



## Bioreduction of iodate in sediment microcosms

FABIOLA GUIDO-GARCIA<sup>1</sup>, GARETH T. W. LAW<sup>2</sup>, JONATHAN R. LLOYD<sup>1</sup>, PAUL LYTHGOE<sup>1</sup> AND KATHERINE MORRIS<sup>1,\*</sup>

<sup>1</sup> Research Centre for Radwaste Disposal and Williamson Research Centre for Molecular Environmental Science, The University of Manchester, Williamson Building, Oxford Road, Manchester M13 9PL, UK

<sup>2</sup> Centre for Radiochemistry Research, The University of Manchester, School of Chemistry, Oxford Road, Manchester M13 9PL, UK

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### ABSTRACT

Iodine-129 is a high-yield fission product formed in nuclear reactors and is a risk-driving radionuclide in both contaminated land and radioactive waste disposal due to its high mobility and long half-life. Here, the bioreduction behaviour of iodate was investigated by tracking iodine speciation and concentration in solution during the development of progressive anoxia in sediment microcosm experiments incubated at neutral pH. Experiments with acetate added as an electron donor showed the expected cascade of terminal electron-accepting processes. Analysis of solution chemistry showed reduction of iodate to iodide during the early stages of metal (Mn(IV) and Fe(III)) reduction, but with no significant retention of iodine species on solids. There was, however, a net release of natural iodine associated with the sediments to solution when robust iron reduction / sulfate reduction had developed. In addition, over 210 days, the controls with no electron donor and the sterile controls showed no Mn(IV) or Fe(III) reduction but displayed modest sorption of iodate to the sediments in the absence of bioreduction. Overall these results show that under oxic conditions iodate may be partially sorbed to sediments over extended periods but that development of mildly reducing conditions leads to the reductive release of iodine to solution as iodide.

**KEYWORDS:** iodate, iodide, speciation, bioreduction, radioactive iodine.

### Introduction

IODINE-129 is of regulatory concern in radioactive waste disposal due to its long half-life ( $t_{1/2} 15.7 \times 10^6$  y), potential for bioaccumulation and its high environmental mobility as the iodide ( $I^-$ ) species (Fuge and Johnson, 1986). It is a high-yield fission product formed in nuclear reactors and is a significant contaminant at nuclear facilities (Hou *et al.*, 2009; Tykva and Berg, 2004). Iodine-129 is considered to be one of the main dose-contributors during the long-term geological disposal of

radioactive wastes, therefore to understand the eventual fate of the radionuclide it is vital to understand its biogeochemical behaviour in the natural environment (Madic *et al.*, 2002; Aimoz, 2012). Geological disposal, which is the preferred management and disposal route for higher-activity waste in the UK, is founded globally on an engineered deep subsurface facility. Deep geological disposal uses a ‘multi-barrier’ approach to contain radionuclides over the long timescales necessary for the bulk of the radionuclides to undergo significant radioactive decay. It is accepted that these barriers will eventually fail and that this could lead potentially to the long-lived fraction of radionuclides migrating to the distant surroundings or ‘far field’ of the geological disposal facility.

\* E-mail: katherine.morris@manchester.ac.uk  
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Iodine-129 with its half life of  $15.7 \times 10^6$  y and its high mobility in the environment is clearly a radionuclide which may impact on the far field at some point in the future.

Iodine exists naturally as the inorganic species iodate and iodide. Under oxic conditions at circumneutral pH, iodate ( $\text{IO}_3^-$ ) dominates and it can be sorbed to mineral phases and sediments (Kodama *et al.*, 2006; Yu *et al.*, 1996). During the development of anoxic conditions, iodate is predicted to be reduced to its lower valence, highly soluble form, iodide ( $\text{I}^-$ ) in the region of Mn(IV) reducing conditions (Lam and Kuypers, 2011) and has been observed during Fe(III) reducing conditions (Fox *et al.*, 2010). Depending on the sediment type, partition coefficient ( $K_d$ ) values for iodate have been reported to be up to  $10^3 \text{ ml g}^{-1}$  (Schwehr *et al.*, 2009; Fukui *et al.*, 1996; Zhang *et al.*, 2011), whilst  $K_d$  values for iodide are routinely below  $10 \text{ ml g}^{-1}$  (Kaplan *et al.*, 2000; Zhang *et al.*, 2011) reflecting the lower sorption of iodide species. Iodate is thought to sorb more strongly to sediments containing significant amounts of iron and manganese oxides, and although the mechanism is not fully understood, the formation of an organic *Me-OIO*<sub>2</sub> bond has been implicated in some studies (Xu *et al.*, 2011). Interestingly, despite the typically small  $K_d$  values for iodine interactions with sediments, several studies have explored the interaction of iodide with different minerals including alumina, ferric-oxides, mono-sulfate (AFm) phases, pyrite, bacteriogenic iron oxides, birnessite, ferromanganese oxides, kaolinite and illitic minerals (Aimoz *et al.*, 2012; Aimoz *et al.*, 2011; Allard *et al.*, 2009; Couture and Seitz, 1983; Kaplan *et al.*, 2000; Kennedy *et al.*, 2011). Bacteriogenic Fe-oxides and illite showed the highest reactivity for iodide under low-pH conditions whilst pyrite, hematite and kaolinite showed limited, if any, sorption (Aimoz *et al.*, 2011; Kennedy *et al.*, 2011; Kaplan *et al.*, 2000). In a study conducted to test iodide sorption to different iron minerals, only magnetite showed significant levels of sorption (Fuhrmann *et al.*, 1998). In addition, Mn is implicated in the redox cycling of iodide, with oxidation of iodine to iodate by  $\delta\text{MnO}_2$  and sorption of iodate to  $\delta\text{MnO}_2$  also possible (Aimoz *et al.*, 2012; Allard *et al.*, 2009; Fox *et al.*, 2009). Organic matter has also shown significant uptake of iodide, and soil humus is considered to be a considerable sink for iodine in soil systems (Shetaya *et al.*, 2012). Indeed, recent work has highlighted the potential for formation of soluble organo-I compounds (Kaplan, 2003;

Kaplan *et al.*, 2013; Xu *et al.*, 2011) again highlighting the complexity of iodine cycling. Previous studies have suggested that inorganic iodate must first be reduced to transient species such as hypiodous acid or  $\text{I}_2$  by organic matter in the soils before it becomes associated with the organic fraction of sediments (Steinberg *et al.*, 2008). By contrast, iodide shows little reaction towards organic matter (Reiller and Moulin, 2002). Iodate sorption to sediments has been shown to be pH dependent, with sediments at low pH with a positive charge favouring sorption of anionic  $\text{IO}_3^-$ , and ambient to alkaline pH sediments with neutral / negative charge favouring desorption of anionic  $\text{IO}_3^-$  (Yoshida *et al.*, 1992). This is pertinent to iodine behaviour during the attempted remediation of contaminated sites. For example, in a remediation process, limestone was used at the Savannah River facility to promote the precipitation of radionuclides such as Pu and U *via* the generation of alkalinity. The limestone addition caused an increase in pH from 3.1 to 3.8 in a radionuclide contaminated plume, and although the concentrations of Pu and U decreased as intended, iodine-129 desorbed from sediments presumably due to the increase in negatively charged mineral surfaces (Kaplan *et al.*, 2011). In the UK,  $^{129}\text{I}$  has been detected in groundwater at the Sellafield site, and globally  $^{129}\text{I}$  is present in radioactive wastes destined for disposal. It is considered one of the key mobile, long-lived radionuclides present over geological timescales (Stamper *et al.*, 2013).

Even though several studies agree that iodide can be formed under reducing conditions, its behaviour during microbial 'bioreduction' scenarios is not fully understood (Fox *et al.*, 2010; Kaplan *et al.*, 2013; Yamaguchi *et al.*, 2006). Bacterial interactions with iodine have been studied, and show that iodate can be reduced directly by iron- and sulfate-reducing bacteria under axenic conditions. Indeed, in one early study, sulfate-reducing species were able to reduce up to 96% of iodate to iodide in matter of hours (Councell *et al.*, 1997). Marine nitrate reducers such as *Pseudomonas*, *Bacillus*, *Achromobacter* and *Vibrio* species have been shown to reduce iodate to iodide, and recent work suggests an enzymatic pathway (Lam and Kuypers, 2011). Furthermore, under the effect of a strong oxidizer (birnessite,  $\delta\text{MnO}_2$ ), iodide was oxidized to elemental iodine and iodate (Allard *et al.*, 2009; Fox *et al.*, 2009) highlighting the likely importance of microbially driven redox cycling processes in predicting iodine speciation and fate in the environment.

*In situ* biostimulation through the addition of electron donors to sediments to promote the development of metal-reducing conditions has been proposed as a strategy for managing Tc and other redox-active radionuclides present as contaminants in groundwater (Lloyd and Renshaw, 2005; Newsome *et al.*, 2014a). Such biostimulation regimes develop reducing conditions, under which the solubility of certain redox-active radionuclides including technetium and uranium is reduced. It is possible, however, that biostimulation aimed at immobilizing Tc(VII) and U(VI) may increase the solubility of iodine if it is present in sediments by promoting iodide formation. In addition, microbial processes are now increasingly being recognized as significant during the deep geological disposal of radioactive wastes (Rizoulis *et al.*, 2012; Behrends *et al.*, 2012). Geological disposal facilities (GDF) for higher-activity wastes are yet to be widely implemented, but the generic design includes a series of ‘multi-barriers’ which are intended to retard migration of radionuclides for as long as possible. However, the engineered barriers will degrade over geological time and long-lived radionuclides will breach the engineered containment and migrate from the repository (Morris *et al.*, 2008). This means understanding iodine-129 biogeochemistry will be important in both natural and engineered environments.

In this contribution, the redox behaviour of iodate was studied in sediment microcosms under conditions of progressive anoxia, to explore its biocycling behaviour in sediments relevant to radioactively contaminated land, thus providing insight into iodine biocycling in shallow subsurface materials. Reflecting this, the speciation of stable iodine-127 (as iodate) at low concentrations (9.96  $\mu\text{M}$ ) was tracked during the development of bioreducing conditions in well characterized sediments collected from near the Sellafield nuclear facility. Acetate was used as an electron donor to stimulate microbial redox processes, and the impact of elevated nitrate concentrations on iodine behaviour during bioreduction was also tested.

## Methods

### Overview

A series of sediment microcosms was established using well-characterized materials from near the Sellafield nuclear facility in northwest England. The sediment was used to prepare microcosms with

acetate as the electron donor and with varying concentrations of nitrate.

### Sample collection

A well characterized sediment, representative of the Sellafield regional geology (Law *et al.*, 2010a), was collected in sterile containers, sealed and stored at 10°C in the dark prior to use.

### Microcosm set-up, sampling and analysis

Sediment microcosms (10.0  $\pm$  0.01 g sediment) were prepared using a range of treatments with a synthetic regional groundwater (100  $\pm$  0.10 ml) containing 0.3 mM NaNO<sub>3</sub>, 0.4 mM MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.09 mM KCl, 0.4 mM MgCl<sub>2</sub>·6H<sub>2</sub>O, 1.6 mM CaCO<sub>3</sub>, 2.9 mM NaHCO<sub>3</sub> and 0.16 mM NaCl (Wilkins *et al.*, 2007). All experiments were run in triplicate in serum bottles that were crimp sealed with butyl rubber stoppers and similar to past work on e.g. U, Tc and Np biogeochemistry (Law *et al.*, 2010a; Law *et al.*, 2010b; Newsome *et al.*, 2014b). Microcosm systems were run with the synthetic regional groundwater and: (a) 10 mM acetate (from a Na-acetate pH 7 stock); (b) 10 mM acetate + 10 mM nitrate (from a pH 7 NaNO<sub>3</sub> stock); and (c) no acetate. The synthetic groundwater had sulfate present at 0.4 mM as an electron acceptor. Sterile (20 min autoclaving at 120°C) and groundwater only controls were also established. In all systems the groundwater pH was adjusted to  $\sim$ 7 prior to the start of the experiment, except for the groundwater only systems where the pH was  $\sim$ 8. Finally, the microcosms and controls were spiked to a concentration of 9.96  $\mu\text{M}$  (2 ppm) of iodate as sodium iodate. All systems were then incubated anaerobically at room temperature (20  $\pm$  2°C) in the dark for 210 days. In addition, to assess abiotic iodate behaviour, pre-reduced sulfate reducing sediments were then autoclaved and reacted with iodate. These microcosms were sampled over one week to assess the rate and extent of any abiotic IO<sub>3</sub><sup>-</sup> reduction.

Sampling was conducted periodically as sediment anoxia developed and sediment slurry was extracted from the microcosms using a sterile syringe and needle, and centrifuged (7000 g) to separate groundwater and sediment. Groundwater samples were analysed for total iodine by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500cx; Brown *et al.*, 2007) and iodine speciation was analysed by chromatographic separation (Hamilton PRP-X100 anion exchange

column) followed by ICP-MS analysis (Brown *et al.*, 2007; Shetaya *et al.*, 2012). Spectrasol (1% CFA-C) was used throughout to minimize build-up of iodine species during analysis (Brown *et al.*, 2007). Samples were stored in the dark at 4°C for a maximum of 4–5 weeks prior to analysis and a mixed iodate/iodide standard was analysed routinely to provide confidence in measurement stability and storage procedures. Total dissolved  $\text{NO}_2^-$ , Mn and Fe concentrations were measured with standard UV-vis spectroscopy methods (Goto *et al.*, 1977; Harris and Mortimer, 2002; Viollier *et al.*, 2000) and aqueous  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were measured by ion chromatography (Dionex AG11-HC). The total bioavailable Fe(III) and the proportion of extractable Fe(II) in the sediment was measured using ferrozine following the method of Lovley and Phillips (1986). The pH and Eh were measured with a digital meter (Denver Instrument Company) and calibrated electrodes. Standards were used routinely to check the reliability of the methods and calibrations typically had  $R^2 \geq 0.99$ . Bulk mineralogy and sediment chemical composition were determined by X-ray fluorescence (Thermo ARL 9400 XRF) and powder X-ray diffraction (Bruker D8 Advance XRD). Total iodine in the sediment as sampled was determined *via* extraction with tetramethylammonium hydroxide (TMAH) followed by ICP-MS analysis (Yamada *et al.*, 1996).

## Results and discussion

### Sediment characteristics

The sediment consisted of quartz, sheet silicates (muscovite and chlorite) and minor albite and microcline, which was consistent with past studies (Law *et al.*, 2010a). The total organic carbon content was low ( $0.56 \pm 0.08$  wt.%) and iron oxides were also found in sediment at 5.3 wt.%. The concentration of iodine extracted from the sediment by 5% TMAH was  $27.5 \pm 0.03$   $\mu\text{mol kg}^{-1}$ .

### Progressive bioreduction

No significant biogeochemical changes were noted in sterile microcosms, or systems without added acetate over 210 days (Fig. 1). The pH in the sterile systems stabilized at pH 6.8 and the pH in groundwater only controls was constant at pH 8.0 (Fig. 1). The microbially active microcosms which were amended with 10 mM acetate showed significant

(>90%) acetate removal at experimental end points consistent with its use as an electron donor. Bioreduction proceeded at different rates depending on the initial nitrate concentration. In the acetate only systems, low concentrations of nitrate (0.32 mM) were present in groundwater, the pH was stable at 6.9, with nitrate reduction starting after two days (Fig. 1a). The systems with acetate and 10 mM nitrate took longer to remove nitrate but complete removal had occurred by day 20 (Fig. 1a). In both systems, transient nitrite was observed in porewaters and in the high-nitrate experiments increasing headspace pressure suggested ingrowth of  $\text{N}_2$  or  $\text{N}_2\text{O}$  from denitrification. In the 10 mM nitrate system the pH also increased from pH 7.1 to pH 8.3 presumably due to alkalinity production during nitrate reduction (Thorpe *et al.*, 2012). In the low nitrate, acetate amended systems, Mn(II) was present in porewater from day 23, followed by Fe(III) reduction as indicated by Fe(II) ingrowth to sediments from day 30 and Fe in porewaters from day 37. For the acetate with 10 mM nitrate systems, metal reduction was delayed with  $\text{Mn}_{(\text{aq})}$  detected by day 44 and  $\text{Fe(II)}_{(\text{aq})}$  from day 66 presumably due to excess nitrate in the experiment. Finally, in experiments with acetate only, sulfate reduction was indicated by a decrease in aqueous sulfate from ~90 days when the Fe(II)/Fe(III) ratio in the solids was >70%. Similarly, in the acetate with 10 mM nitrate systems, sulfate reduction was observed from ~90 days when Fe(II)/Fe(III) ratios were >~70% with essentially complete reduction in both systems by 210 days (Fig. 1e).

### Iodine fate during bioreduction

No changes in iodine speciation were evident in the groundwater-only system, with essentially all of the added iodate remaining in solution throughout the incubation (Fig. 2a). Interestingly, there was evidence for modest sorption of iodine to sterile sediments over the duration of the experiment, with  $8.43 \pm 0.38$   $\mu\text{M}$  total iodine present in solution at day 210 (15% removal,  $K_d = 3.04$   $\text{ml g}^{-1}$ ). This removal from solution was attributed to sorption to sediments although it is clear that in sterile oxic systems, the extent of sorption was limited with >85% of the iodine in solution at 210 days. Indeed, iodate was the dominant species in the system at the end of the experiment ( $73 \pm 2\%$  iodate and  $10 \pm 3\%$  iodide; Fig. 2b). In the systems without added acetate, again there was no evidence for iodate reduction, reflecting the fact there were negligible

## BIOREDUCTION OF IODATE IN SEDIMENT MICROCOSMS

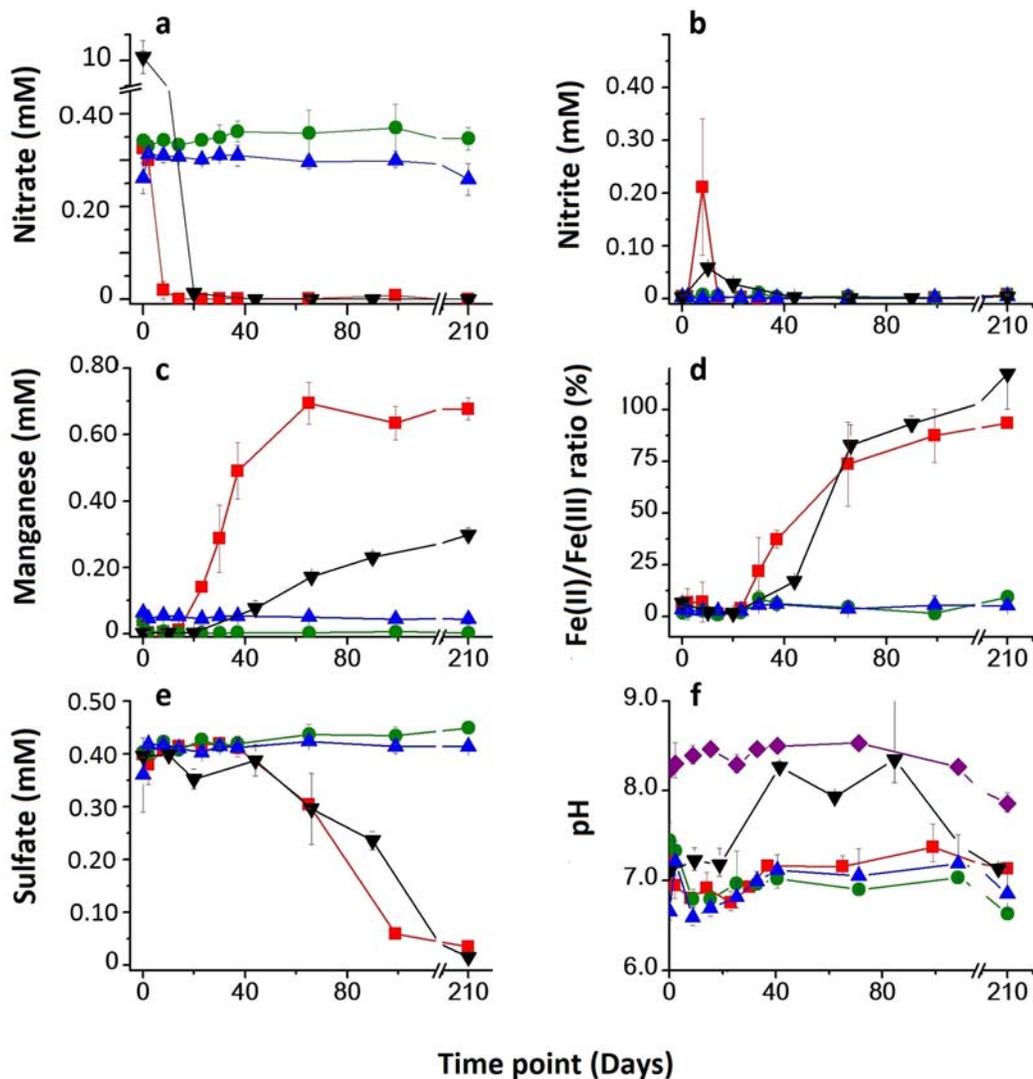


FIG. 1. Sediment microcosm incubation time data (0–250 days). (a)  $\text{NO}_3^-$ ; (b)  $\text{NO}_2^-$ ; (c) Mn (aq); (d) Percent of 0.5 N HCl extractable Fe present as Fe(II) in sediments; (e) groundwater  $\text{SO}_4^{2-}$ ; and (f) groundwater pH. Note: ■ = acetate amended systems, ● = no added acetate systems, ▲ = sterile control systems, ▼ = acetate and [10 mM] nitrate amended systems, ◆ = groundwater only. Error bars are 1  $\sigma$  of triplicate microcosm experiments (where not visible, error bars are within the symbol size).

changes in other biogeochemical indicators (Fig. 1) and confirming that natural levels of organic electron donor were very low in these sediments consistent with past work (Law *et al.*, 2010a). Here, total iodine analyses again showed modest levels of sorption of iodate to sediments, similar to the sterile systems. Total iodine data showed  $6.16 \pm 1.06 \mu\text{M}$  in solution at 210 days ( $46 \pm 7\%$  removal,  $K_d =$

$4.61 \text{ ml g}^{-1}$ ; Fig. 2c). Again, speciation data suggested that iodate dominated the aqueous speciation at 210 days. This longer term and modest sorption of iodate in these experiments is similar to past work (Xu *et al.*, 2011; Shetya *et al.*, 2012).

In the acetate-only bioreduction experiment, the total iodine remaining in solution showed a modest but significant increase from the added  $9.96 \mu\text{M}$  to

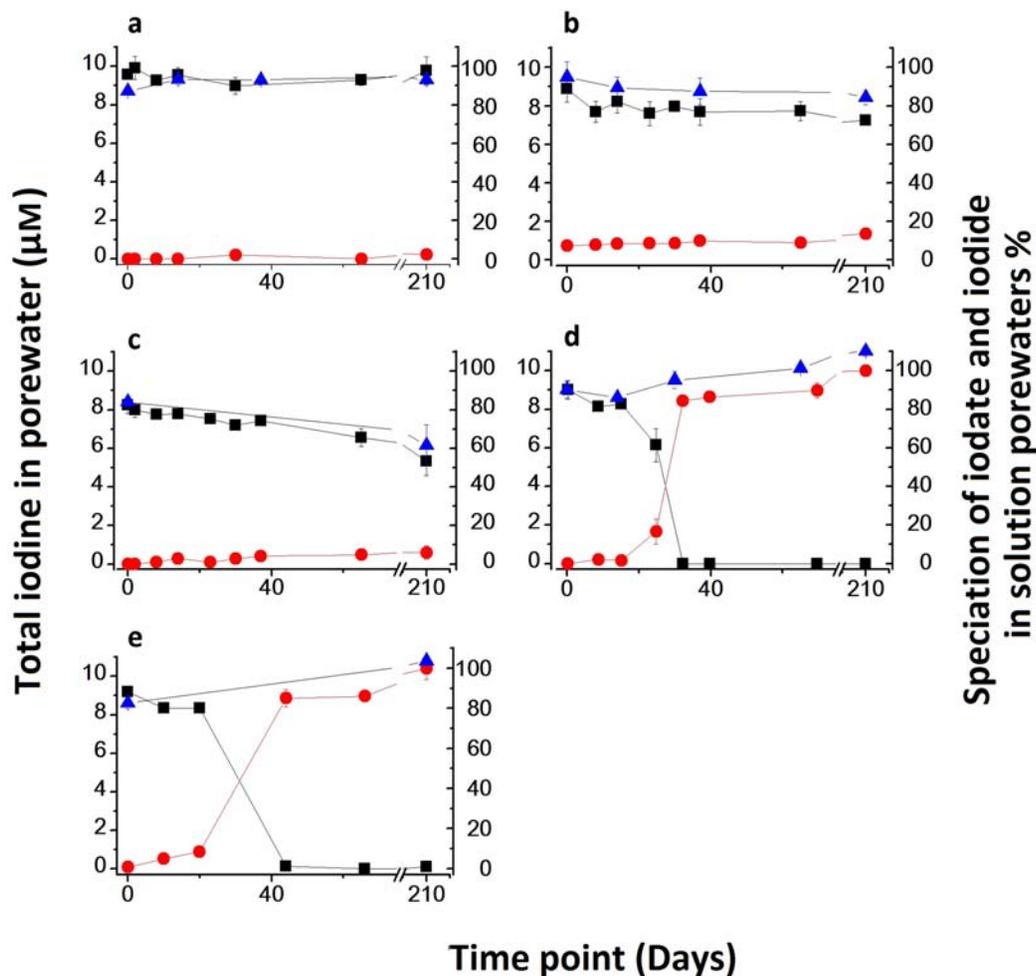


FIG. 2. Iodate reduction-time data (0–250 days) from: (a) groundwater only experiments; (b) sterile control; (c) no acetate system; (d) acetate amended system; and (e) acetate and [10 mM] amended system. ▲ = total iodine in porewater ( $\mu\text{M}$ ), ■ =  $\text{IO}_3^-$  (%), ● = % $\text{I}^-$  (%). Error bars are  $1\sigma$  experimental uncertainty from triplicate microcosm experiments (where not visible, error bars are within the symbol size).

$11.0 \pm 0.27 \mu\text{M}$  by day 210 where the  $\text{Fe(II)/Fe(III)}$  ratio was  $>70\%$  and sulfate reduction had developed in the microcosm. The extractable iodine in the sediment was measured using TMAH extractions as  $27.5 \mu\text{M kg}^{-1}$ . Mass balance calculations suggest that in microcosms up to  $2.8 \mu\text{M I}^{-1}$ , additional iodine could be supplied by release of this pool of natural iodine bound to sediments. Indeed, in an acetate stimulated control experiment with no added iodate, there was a release of  $\sim 2.0 \mu\text{M I}^{-1}$  iodide to solution over 210 days (data not shown) again highlighting reductive release of the natural pool of iodine in these samples. This reductive release

pathway for natural, sediment bound iodine has also been observed in other studies (Fox *et al.*, 2010, Yamaguchi *et al.*, 2006).

The aqueous speciation data for iodine in the acetate-only systems showed that the iodate levels decreased as iodide increased in porewaters. The iodate in solution was removed by day 30 leaving essentially all iodine in solution speciated as iodide (Fig. 2d). By 30 days Mn reduction was established and the  $\text{Fe(II)/Fe(III)}$  ratio in sediments was 20% indicating that early metal-reducing conditions were established at the point of essentially complete iodate reduction to iodide. This is in agreement

with Lam and Kuypers (2011), who suggest that iodate is theoretically reduced at the same time as manganese reduction. Interestingly, when pre-reduced autoclaved sediments (with 100% Fe(II)) were spiked with 9.96  $\mu\text{M}$   $\text{IO}_3^-$ , essentially complete reduction of iodate to iodide occurred over 1 week. This confirms that abiotic reduction of iodate is possible in these systems, where both Fe(II) and sulfide are present and in agreement with past work (Councell *et al.*, 1997).

In the acetate with 10 mM nitrate systems, iodine followed a similar pattern to the acetate only experiment but the onset of iodate reduction was delayed to 44 days, reflecting the elevated nitrate concentrations in solution; an extended period of nitrate reduction was observed in the microcosms before iodate was reduced (Fig. 2e). Again, total iodine increased to  $10.8 \pm 0.2 \mu\text{M}$  during the incubation period and again this suggests that some of the sediment-bound iodine in the system was being released as a consequence of the microbially mediated generation of reducing conditions. Aqueous speciation measurements suggested that in the first 20 days of incubation, iodine speciation was dominated by iodate with significant reduction to iodide occurring by day 44. At this point, nitrate had been completely removed from porewaters, Mn concentration in porewaters had increased and Fe(II)/Fe(III) ratios in sediments were  $17 \pm 1.0\%$  suggesting that early metal-reducing conditions had developed by the point at which iodate was reduced to iodide. Finally, in both 10 mM and acetate-only systems the final concentrations of iodide accounted for all the iodine present in solution and in fact were higher than the original spike. This confirmed that the aqueous species accounted for essentially all of the iodine in the experimental pool.

## Conclusions

The results of this study shows that in sterile and no-electron-donor control experiments, iodate can be sorbed to sediments over several months. In addition, development of early metal-reducing conditions leads to complete reduction of iodate to iodide: all iodide that forms is released into solution. Furthermore, in both microbially active experiments, the total iodine measurements suggested a net release of iodide from sediments during bioreduction. This suggests that an additional source of natural sediment bound iodine was released to solution as iodide under metal- or

sulfate-reducing conditions. In many systems, bioreduction has been shown to retard migration of radionuclides such as uranium and technetium (Newsome *et al.*, 2014a), but the enhanced levels of iodine detected in solution under anaerobic conditions, are consistent with bioreduction causing an indirect reductive solubilization of iodine through formation of iodide. When considering the long-term management of radioactive-contaminated land and the disposal of radioactive waste, this study suggests that  $^{129}\text{I}$  may be less mobile in oxic environments where the  $\text{IO}_3^-$  species will dominate. Further work is needed to define the point in the biogeochemical cascade at which iodate reduction occurs and also its fate on sediment reoxidation with air and nitrate.

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