools, low soil moisture and more oxidising conditions.

The important ecosystem services provided by floodplains and their general proximity to potentially damaging agricultural and urban nutrient sources means there is an imperative to understand nutrient processes, fluxes and attenuation mechanisms within. Due to the complex