



## Cycling of iodine by microalgae: Iodine uptake and release by a microalgae biofilm in a groundwater holding pond



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### ABSTRACT

Biological iodine cycling has been widely studied in marine environments, but rarely considered in terrestrial waters. In this work, a microalgae biofilm, with an iodine content of  $350 \pm 29 \text{ mg kg}^{-1}$ , is shown to potentially be a significant iodine cyclor in a groundwater holding pond. Cultivation of the biofilm in extracted groundwater was carried out at bench scale. In parallel, iodine release from an iodine-rich biofilm kept in the dark was monitored. Iodine uptake and release were found to be proportional to algal growth and decay, with the maximum growth rate and specific decay rate being  $0.53 \pm 0.05 \text{ g m}^{-2} \text{ d}^{-1}$  and  $0.12 \pm 0.02 \text{ d}^{-1}$  respectively. Iodine uptake and release in an engineered groundwater holding pond ( $1 \text{ m}^3:1 \text{ m}^2 \times 1 \text{ m}$ ) was simulated. The results indicated that bioaccumulation causes non-steady state conditions in such ponds, and in extreme circumstances decay events can elevate iodine concentrations to problematic levels.

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### 1. Introduction

Iodine cycling in the marine environment has been widely studied, but little is known about iodine cycling in terrestrial aquatic systems (Gilfedder et al., 2008). In aquatic systems iodine is present as inorganic iodine and in microorganisms as organic iodine (the biological iodine pool). In marine environments the biological iodine pool is known to play an important role in global iodine cycling, as some macroalgae (seaweed) can accumulate large amounts of intracellular iodine as antioxidant to counter elevated oxidative stress during photosynthesis (Kupper et al., 2008, 1998). In terrestrial aquatic systems the story is less well documented, but it has recently been concluded that biological activity contributes to storage of iodine in lake sediments, with a strong flux of iodine from that pool being occasionally observed (Gilfedder et al., 2008). In this paper, the contribution of microalgae to iodine cycling in terrestrial aquatic systems is considered, with a view to understanding the role that iodine hold-up in microalgae and subsequent cycling as microalgae decays could play in determining iodine concentrations in the water column. Specifically, we quantify the potential consequence of an increase in iodine concentration if the iodine accumulated in microalgae is at some point rapidly released.

The presence of iodine in surface and groundwater has been widely reported (Álvarez et al., 2015; Leybourne and Cameron 2006; Schall et al., 1994; Schwehr and Santschi 2003; Zhang et al., 2011), with the relevant species including: iodide, iodate and organically bound iodine. In this work, an engineered open aquatic system fed with alkaline brackish groundwater is considered. In such alkaline ( $\text{pH} > 9$ ) conditions (Zaman et al., 2015), iodine is mainly present as iodide (Gottardi 2001). Groundwater fed systems are particularly interesting as iodine content can be very high ( $> 100 \text{ mg L}^{-1}$  (Leybourne and Cameron 2006; Tang et al., 2013)) compared to the content reported in surface water ( $0\text{--}0.02 \text{ mg L}^{-1}$ ) and seawater ( $0.02\text{--}0.05 \text{ mg L}^{-1}$ ) (Gilfedder et al., 2006; Korobova 2010; Whitehead 1979). Therefore, low iodine concentration by groundwater standards is still elevated compared to typical surface water and seawater. Technologies to reduce iodine content may therefore be widely required in desalination plants that treat groundwater. Australian drinking water standards state that iodide in drinking water should not exceed  $0.5 \text{ mg L}^{-1}$  (NHMRC 2011). This guideline means that for a single stage RO process, with typical 85% iodide rejection and 1:3 reject/flux ratio, an iodide content of  $2.5 \text{ mg L}^{-1}$  can be problematic as a potable water supply (Watson et al., 2012).

There are long-term studies showing that iodine content in terrestrial aquatic systems is influenced by the organic iodine pool. For example, Gilfedder et al. (2008) showed that organo-I accounted for more than 85% of the total iodine in a headwater lake (Mummelsee)

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(Gilfedder et al., 2008). They observed the total iodine content in the lake water increases with depth. This phenomenon was believed to be owing to the release of iodine from the high iodine content ( $11.8 \pm 1.7 \text{ mg kg}^{-1}$ ) lake sediments. Organisms that accumulate iodine include bacteria and macro- and microalgae. Some iodine accumulating bacteria have been isolated and discovered to have an intracellular iodine content of  $300 \text{ mg kg}^{-1}$  (Amachi et al., 2005). Iodine accumulation in macroalgae has been widely studied. It has been shown that the iodine content in some brown algae species can be up to  $40,000 \text{ mg kg}^{-1}$  (4% by weight) (Kupper et al., 1998). Organically bound iodine is also associated with microalgae. Compared with macroalgae, there are relatively few studies about iodine in microalgae. Radioactive labelling has been recently used to show that many microalgae species can accumulate iodine (Fukuda et al., 2014). For example, *Chlorella* sp. can accumulate iodine to a content of  $1,300 \text{ mg kg}^{-1}$  (Niedobova et al., 2005) and the iodine content in cyanobacteria *Spirulina platensis* can be as high as  $2,000 \text{ mg kg}^{-1}$  (Mosulishvili et al., 2002). However, there are no reports considering the contribution of microalgae iodine uptake and release to water quality.

Iodine mass transfer between the organic iodine pool and water environment can be caused by a variety of biological activities, such as iodine adsorption or excretion in response to environmental pressures (oxidative stress, salinity change, enzymatic catalysis) during cell growth (Kupper et al., 2008; Kupper et al., 1998; Nitschke and Stengel, 2014) and settled biomass decomposition (Gilfedder et al., 2006; Gilfedder et al., 2010). The organic iodine pool is not the only influence on iodine concentration in lake, river and marine systems. There are many other significant factors, such as atmospheric deposition, soil sorption and desorption, precipitation and evaporation (Abdel-Moati, 1999; Gilfedder et al., 2010; Leblanc et al., 2006). Nevertheless, in some non-steady state aquatic environments with relatively large organic iodine pools there is certainly potential for biological iodine uptake and release to be a prominent influence on iodine concentration. This is supported by laboratory data, which shows that cultivation of some iodine accumulating microalgae and bacteria on synthetic growth media can result in complete depletion of iodine in the bulk (from  $75 \text{ mg L}^{-1}$  to essentially  $0 \text{ mg L}^{-1}$  within 24 h) (Gomez-Jacinto et al., 2012).

In this study, we consider a microalgae biofilm as an important biological iodine pool that can contribute significant iodine flux in a terrestrial aquatic environment. The objective of the work is twofold: (i) to quantify the iodine content in microalgae that grows in an engineered pond fed with groundwater, and (ii) to quantify the uptake and release of iodine by that microalgae with the view to assessing the potential for iodine concentrations to exceed potable limits as the result of a rapid release of iodine that has accumulated within the microalgae. It is acknowledged that many environmental factors would likely contribute to the extent of the impact, and even to the potential for the rapid release scenario to occur. Understanding those factors should be the focus of future research.

## 2. Materials and method

The potential influence of the biological iodine pool to liquid phase iodine concentration was assessed by iodine uptake and iodine release experiments. Cultivation of a microalgae biofilm in extracted groundwater was carried out at bench scale. In parallel, iodine release from an iodine-rich microalgae biofilm kept in the dark was monitored.

A non-steady state mass balance model was developed to simulate the potential effect of iodine uptake and release on iodine concentration in a liquid column.

### 2.1. The groundwater

Fig. 1 shows an engineered holding pond for groundwater storage and a typical treatment train for management of that water. The facility considered in this work is located in inland Queensland, Australia and has the capacity to manage  $12 \text{ ML d}^{-1}$ . Pond 1 is the main storage pond that holds extracted groundwater. The pond water goes through a microfiltration (MF) process to remove suspended solids, and is then fed to a reverse osmosis system for desalination. The suspended solids rejected by the MF membrane are returned to Pond 1. After reverse osmosis, fresh water is stored and used. Concentrated brine water is stored in another smaller pond (Pond 2) for further treatment.

Table 1 shows the characteristics of the groundwater used in this study. The water is brackish and alkaline (Buchanan et al., 2013). Iodine content in the water used in this study is around  $2 \text{ mg L}^{-1}$ , which is much higher than some reported high-iodine waters (Tang et al., 2013).

### 2.2. Cultivation of microalgae in extracted groundwater

Water from Pond 1 was added to 5 L large glass beakers and supplemented with double strength f/2 medium (Murashige and Skoog 1962) which provided sufficient nitrogen ( $23.3 \text{ mg L}^{-1}$ ) and phosphorus ( $2.89 \text{ mg L}^{-1}$ ) for algae cultivation (Table 1). The water was illuminated with fluorescent light ( $80 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) at  $25^\circ\text{C}$  for 40 days. A microalgae biofilm that adhered to the walls of the cultivation vessel was obtained. The iodine content in the biofilm material was quantified.

### 2.3. Iodine uptake by the microalgae biofilm

#### 2.3.1. Inoculation

Polyethylene biofilm carriers (4 cm diameter  $\times$  2 cm height, equal weight) were placed in 1 L measuring cylinders and soaked with groundwater supplemented with double strength f/2 medium. The culture was incubated under the same environmental conditions described in Section 2.2. After about 80 days, the carriers covered with biofilm were removed and placed on a  $200 \mu\text{m}$  pore size mesh for drainage. After 20 min of drainage, five carriers with

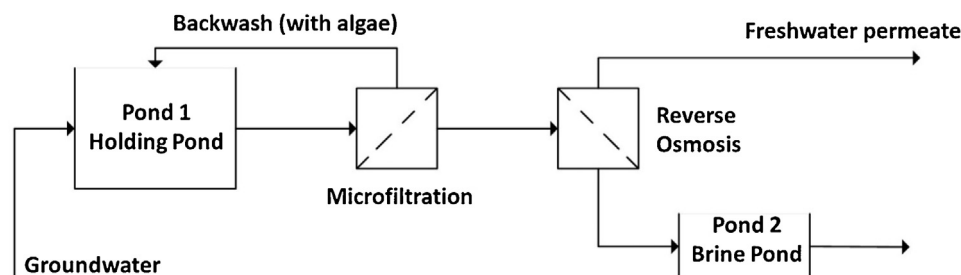


Fig. 1. Schematic of a typically designed engineering holding pond for groundwater storage.

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