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Effective removal of bromate in nitrate-reducing anoxic zones during managed aquifer recharge for drinking water treatment: Laboratory-scale simulations

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ABSTRACT

The removal of bromate (BrO_3^-) as a by-product of ozonation in subsequent managed aquifer recharge (MAR) systems, specifically in anoxic nitrate (NO_3^-)-reducing zones, has so far gained little attention. In this study, batch reactors and columns were used to explore the influence of NO_3^- and increased assimilable organic carbon (AOC) due to ozonation pre-treatment on BrO_3^- removal in MAR systems. 8 m column experiments were carried out for 10 months to investigate BrO_3^- behavior in anoxic NO_3^--reducing zones of MAR systems. Anoxic batch experiments showed that an increase of AOC promoted microbial activity and corresponding BrO_3^- removal. A drastic increase of BrO_3^- biodegradation was observed in the sudden absence of NO_3^- in both batch reactors and columns, indicating that BrO_3^- and NO_3^- competed for biodegradation by denitrifying bacteria and NO_3^- was preferred as an electron acceptor under the simultaneous presence of NO_3^- and BrO_3^-. However, within 75 days' absence of NO_3^- in the anoxic column, BrO_3^- removal gradually decreased, indicating that the presence of NO_3^- is a precondition for denitrifying bacteria to reduce BrO_3^- in NO_3^--reducing anoxic zones. In the 8 m anoxic column set-up (retention time 6 days), the BrO_3^- removal achieved levels as low as 1.3 μg/L, starting at 60 μg/L (98% removal). Taken together, BrO_3^- removal is likely to occur in vicinity of NO_3^--reducing anoxic zones, so MAR systems following ozonation are potentially effective to remove BrO_3^-.

1. Introduction

Managed aquifer recharge (MAR), such as artificial recharge and dune filtration, is a natural water treatment process that induces surface water to flow through the soil. After soil passage, the water is abstracted by vertical or horizontal wells (Bouwer, 2002; Tufenkji et al., 2002). In some European countries, water utilities use MAR as a robust and cost-effective water treatment process to supply drinking water without needing to use chlorination as a disinfection process because of its pathogen removal ability (Lekkerkerker, 2012; Maeng, 2010; Van der Hoek et al., 2014). Additionally, MAR has proven to be an effective barrier for multiple organic micropollutants (OMPs) present in surface waters during drinking water production due to filtration, sorption, ion-exchange, precipitation and biological degradation (Kim et al., 2015; Laws et al., 2011; Postigo and Barceló, 2015). However, some highly persistent trace organic compounds can still be detected in MAR filtrate (Drewes et al., 2003) and may reach the drinking water supply (Ternes et al., 2002).

Ozonation is a powerful process for the removal of many OMPs, and the combination of MAR with ozonation as a pre-treatment has been suggested as a comprehensive treatment system to effectively remove various OMPs during drinking water production (Lekkerkerker-Teunissen et al., 2012; Lekkerkerker et al., 2009; Oller et al., 2011). However, bromate (BrO_3^-), a genotoxic

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carcinogen (Ahmad et al., 2013), may be formed when ozonation is applied in the treatment of bromide-containing water (Assuncao et al., 2011; Haag and Holgne, 1983; Kurokawa et al., 1990). WHO, USEPA, and the European Union have set drinking water regulations for the maximum allowable concentration of BrO_3^- at 10 μg/L (Carney, 1991; EU, 1998; Forum, 2005; WHO, 2011).

BrO_3^- cannot be easily eliminated using conventional treatment technologies due to its high solubility and stability in water (Butler et al., 2005) and its weak sorption characteristics to common soil and sediment components. Several studies involving different chemical, physical and biological techniques have been conducted (Bhatnagar and Sillanpää, 2012; Hijnen et al., 1999; Jia et al., 2015; Wang et al., 2009; Xu et al., 2015a; Zhang et al., 2015). Microbial BrO_3^- reduction may be an effective treatment strategy because microbiological reduction of BrO_3^- has been observed in anaerobic activated sludge columns, biologically active carbon filters and denitrifying bioreactors (Hijnen et al., 1999; Kirisits et al., 2001; Van Ginkel et al., 2005). The study of Van Ginkel et al. (2005) showed that BrO_3^- reduction was detected only in the absence of O_2 in a microbial culture from activated sludge. However, some other studies found that BrO_3^- reduction could also take place in the presence of O_2. For example, a biological activated carbon (BAC) filter almost completely reduced 60 μg/L BrO_3^- to Br^- at both 2 and 8 mg/L influent dissolved oxygen (DO) concentrations (Liu et al., 2012). Therefore, redox condition may be one of the important factors impacting BrO_3^- removal in MAR systems. Hijnen et al. (1995) isolated denitrifying organisms that were able to reduce BrO_3^- with ethanol as the electron donor and carbon source. Hijnen et al. (1999) showed that BrO_3^- was removed in a denitrifying bioreactor fed with methanol. However, they demonstrated that BrO_3^- removal in a denitrifying bioreactor did not seem to be a realistic option in drinking water treatment due to the long contact times required for BrO_3^- removal and extensive post treatment necessary to remove excessive methanol and released biomass. The anoxic zone within MAR systems might be effective in reducing BrO_3^-, as retention times in the subsurface are days to months. However, there has been only one study (Hübner et al., 2012) concerning the removal of BrO_3^- in MAR systems since Hijnen et al. (1999) and Kruithof and Meijers (1995) mentioned that soil passage under anoxic conditions, such as artificial recharge and river bank filtration, may enable BrO_3^- removal from ozonated water. Only recently, Hübner et al. (2016) studied BrO_3^- removal in 1 m sand columns, with a focus on treatment of secondary effluent (wastewater) instead of drinking water treatment. They observed that BrO_3^- was effectively reduced under anoxic conditions instead of oxic conditions and that NO_3^- and BrO_3^- were consumed as electron acceptors simultaneously in small-scale columns. However, because microbial biodegradation in secondary effluent differs given high dissolved organic carbon (DOC) and NO_3^- concentrations, these findings cannot be directly translated to surface water infiltration sites for drinking water production. Water composition (e.g. NO_3^-, SO_4^{2-}, ClO_3^- and ClO_4^-) is known to affect BrO_3^- reduction in reactors (Demirel et al., 2014; Fan et al., 2006; Kirisits et al., 2001; Xu et al., 2015b), so it is likely to affect biological BrO_3^- reduction during MAR as well.

Several microbial BrO_3^- conversion pathways have been described in literature. BrO_3^- was reduced to bromide by denitrifying and ClO_3^--reducing enrichments, possibly via co-metabolic action of NO_3^- reductase and ClO_3^- reductase enzymes (Downing and Nerenberg, 2007). Other studies suggested the existence of a specific BrO_3^- reduction pathway (Davidson et al., 2011). Additionally, the aerobically expressed selenate reductase of *Enterobacter cloacae* is capable of low rates of BrO_3^- reduction (Ridley et al., 2006), indicating that oxic bacteria might also be capable of BrO_3^- reduction. Therefore, although different BrO_3^- removal pathways have been identified, it is unknown whether these pathways exist during MAR soil passage.

The objectives of this study were to explore the BrO_3^- removal in NO_3^--reducing anoxic zones of MAR systems and the potential mechanisms behind this removal. Specifically, the influence of (a) increased assimilable organic carbon (AOC) concentrations (due to ozonation pre-treatment) and (b) NO_3^- long-term presence, sudden absence and long-term absence and (c) BrO_3^- removal performance with infiltration retention time in 8 m anoxic zones were investigated in order to evaluate the feasibility of BrO_3^- removal by MAR systems.

2. Materials and methods

2.1. Water and sand

The water used in this study was collected every two weeks from the MAR site of Dunea, a drinking water company in the Netherlands. The composition of MAR influent water is shown in Table S1 in the supplemental information. The sand used in batch reactors and column reactors was collected from a 1 m depth from the MAR site of Dunea. Chemicals $NaBrO_3$, $NaNO_3$, CH_3COONa, K_2SO_4 and Purolite A520E resin were purchased from Sigma (St Louis, MO, United States). All chemicals were of AR grade. All solutions used in this study were prepared using water from a Millipore Milli-Q system.

2.2. Batch experiments

To investigate the role of increased AOC from ozonation as a pretreatment for MAR and the influence of NO_3^- on BrO_3^- removal, batch experiments using 15 glass bottles with a volume of 500 mL were performed for approximately 3 months under anoxic conditions. The batch reactors were filled with 100 g sand and 400 mL MAR water. This ratio of MAR water and sand was chosen from previous literature that also focused on MAR studies (Wang et al., 2016). Anoxic conditions were provided by stripping the water with nitrogen gas for 15 min then sealing the bottles with rubber stoppers and plastic caps. All batch reactors were placed in a dark room with temperature control (11.5 ± 0.5 °C). A 60 day acclimation period was necessary to stabilize the batch reactors with respect to DOC removal (fill-and-draw mode during the acclimation period, hydraulic retention time (HRT) 7 d). Next, the 15 bottles were divided into 5 groups with different DOC concentrations and different NO_3^- concentrations as shown in Fig. 1a. Three batch reactors as reference (group 1) to distinguish BrO_3^- adsorption from biological BrO_3^- removal in group 2 were autoclaved at 121 °C for 40 min to inactivate bacteria. Ozonation can oxidize a part of DOC into biodegradable DOC, so 1 mg/L of additional C-CH_3COONa was dosed in group 3 to investigate the effect of ozonation pretreatment on BrO_3^- removal. The aim of groups 4 and 5 was to assess the effect of the sudden absence of NO_3^- on BrO_3^- removal. The microbial community may change in the absence of NO_3^- after a certain time. To achieve BrO_3^- removal as early as possible before microbial community change, 4 mg/L C-CH_3COONa was dosed into groups 4 and 5 to promote microbial activity. Also for groups 4 and 5, the concentration of NO_3^- initially present in the MAR water was measured daily until it fell below the detection limit, 0.89 mg/L. Then, 10 mg/L NO_3^- was dosed to group 4 and not to group 5.60 μg/L BrO_3^- was dosed to all batch reactors after the acclimation period and the above described different treatments. BrO_3^-, NO_3^-, sulfate (SO_4^{2-}), adenosine triphosphate (ATP) and DOC samples were collected from groups 1–3 at day 7 and day 21. For groups 4 and 5, samples were collected after 2.7 h because of the high microbial