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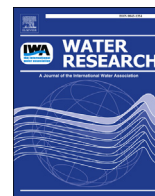To cite this publication, please use the final published version (if applicable).
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Effective removal of bromate in nitrate-reducing anoxic zones during managed aquifer recharge for drinking water treatment: Laboratory-scale simulations

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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^-.

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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 micro-pollutants (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

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
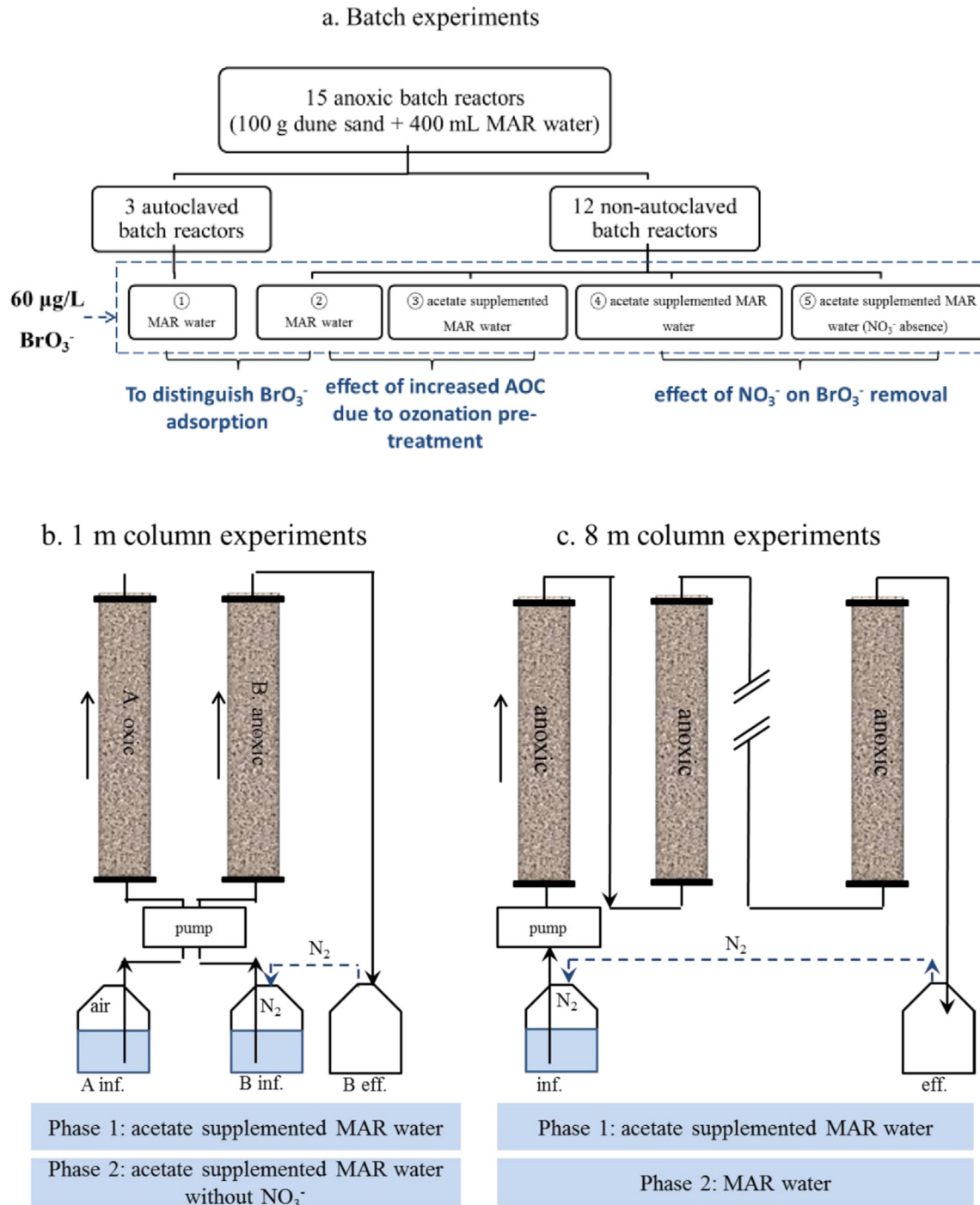
Fig. 1. Batch and column experimental designs.

activity in these groups caused by the 4 mg/L C-CH$_3$COONa dose.

2.3. Column experiments

All columns (L = 1 m, D = 36 mm) shown in Fig. 1b and c were constructed from PVC (L = 1 m, D = 36 mm). A peristaltic multi-channel pump (205 S, Watson Marlow, The Netherlands) using Marprene® pump tubes (d = 0.63 mm, Watson Marlow, The Netherlands) was connected to the columns by dark polyamide tubing (d = 2.9 mm, Festo, The Netherlands) to feed both columns. The columns were operated in continuous up-flow mode at

11.5 ± 0.5 °C, corresponding to the natural aquifer temperature, in a dark room to prevent algal growth.

To avoid the leaching of soil/sand grains, both the top and bottom of the column were fitted with perforated PVC plates (30 holes, d = 0.8 mm) that were covered with filter cloth (45 μm, Top7even net & mesh, The Netherlands). The oxic column was fed from a 10 L open glass bottle with Dunea MAR influent water, and the anoxic columns were fed from 10 L sealed glass bottles with N$_2$ flushing as pre-treatment. Feed bottles were washed twice with acetone and flushed several times with demineralized water before refilling to avoid biofilm formation.

Before starting the BrO_3^- experiment, these columns had been acclimated for 3 months until steady state conditions were reached with respect to DOC removal and NO_3^- removal.

2.3.1. 1 m oxic and anoxic sand columns

To investigate BrO_3^- biodegradation performance in oxic zones and anoxic NO_3^- reducing zones of MAR systems and to study the influence of NO_3^- on BrO_3^- removal, column experiments using a 1 m oxic sand column simulating oxic zones and a 1 m anoxic sand column simulating anoxic zones of MAR systems were carried out in the presence and absence of NO_3^-. The hydraulic retention time was 22 h for both columns, corresponding to a filtration velocity of 1 m/day.

The experiment lasted 13 months in total: a 3 months acclimation period followed by a 10 month period divided into two phases. In the first phase, NO_3^- was present in the influent water, while in the second phase, NO_3^- was absent. During the 13 months experiment, 150 μg/L C-CH_3COONa was dosed to the influent water of both oxic and anoxic columns to simulate the increased AOC from ozonation since, in practice, the ozonation pre-treatment before MAR increases the AOC (Hammes et al., 2006; Orlandini et al., 1997; Sarathy et al., 2011; Van Der Hoek et al., 1998) and as reported by Hammes et al. (2006) 60—90% of the AOC consists of organic acid carbon. BrO_3^- formation at concentrations ranging from <2 to 293 μg/L has been reported during ozonation of natural waters under normal drinking water treatment conditions (Amy et al., 2000; Glaze et al., 1993; Krasner et al., 1993; Van Der Hoek et al., 1998), but in 100 investigated drinking water utilities BrO_3^- concentration was within the range of <2—60 μg/L after ozonation of water containing 2—429 μg/L Br^- (Butler et al., 2005; Kirisits and Snoeyink, 1999). For this study it was decided to investigate the upper value of this range, so 60 μg/L BrO_3^- was dosed to the influent of the oxic column and anoxic columns. A summary of BrO_3^- and AOC formed during ozonation based on existing literature (Agbaba et al., 2016; Escobar and Randall, 2001; Huang and Chen, 2004; Orlandini et al., 1997; Van Der Hoek et al., 1998) is presented in Table S2. The influent water of these columns was NO_3^- containing MAR water in phase 1, while in phase 2 the influent was NO_3^- free MAR water. NO_3^- free water was produced by using a strong base anion exchange resin Purolite A520E (ratio of water and resin: 2 L/20 g) to remove NO_3^- to below the detection limit (0.89 mg/L). The water was in contact with the resin were for a period of 12 h. The ion exchange resin, used to remove NO_3^- from the MAR water, was pre-treated as follows. Firstly, A520E resin was soaked in both 1 M NaOH solution followed by 1 M HCl solution or one day each to remove impurities. Afterwards, the resin was washed several times using demineralized water until pH 7 was reached. Finally, the clean resin was dried in an oven at 80 °C for 24 h and kept in a desiccator until use. Since Purolite A520E resin removes not only NO_3^- but also a portion of SO_4^{2-}, 50 mg/L SO_4^{2-} was dosed back to the influent water in phase 2. Influent water samples and corresponding effluent water samples were collected every 1—2 weeks during each phase to measure BrO_3^-, NO_3^- and SO_4^{2-} concentrations. DO concentrations in the influent and effluent of oxic and anoxic columns were measured to confirm oxic and anoxic conditions.

2.3.2. 8 m anoxic columns

A long anoxic column set-up consisting of eight 1 m columns in series was used for 10 months to better simulate anoxic zones of MAR systems since the retention time, 6 days, was much longer than the above 1 m anoxic column in Section 2.3.1. The objective of the long anoxic column was to further investigate BrO_3^- biodegradation with respect to retention time in anoxic NO_3^--reducing zones and to further assess the role of AOC formation, as a result of ozonation pre-treatment, on BrO_3^- biodegradation.

The whole experiment consisted of a 4 months acclimation period followed by two phases with and without an extra 150 μg/L C-CH3COONa in the influent water. Each phase was carried out for 3—4 months to establish a stable BrO_3^- removal. Water samples were collected 4—7 times at depth 0 m, 1 m, 3 m and 8 m, that is retention time 0, 0.75, 2.25 and 6 days, during each phase to measure BrO_3^-, NO_3^- and SO_4^{2-} concentrations. DO concentrations in the influent and effluent were measured to confirm anoxic conditions.

2.4. Sample analysis

Dissolved oxygen (DO), temperature and pH were measured with a multimeter (SenTix® 940 IDS probe, Multi 340i, WTW, Germany) directly in the feed bottle or in a flow through cell connected to the influent or effluent tubes of the columns.

BrO_3^-, NO_3^- and SO_4^{2-} samples were analysed by ion chromatography at Het Waterlaboratorium (Haarlem, The Netherlands). Following ion chromatography, BrO_3^- was also analysed by conductivity detection. 30 mL samples were pre-treated by filtration on barium and silver loaded on guard columns to remove sulfate and chloride respectively, followed by a H^+ column for the removal of Ag^+ ions leaching from the Ag^+ column. 2000 μl of the sample was subsequently concentrated on a positively charged anion exchange column (Dionex IonPac AG9SC). The anions on the ion exchange column were eluted with 1.5 mL/min of a 0.7 mM $NaHCO_3$ solution and separated on an ion exchange analytical column (Dionex IonPac AS9SC). Detection was performed by using suppressed conductivity. The measured BrO_3^- concentration was confirmed using a two point calibrated UV absorption measurement at a wavelength of 200 nm. The BrO_3^- detection limit was 0.5 μg/L. NO_3^- and SO_4^{2-} were analysed with a ProfIC 15 - AnCat ion chromatograph (Metrohm 881 anion (suppressed) and 883 cation system) (Metrohm, Switzerland) after filtering through 0.45 μm filters (Whatman, Germany). A Supp 150/4.0 anion column was used with 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ eluent for the anions measurement. Regenerant for the suppressor was 50 mM H_2SO_4. Detection limits of NO_3^- and SO_4^{2-} were 0.89 mg/L and 0.5 mg/L, respectively. DOC was measured with a Shimadzu TOC analyser according to the protocols described in Wang et al. (2016).

3. Results

3.1. Batch reactor experiments

3.1.1. Effect of increased AOC due to ozonation as pre-treatment

Fig. 2 presents BrO_3^- concentrations over 7 days (Fig. 2a) and 21 days (Fig. 2b) in anoxic batch reactors with MAR water and acetate supplemented MAR water and autoclaved batch reactors with MAR water. In the reference experiments with autoclaved batch reactors, BrO_3^- degradation over 7 days and 21 days was not observed, indicating BrO_3^- adsorption did not occur. Therefore, the BrO_3^- removal was caused by biodegradation instead of adsorption, which is in agreement with the studies of Xie and Shang (2006) and Weast (1986). Though differences were small, bromate removal was found not to be significant ($p > 0.05$) in MAR water, while removal was observed in acetate supplemented MAR water. Slightly more BrO_3^- was removed in acetate supplemented MAR water after 21 days (9 μg/L, 16.9%) compared to 7 days (2.4 μg/L, 4.2%).

Fig. 3 presents NO_3^- concentrations over 7 days (Fig. 3a) and 21 days (Fig. 3b) in anoxic batch reactors with MAR water (group 2) and acetate supplemented MAR water (group 3). NO_3^- was not significantly biodegraded in MAR water ($p > 0.05$), while NO_3^- was biodegraded in acetate supplemented MAR water over 7 days
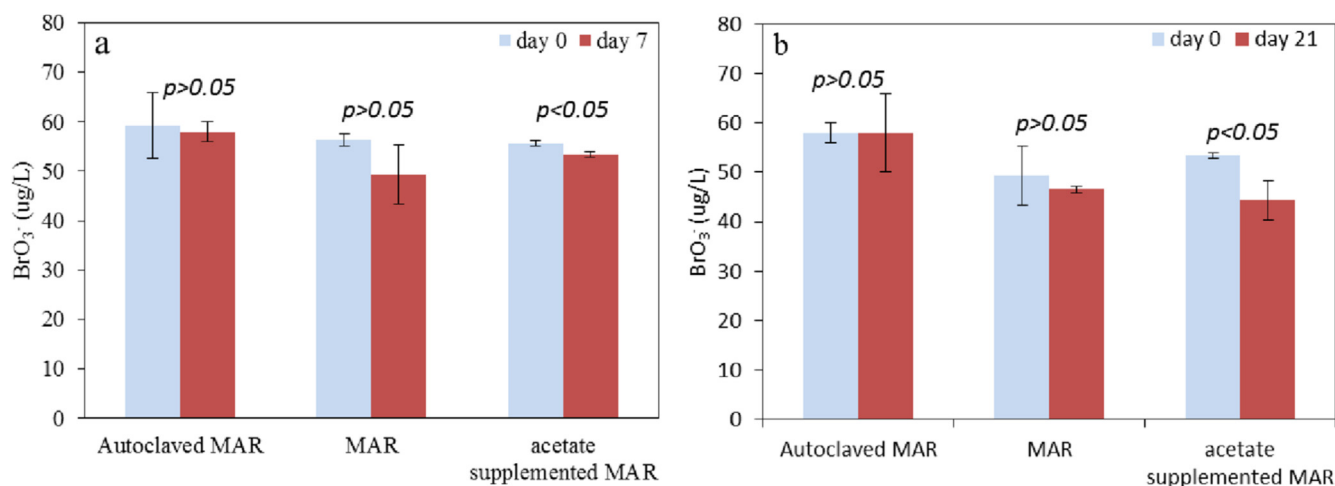
Fig. 2. BrO_3^- removal in autoclaved and non-autoclaved batch reactors with MAR water and acetate supplemented MAR water over 7 days (a) and 21 days (b). An additional 1 mg/L AOC from CH_3COONa solution was added to MAR water to create the acetate supplemented MAR water. All batch reactors were in anoxic conditions at 11.5 ± 0.5 °C (n = 3).
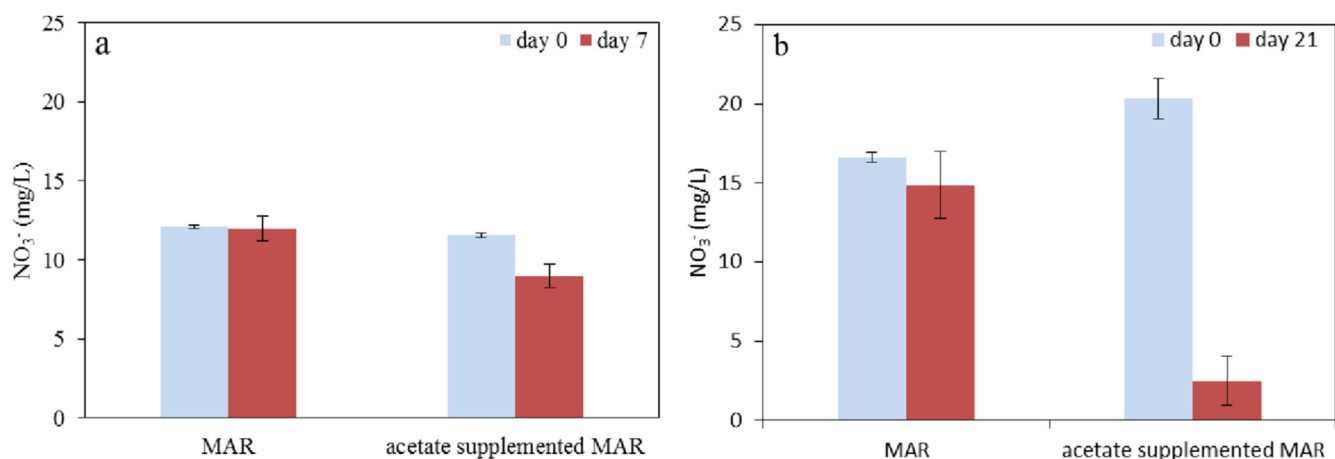

Fig. 3. NO_3^- removal in anoxic batch reactors with MAR water and simulated ozonation-MAR water over 7 days (a) and 21 days (b). An additional 1 mg/L AOC from CH_3COONa solution was added to MAR water to create the acetate supplemented MAR water. T = 11.5 ± 0.5 °C (n = 3).

(2.6 mg/L, 22.7%. $p < 0.05$), and at a greater magnitude after 21 days (17.8 mg/L, 87.8%. $p < 0.05$). These results demonstrate that the retention time as well as the availability of AOC is an important factor influencing BrO_3^- and NO_3^- biodegradation, with NO_3^- degradation occurring faster than BrO_3^- degradation.

3.1.2. Presence of NO_3^-

The influence of NO_3^- on BrO_3^- removal was investigated in anoxic batch reactors containing acetate supplemented MAR water in the presence and sudden absence of NO_3^- (Fig. 4). No BrO_3^- biodegradation ($p > 0.05$) was observed in batch reactors with an initial NO_3^- concentration of 6.1 mg/L, while a clear decrease of NO_3^- ($p < 0.05$) from 6.1 mg/L to 3.8 mg/L was observed after 2.7 h. In case of a sudden absence of NO_3^- in the batch reactors (lower than 0.89 mg/L), BrO_3^- was reduced from 47 µg/L to 35 µg/L in 2.7 h ($p < 0.05$), indicating that NO_3^- and BrO_3^- compete for biodegradation.

3.2. 1 m column experiments

3.2.1. Oxic and anoxic zones

The removal of BrO_3^-, NO_3^- and SO_4^{2-} in 1 m oxic and anoxic

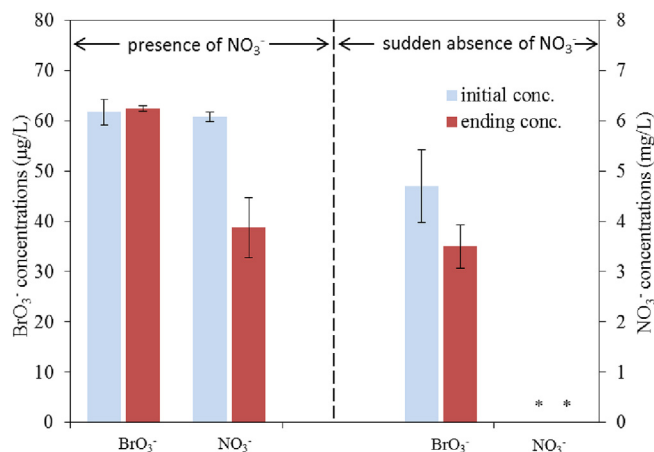**Fig. 4.** BrO_3^- and NO_3^- removal in batch reactors with acetate supplemented MAR water in the presence and sudden absence of NO_3^- within 2.7 h * indicates measurements below the detection limit. T = 11.5 ± 0.5 °C (n = 3).

columns (retention time 22 h) for 98 days are shown in Fig. 5. BrO_3^- removal was slightly higher in the anoxic column (8%) than in the oxic column (5.7%), although the difference was not significant ($p < 0.05$). 10.7% NO_3^- was removed in the anoxic column, indicating anoxic conditions were indeed reached. In the oxic column, NO_3^- was not converted and passed through the column. No significant SO_4^{2-} removal in both oxic and anoxic columns was observed, so neither columns reached SO_4^{2-}-reducing conditions.

3.2.2. Effect of NO_3^-

The 1 m columns were operated in two subsequent phases: during phase 1 (day 0−98), 10.3 ± 1.8 mg/L NO_3^- was present in the influent, whereas during phase 2 (day 98−209), NO_3^- was extracted from the influent until the concentration was lower than 0.89 mg/L. Fig. 6 presents BrO_3^- removal in the oxic and anoxic columns with long-term presence and absence of NO_3^-. During phase 1, the BrO_3^- removal in the oxic column (1.3−11.2%) and anoxic column (3.9−11.7%), with a 22 h retention time, was not highly effective. However, during phase 2, the sudden absence of NO_3^- in the influent water at day 98 resulted in sharp initial increases of BrO_3^- reduction (82.5% in anoxic column and 13.6% in oxic column), after which BrO_3^- removal decreased to 61.4% in the anoxic column and 0.32% in the oxic column in day 98−99.5. After that, the oxic column had a very limited BrO_3^- removal of 0−3.3% lower than that in the presence of NO_3^-, whereas the BrO_3^- removal in the anoxic column gradually decreased and finally returned to a steady 5.5−12.9% during 99.5−209 days.

3.3. 8 m column experiments

3.3.1. Effect of infiltration retention time

In order to investigate the effect of infiltration retention time during MAR, a series of columns (8 m total, 6 days retention time) was operated with MAR influent water for several months. Fig. 7 presents the continuous BrO_3^- removal during the final 2 months for 1, 3 and 8 m infiltration depth. In the first 1 m (corresponding to a retention time of 0.75 day), no clear BrO_3^- and NO_3^- removal was observed. After 3 m infiltration (corresponding to a retention time of 2.25 days), BrO_3^- and NO_3^- remaining concentrations were clearly lower than the influent concentrations with 20.4% BrO_3^- and 15.8% NO_3^- removal. After 8 m of soil passage, 48.2% BrO_3^- and 30.2% NO_3^-
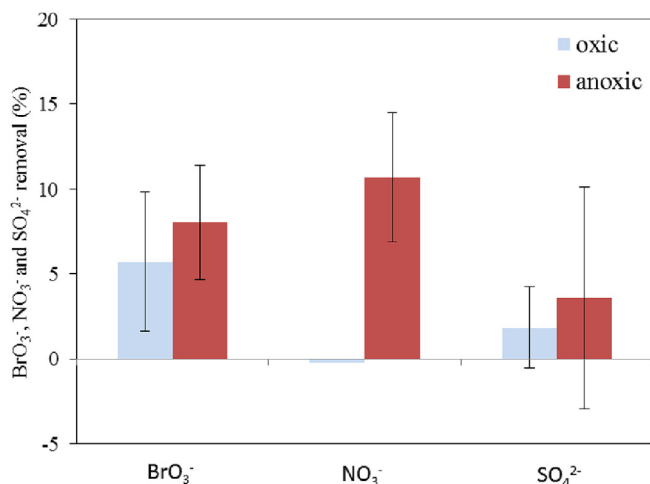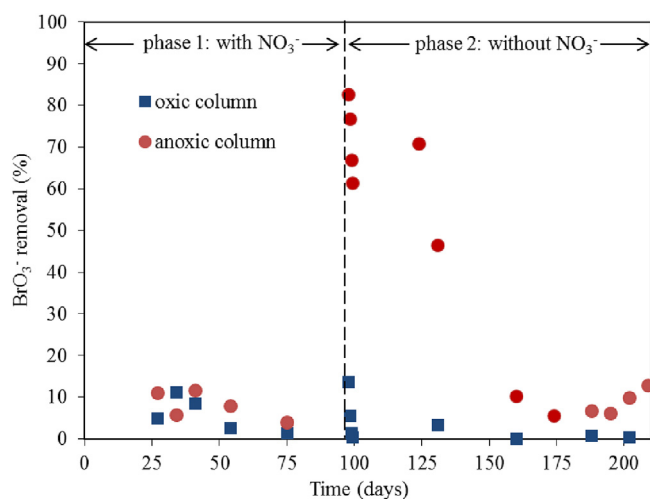

Fig. 6. BrO_3^- removal in the 1 m oxic and anoxic columns containing acetate supplemented MAR water as influent with 10.3 ± 1.8 mg/L NO_3^- (phase 1: 0−98 days) and acetate supplemented MAR water as influent with NO_3^- below than detection limit (0.89 mg/L) (phase 2: 98−209 days). 150 μg/L AOC from a CH_3COONa solution was added to the MAR water to compose acetate supplemented MAR water. The dashed line at day 98 separates phase 1 and phase 2. Influent BrO_3^- was 56.6 ± 6.45 μg/L. Influent DO in the oxic column and anoxic column was 8.52−10.74 mg/L and below 0.6 mg/L respectively. T = 11.5 ± 0.5 °C.
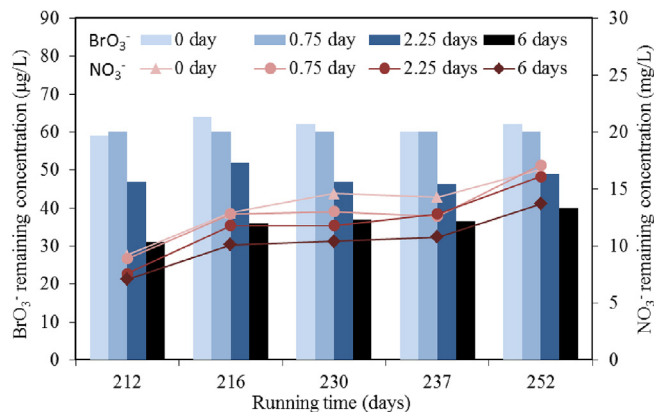

Fig. 7. BrO_3^- removal and normalized concentrations of BrO_3^- and NO_3^- in the 8 m anoxic column set-up containing MAR water as the influent. BrO_3^- and NO_3^- in the influent were 63 ± 4 μg/L and 13 ± 3.8 mg/L respectively. Influent DO was below 0.6 mg/L. T = 11.5 ± 0.5 °C.

were removed and the. Final BrO_3^- concentration reached with a retention time of 6 days was 29.6 μg/L.

3.3.2. Effect of increased AOC due to ozonation pre-treatment

Fig. 8 presents concentrations of BrO_3^-, NO_3^- and SO_4^{2-} along the column height of the 8 m anoxic columns in series containing acetate supplemented MAR water (phase 1, Fig. 8a) and MAR water (phase 2, Fig. 8b), respectively. Fig. 8a shows that BrO_3^- was removed by 8%, 59% and 98%, at a depth of 1 m, 3 m and 8 m, respectively. NO_3^- was removed by 8%, 51% and 80% at a depth of 1 m, 3 m and 8 m, respectively. Consequently, at the end of the 8 m column, corresponding to an infiltration retention time of 6 days, the BrO_3^- concentration was as low as 1.3 μg/L and the NO_3^- concentration was 1.1 mg/L. No SO_4^{2-} removal was observed in this column set-up with and without the increased AOC concentration as a result of ozonation pre-treatment, indicating no SO_4^{2-}-reducing conditions were reached. Comparison of the NO_3^- and

Fig. 5. BrO_3^-, NO_3^- and SO_4^{2-} removal in oxic and anoxic columns with acetate supplemented MAR water as the influent. 150 μg/L AOC from CH_3COONa solution was added to MAR water to compose the acetate supplemented MAR water. The concentrations of BrO_3^-, NO_3^- and SO_4^{2-} were 58.9 ± 3.1 μg/L, 10.3 ± 1.8 mg/L and 51.9 ± 10.1 mg/L respectively. T = 11.5 ± 0.5 °C. n = 5.
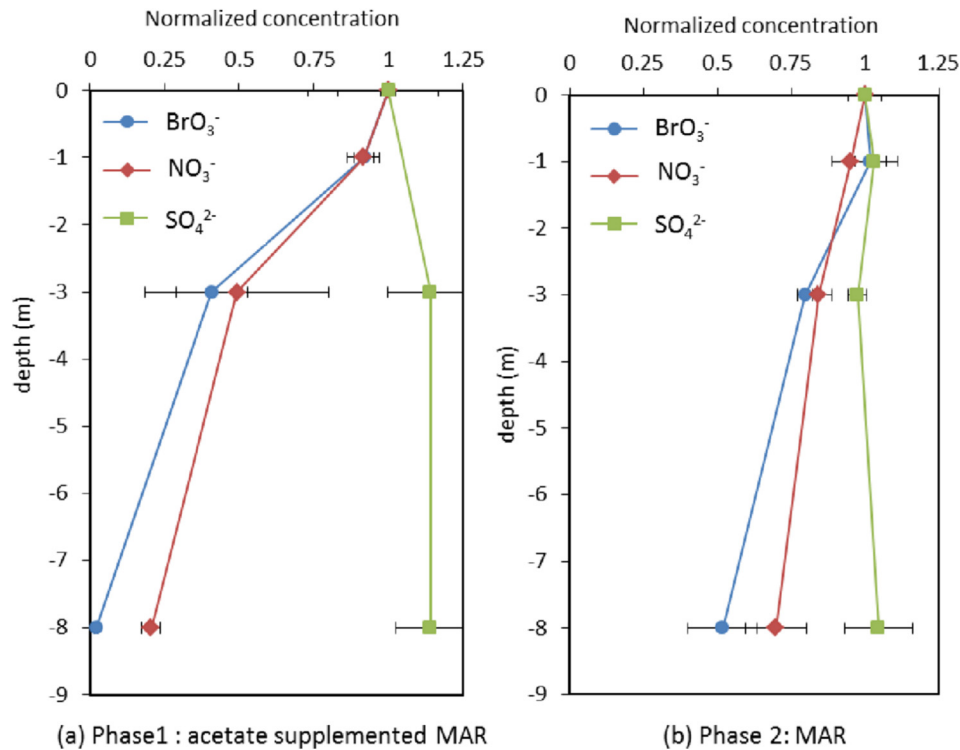
Fig. 8. Average concentrations (n = 5–8) of BrO_3^-, NO_3^- and SO_4^{2-} with depth in the 8 m anoxic column during phase 1 with acetate supplemented MAR water (a) and during phase 2 with only MAR water (b). 150 µg/L AOC from CH_3COONa solution was added to MAR water to compose the acetate supplemented MAR water. BrO_3^-, NO_3^- and SO_4^{2-} concentrations in the influent water were 61.83 ± 5.18 µg/L, 10.7 ± 6 mg/L and 52.5 ± 8.5 mg/L. Mostly, influent DO was below 0.6 mg/L. T = 11.5 ± 0.5 °C.

BrO_3^- removal efficiencies of the two phases consistently shows better BrO_3^- and NO_3^- removal over the height of the column, indicating that the addition of 150 µg/L C-CH3COONa resulted in substantially higher BrO_3^- and NO_3^- removals.

4. Discussion

4.1. Role of NO_3^- in BrO_3^- removal

As stated in the introduction, it has been reported by other authors that biological BrO_3^- reduction is a side reaction of the NO_3^- reduction pathway (Butler et al., 2005; Korom, 1992), and BrO_3^- can be biodegraded by several other anoxic bacteria instead of denitrifying bacteria (Davidson et al., 2011). Both anoxic batch reactors and 1 m anoxic column experiments showed that BrO_3^- removal in the presence of NO_3^- was low and NO_3^- biodegradation was higher, indicating that BrO_3^- biodegradation can occur in the presence of NO_3^-. BrO_3^- removal suddenly increased due to the sudden absence of NO_3^-, indicating that BrO_3^- and NO_3^- in MAR systems may compete for biodegradation by denitrifying bacteria, and denitrifying bacteria prefer NO_3^- over BrO_3^- although the biodegradation of NO_3^- and BrO_3^- occur simultaneously in anoxic NO_3^--reducing zones. In Fig. 8, the BrO_3^- biodegradation rate may initially appear higher than NO_3^- biodegradation rate in 1–8 m, but actually the mass of NO_3^- reduction (phase 1: 2.02 mg/L/m in 1–8 m, phase 2: 0.63 mg/L/m in 1–8 m) was much higher than the mass of BrO_3^- biodegradation (phase 1: 20.59 µg/L/m, phase 2: 10.27 µg/L/m in 1–8 m).

Some studies demonstrated the potential role of NO_3^- reductase in BrO_3^- reduction (Davidson et al., 2011; Hijnen et al., 1995). It can be observed from Fig. 8 that both NO_3^- and BrO_3^- biodegradation rates in the first 1 m column passage were lower than from 1 to 3 m. One potential explanation for this result is that even if the anoxic

condition were achieved in the first 1 m, DO became lower with increasing retention time and resulted in more active NO_3^- reductase (Bell et al., 1990; Cavigelli and Robertson, 2000), and correspondingly more NO_3^- and BrO_3^- biodegradation. NO_3^- and BrO_3^- biodegradation rates reduced in 3–8 m soil passage than higher up in the column, which can be potentially explained by AOC becoming insufficient as retention time increased and therefore lowered the level of microbial activity.

In the 1 m anoxic column, a rapid decrease of BrO_3^- removal was observed in 1.5 days (running time 98–99.5 days) following an increase due to the sudden absence of NO_3^-. Subsequently, a gradual decrease of BrO_3^- biodegradation within 2.5 months (phase 2 in Fig. 6) was observed. This study is the first documentation of BrO_3^- removal in the long-term absence of NO_3^-. Korner and Zumft (1989) concluded that the presence of nitrogen oxides was a prerequisite to promote the synthesis and the activity of denitrification enzymes. Several other studies (Cove, 1966; Saleh-Lakha et al., 2009; Sun et al., 2016) reported that NO_3^- absence or limited NO_3^- leads to a decrease of denitrification functional genes, and NO_3^- reductase activity decay or denitrification rate decrease in several hours in pure microbial species and mixed microbial strains. Therefore, the rapid decrease of BrO_3^- removal in the 8 m column from 82.5% to 61.4% in 1.5 days (running time 98–99.5 days) can potentially be explained by the limitation of NO_3^- reductase activity of denitrifying bacteria by a NO_3^- concentration below detection limit (0.89 mg/L). The gradual decrease of BrO_3^- biodegradation fits the first-order kinetic model with the first-order decay constant 0.034/day (Fig. S1 in the supplemental information). The decay of heterotrophic bacteria due to a lack of substrate is a relatively slow process, particularly under anoxic conditions. Lin (2008) showed that when NO_3^- or glucose were limited in a moving-fixed bed biofilm reactor, denitrifying bacterial biomass decayed from 100% to 51.5% in 11 days with a first-order kinetic coefficient of 0.061/day. Although the

decay rate of denitrifying bacteria reported in the previous study (Lin, 2008) is faster (double) than the observed BrO$_3^-$ removal decrease, given that these experiments were performed under different conditions (including higher temperatures; 20—25 °C vs 11 °C), the results of Lin (2008) indicate the hypothesized relationship between denitrifying bacteria biomass and BrO$_3^-$ removal.

4.2. Ozonation as MAR pre-treatment

Figs. 2, 3 and 7 show that in both the batch experiments and the 8 m column experiment, the addition of extra C-CH$_3$COONa, simulating formation of AOC during ozonation pre-treatment, resulted in slight but significantly higher NO$_3^-$ and BrO$_3^-$ reductions. This observation is similar to the results of Kirisits et al. (2001) who showed that the increase of DOC as an external electron donor resulted in the increase of BrO$_3^-$ reduction in a BAC filter. The addition of extra carbon stimulated microbial growth, which was monitored with ATP measurements. Biomass in the batch reactors with 1 mg/L C-CH$_3$COONa addition was approximately two times as high as in the reference reactors (3.3 ng/mL and 1.5 ng/mL respectively; Fig. S2). This result suggests that an increase of AOC as a result of the ozonation pre-treatment can promote microbial activity and therefore BrO$_3^-$ removal in subsequent MAR systems.

Inevitably, the ozonation pre-treatment not only affects the AOC concentration but also causes high concentrations of dissolved oxygen (DO) in the MAR influent water. In the column studies, BrO$_3^-$ reduction was much higher in the anoxic column than in the oxic column, indicating that biological reduction of BrO$_3^-$ predominantly occurs in anoxic zones instead of oxic zones in MAR systems. This result is in agreement with previous studies (Hübner et al., 2016; Kirisits et al., 2001; Liu et al., 2012). Hijnen et al. (1995) found that BrO$_3^-$ reduction was inhibited by oxygen. Controlled column studies simulating MAR revealed inefficient BrO$_3^-$ removal under oxic conditions in the study of Hübner et al. (2012). This observation can be potentially explained by DO being preferred over BrO$_3^-$ (and NO$_3^-$) as a competing electron acceptor. It is therefore recommended to design ozonation-MAR systems in such a way that anoxic zones develop, which can generally be achieved by extending the subsurface retention time. Depending on site-specific water quality and hydrogeological conditions, oxic zones are usually found in the first several meters with a retention time of a couple of hours to days (Bertelkamp et al., 2016). Therefore, the ozonation effluent with high oxygen concentrations is not likely to limit biological BrO$_3^-$ reduction in most MAR systems.

4.3. Redox conditions in MAR

Fig. S3 in the supplemental information shows redox conditions in MAR systems and the theoretical sequence of terminal electron acceptor processes. The initial infiltration phase in MAR systems are usually oxic, followed first by NO$_3^-$-reducing and then Fe/Mn-reducing zones (Bertelkamp et al., 2016; Lekkerkerker-Teunissen et al., 2012; Maeng et al., 2010; Schmidt et al., 2011). This study only focused on BrO$_3^-$ removal in oxic and NO$_3^-$-reducing anoxic zones.

In the oxic column, the observed slight BrO$_3^-$ reduction (Fig. 6) is an indication that minor BrO$_3^-$ reduction by oxic bacteria in MAR systems can also take place. Based on the absence of NO$_3^-$ removal in the oxic column, it can be concluded that no denitrifying bacteria or anoxic microniches were present in this column. Therefore, BrO$_3^-$ reduction by denitrifying bacteria in this oxic column can be excluded.

In the current study, the retention time in the 8 m anoxic column was 6 days. 60 μg/L BrO$_3^-$ was biodegraded to 1.3 μg/L and 29.6 μg/L in this long anoxic column set-up with and without

increased AOC, respectively. In practice, travel times (weeks, months or even years) for MAR systems are much longer than those used in this study (Baumgarten et al., 2011; Grünheid et al., 2005; Stauder et al., 2012). With a greater retention time of the anoxic NO$_3^-$-reducing zones in MAR systems, more BrO$_3^-$ than in the 8 m anoxic column with 6 days retention time may be biodegraded, as the travel time is longer and thus the reaction time is also longer. In addition, the concentration of NO$_3^-$ as a competitor of BrO$_3^-$ reduction by denitrifying bacteria becomes lower and lower. Therefore, BrO$_3^-$ biodegradation should be more efficient with greater retention time in anoxic zones, especially in the zone immediately after NO$_3^-$ depletion, i.e. at the interface of the anoxic denitrification zone and the Fe/Mn oxide reduction zone. Additional evidence of this inference is illustrated by the study of Hübner et al. (2016), in which it was observed that BrO$_3^-$ removal in the presence of low NO$_3^-$ concentrations was significantly higher than in the presence of high NO$_3^-$ concentrations.

5. Conclusions

This study focused on the effect of NO$_3^-$ and the role of increased AOC concentrations on the removal of BrO$_3^-$ in NO$_3^-$-reducing anoxic zones of MAR systems. The following conclusions can be drawn:

- BrO$_3^-$ and NO$_3^-$ compete for reduction by denitrifying bacteria, but BrO$_3^-$ reduction and NO$_3^-$ reduction can occur simultaneously even if denitrifying bacteria prefer NO$_3^-$ to BrO$_3^-$ as an electron acceptor.
- The presence of NO$_3^-$ is a precondition for denitrifying bacteria to reduce BrO$_3^-$ in NO$_3^-$-reducing anoxic zones of MAR systems.
- An increase of AOC as a result of ozonation pre-treatment promotes microbial activity and therefore BrO$_3^-$ removal in subsequent MAR systems.
- In the 8 m long anoxic column (retention time 6 days) simulating anoxic NO$_3^-$-reducing zones of MAR systems, BrO$_3^-$ biodegraded to a concentration of 1.3 μg/L, indicating that BrO$_3^-$ biodegradation by denitrifying bacteria can happen in anoxic NO$_3^-$-reducing zones of MAR systems.
- MAR systems following ozonation are potentially effective to biodegrade BrO$_3^-$, provided that anoxic NO$_3^-$ reducing conditions are reached in MAR systems.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2017.11.052.

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