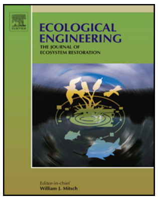
Ecological Engineering xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng



Spatio-temporal analysis of factors controlling nitrate dynamics and potential denitrification hot spots and hot moments in groundwater of an alluvial floodplain

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ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form 13 October 2015
Accepted 18 December 2015
Available online xxx

Keywords:
Groundwater
Denitrification
Nitrate
Wetland
Floodplain

ABSTRACT

Nitrate (NO_3^-) contamination of freshwater systems is a global concern. In alluvial floodplains, riparian areas have been proven to be efficient in nitrate removal. In this study, a large spatio-temporal dataset collected during one year at monthly time steps within a meander area of the Garonne floodplain (France) was analysed in order to improve the understanding of nitrate dynamic and denitrification process in floodplain areas. The results showed that groundwater NO_3^- concentrations (mean 50 mg NO_3^- L^{-1}) were primarily controlled by groundwater dilution with river water (explaining 54% of NO_3^- variance), but also by nitrate removal process identified as denitrification (explaining 14% of NO_3^- variance). Dilution was controlled by hydrological flow paths and residence time linked to river-aquifer exchanges and flood occurrence, while potential denitrification (DEA) was controlled by oxygen, high dissolved organic carbon (DOC) and organic matter content in the sediment (31% of DEA variance). DOC can originate both from the river input and the degradation of organic matter (OM) located in topsoil and sediments of the alluvial plain. In addition, river bank geomorphology appeared to be a key element explaining potential denitrification hot spot locations. Low bankfull height (LBH) areas corresponding to wetlands exhibited higher denitrification rates than high bankfull height (HBH) areas less often flooded. Hydrology determined the timing of denitrification hot moments occurring after flood events. These findings underline the importance of integrating dynamic water interactions between river and aquifer, geomorphology, and dual carbon source (river and sediment) when assessing nitrate dynamics and denitrification patterns in floodplain environments.

1. Introduction

Nitrate contamination of groundwater through point source and diffuse pollution has long attracted world-wide attention (Power and Schepers, 1989; Bijay-Singh et al., 1995; Zhang et al., 1996; Arrate et al., 1997; Carpenter et al., 1998; Jégo et al., 2012). Nitrate pollution from agricultural sources is considered to be the main cause of groundwater degradation in the European Union (Sutton et al., 2011). In Europe and North America, up to 90% of floodplain areas are cultivated (Tockner and Stanford, 2002). Agricultural land use, in combination with factors such as shallow groundwater, high permeability of alluvial deposits and interconnections with surface water, make alluvial aquifers particularly vulnerable to nitrate diffuse pollution (Arauzo et al., 2011). As a result, nitrate concentrations exceeding the limit of 50 mg-NO_3^- L^{-1} set for groundwater systems in Europe by the Nitrate Directive (91/676/EEC) and the Groundwater Directive (2006/118/EEC) have been reported for several shallow aquifers in floodplain areas (Baillieux et al., 2014; Sánchez-Pérez et al., 2003).

Floodplain environments are characterised by strong surface water-groundwater interactions that are important for aquifer water composition (Amoros et al., 2002; Sun et al., 2015). Nitrate contamination in shallow aquifers can therefore be mitigated by the dilution resulting from mixing with river water containing low nitrate concentrations (Pinay et al., 1998; Baillieux et al., 2014). Nitrate mass removal also occurs through natural biogeochemical processes such as plant uptake, denitrification, dissimilatory nitrate reduction to ammonium and microbial immobilisation,

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http://dx.doi.org/10.1016/j.ecoleng.2015.12.031

Please cite this article in press as: Bernard-Jannin, L., et al., Spatio-temporal analysis of factors controlling nitrate dynamics and potential denitrification hot spots and hot moments in groundwater of an alluvial floodplain. Ecol. Eng. (2015), http://dx.doi.org/10.1016/j.ecoleng.2015.12.031

among which denitrification is reported to be the most important in groundwater (Korom, 1992; Burt et al., 1999; Rivett et al., 2008).

Denitrification is the anaerobic reduction of nitrate (NO_3^-) into gaseous compounds (nitrous oxide or dinitrogen) by microorganisms. Denitrification in groundwater is linked to: (i) presence of nitrate, denitrifying bacteria and organic carbon (OC) as electron donor, (ii) anaerobic conditions and (iii) favourable environmental conditions in terms of *e.g.* temperature and pH (Rivett et al., 2008). However, among all these factors, availability of OC has been identified as the major limiting factor in nitrate-contaminated groundwater (see Rivett et al. (2008) for a review).

Riparian zones are located at the interface between aquatic and terrestrial environments (Vidon et al., 2010). In these areas, where surface water rich in organic matter (OM) meets groundwater containing abundant nutrients, denitrification is promoted (Hill et al., 2000; Sánchez-Pérez et al., 2003). Therefore riparian areas have been shown to be efficient in nitrate pollution mitigation (Vidon and Hill, 2006; Dosskey et al., 2010; Naiman et al., 2010). In these systems, the hydrological exchanges at the river/groundwater interface can have a significant impact on denitrification rates in the aquifer (Baker and Vervier, 2004; Lamontagne et al., 2005). Such exchanges recharge aquifer with river water rich in OM, stimulating denitrification in groundwater (Iribar, 2007; Sánchez-Pérez et al., 2003). The location of the denitrification process is driven by advective flux, where flow paths lead organic matter and nitrate to meet (Seitzinger et al., 2006), at points defined as hot spots by McClain et al. (2003). At the scale of the floodplain section, denitrification is usually triggered by NO_3^- input from upland areas and hot spots can be located at the interface between the upland and riparian zones, between the riparian zone and the stream or within the riparian zone (McClain et al., 2003). At this scale, the efficiency of the riparian area in nitrate removal is reported to be related to hydrogeomorphic characteristics associated with geological and hydrological settings (Groffman et al., 2009), such as water residence time (Seitzinger et al., 2006). In addition, the occurrence of hot spots may vary in time, especially in environments with strong temporal variations in hydrological conditions. For example, denitrification rates have been found to be higher in high flow conditions (Baker and Vervier, 2004; Iribar, 2007; Peter et al., 2011), within periods corresponding to hot moments (McClain et al., 2003). Therefore, studies on denitrification processes need to take into account both spatial and temporal scale with suitable resolution in order to accurately describe the processes at stake and their impact on nitrate dynamics.

The main objective of this study was to examine the occurrence of potential denitrification hot spots and hot moments and their relationship to environmental conditions, in order to improve knowledge on nitrate dynamics in floodplains. Based on a high spatial resolution dataset collected during 12 monthly sampling campaigns, we sought to: (i) identify the factors best explaining nitrate concentrations variations and explored their spatio-temporal patterns; (ii) identify the factors best explaining potential denitrification rates measured in aquifer sediment samples; and (iii) analyse the occurrence of denitrification hot spots/hot moments according to the controlling factors in order to develop a conceptual diagram of denitrification process in floodplain environments.

2. Materials and methods

2.1. Study site

The study area, which covers about 50 ha, is located within a 2 km long meander in the middle section of the Garonne river watershed, close to the village of Monbéqui in south-west France (Fig. 1). Mean annual precipitation in the area is 660 mm. The drainage area of the Garonne watershed at the study site is about 13,730 km^2, with annual average flow of 190 m^3 s^{-1} and a range from 98 m^3 s^{-1} (1989) to 315 m^3 s^{-1} (1978) over the past 41 years. The driest month is August, with 76 m^3 s^{-1} on average, and the wettest is May, with 343 m^3 s^{-1} on average. The daily flow is highly variable, ranging from 10 m^3 s^{-1} during the severe drought in August 1991 to 2930 m^3 s^{-1} during the largest flood event recorded, on 6 November 2000 (www.hydro.eaufrance.fr). The two-year return period flood corresponds to daily flow of 1400 m^3 s^{-1}. The floodplain comprises 4–7 m of quaternary sand and gravel deposits (mean saturated hydraulic conductivity 10^{-3} m s^{-1}), overlying impermeable molassic bedrock. In this area the Garonne River fully penetrates the alluvial formation, so that the riverbed lies on the impermeable substratum. The alluvial deposits are covered with a silty soil layer 1–2 m deep and containing 1.5% OM on average (Jégo et al., 2012). The connection between aquifer and the Garonne river is strongly influenced by hydrological conditions (Sun et al., 2015). The floodplain is heavily cultivated (irrigated maize, sunflower, sorghum, wheat), leading to major nitrate influx into the groundwater. Concentrations of 100 mg-NO_3^- L^{-1} are common (Sánchez-Pérez et al., 2003). A small area of riparian forest, mainly composed of willow (*Salix alba*) and ash trees (*Fraxinus excelsior*), is located close to the river at a lower elevation than the rest of the study area, and is separated from the agricultural fields by plantations of poplar (*Populus alba*) (Fig. 1). The geomorphology of the river bank on the right side of the river can be separated into two types: Low bankfull height type (LBH) corresponding to the profile A–A′ (Fig. 1), which is regularly flooded as the groundwater level is often close to the surface and can be designated as permanent wetland; and high bankfull height type (HBF), corresponding to the profile B–B′, which is only flooded during the highest floods (greater than two-year return period flood events). Three piezometers (P6, P9 and P13) are located within a LBH area.

Previous studies carried out on this area have demonstrated the role of DOC borne by the river into the aquifer in denitrification (Sánchez-Pérez et al., 2003) and the importance of the sediment-attached bacterial community for aquifer denitrification (Iribar et al., 2008). In addition, modelling studies have shown the importance of river-aquifer exchanges for groundwater composition (Weng et al., 2003; Peyrard et al., 2008; Sun et al., 2015) and the impact of agricultural practices on nitrate leaching into the shallow aquifer (Jégo et al., 2012).

2.2. Sampling

A network of 22 piezometers (internal diameter 51 mm, with 1 mm slots) was installed throughout the study site between the Garonne river and the agricultural fields (Fig. 1). Water samples were collected within each piezometer during monthly sampling campaigns from April 2013 to March 2014, providing a high-spatial resolution dataset with around 50–100 m between sampling points. In four of these campaigns, called full campaigns, additional sediment sampling was performed (Fig. 2).

After measuring water table depth (WD), as the distance between soil surface and water table surface, water was pumped with a thermal motor pump and physico-chemical parameters in water were measured once electrical conductivity (EC) had stabilised (Sánchez-Pérez et al., 1991a, 1991b). Dissolved oxygen (DO), temperature (T), pH and EC were measured using a portable metre (WTW Multi 3420) and specific probes. Water samples were then filtered through 0.45 μm cellulose acetate membrane filters. Anion concentrations, *i.e.* nitrate (NO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}), and cation concentrations, *i.e.* calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+)

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