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The biogeochemical effect of seaweeds upon close-to natural concentrations of dissolved iodate and iodide in seawater − Preliminary study with *Laminaria digitata* and *Fucus serratus*

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Abstract

Toward assessing the biogeochemical significance of seaweeds in relation to dissolved iodine in seawater, the effect of whole seaweeds (*Laminaria digitata* and *Fucus serratus*) upon iodide and iodate, at essentially natural concentrations, has been studied. The weeds were carefully removed from the sub-littoral zone of the Menai Straits and exposed to iodide and iodate at their natural temperature (6 °C), but under continuous illumination. *Laminaria digitata* was found to decrease the concentration of iodate with an exponential rate constant of 0.008−0.24 h^{-1}. This is a newly discovered process which, if substantiated, will require an entirely new mechanism. Generally, apparent iodide concentration increased except in a run with seawater augmented with iodide, where it first decreased. The rate constant for loss of iodide was 0.014−0.16 h^{-1}. Meanwhile, *F. serratus* was found not to decrease iodate concentrations, as did *L. digitata*. Indeed, after ~30 h iodate concentrations increased, suggesting that the weed may take in iodide before oxidising and releasing it. If substantiated, this finding may offer a way into one of the most elusive of processes within the iodine cycle − iodide oxidation. With both seaweeds sustained long-term increases of apparent iodide concentration are most easily explained as a secretion by the weeds of organic matter which is capable of reducing the Ce(IV) reagent used in determination of total iodine. Modelling of the catalytic method used is provided to support this contention. The possibility of developing this to measure the strain that seaweeds endure in this kind of biogeochemical flux experiment is discussed. A Chemical Oxygen Demand type of approach is applied using Ce(IV) as oxidant. The results of the iodine experiments are contrasted with the several investigations of ^{131}I interaction with seaweeds, which have routinely used discs of weed cut from the frond. It is argued that experiments conducted with stable iodine may measure a different variable to that measured in radio-iodine experiments.

Keywords: iodide; iodate; iodine; seaweeds; *Laminaria* sp.; *Fucus* sp.; seawater

1. Introduction

The element iodine is present generally in seawater at a concentration of about 0.45 μM as dissolved iodide and iodate (Sugawara and Terada, 1957; Barkley and Thompson, 1960; Wong, 1991; Truesdale et al., 2000), with a significant organic-I fraction in near-shore environments (Truesdale, 1975; Wong and Cheng, 1998). While iodate represents by far the greatest proportion in the deep sea, iodide can make up approximately one-half in near-surface waters both off temperate coasts (Truesdale, 1978a) and in the tropical and sub-tropical oceans (Elderfield and Truesdale, 1980; Truesdale, 1994a; Truesdale and Bailey, 2002). A small particulate-iodine contribution exists (Wong et al., 1976). In anoxic conditions, e.g., the Black Sea, the Orca Trench, iodide predominates (Wong and Brewer, 1977; Luther, 1991; Truesdale et al., 2001).

The reason for iodide accumulation in oxic waters is by no means clear. Most attention has been given to a phytoplanktonic influence but major inconsistencies still exist. Thus, hydrographic studies of temperate waters do not show any reliable connection between the spring algal bloom and a reduction of iodate concentration (Truesdale, 1978a, 1994b; Truesdale and Jones, 2000). Also, mesocosm experiments

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with added nutrients have not demonstrated any significant reduction (Truesdale et al., 2003a). Finally, although some workers have reported that dense algal cultures reduce iodate (Sugawara and Terada, 1967; Moisan et al., 1994; Chance et al., 2007), others have found it to happen only at higher than ambient concentrations (Waite and Truesdale, 2003), or barely at all (Truesdale, 1978a; Butler et al., 1981). Jickells et al. (1988) and Tian et al. (1996) suggested that iodate reduction in warm ocean waters may be a function of regenerated rather than new production, that is, rely upon such compounds as ammonium rather than nitrate. Meanwhile, the photochemical reduction of iodate, initiated by organic matter, was investigated by Spokes and Liss (1996), with somewhat uncertain results. Also, Truesdale (2007) demonstrated that at natural concentrations in seawater, the known photochemical reduction of iodate by iodide could not account for the degree of iodate reduction in seawater. Against this background, Truesdale and Upstill-Goddard (2003) hypothesised that iodate reduction in temperate coastal waters may depend upon the injection, by tidal-currents, of water into the sedimentary anoxic zone, where iodate could be reduced by reaction with sulfide (Jia-Jhong and Whitfield, 1986). Such a mechanism would only apply to relatively shallow water and would produce a generally diffuse coastal source of iodide. As it could not represent the upper part of the oceanic water column it has the disadvantage that two distinct reduction mechanisms might be needed, one for tropical oceans and another for temperate zone waters. Nonetheless, the sediment-penetration idea would be generally consistent with the two end-member mixing regime for iodate observed on the European shelf, involving onshore and offshore water types. Potentially this eliminates any need to involve estuaries in explaining reduced iodate concentrations in coastal waters. Thus, iodate reduction has been observed in several estuaries (Smith and Butler, 1979; Takayanagi and Cossa, 1985; Upstill-Goddard and Elderfield, 1988) but generally only in the upper, shallow reaches of the estuary (Luther and Cole, 1988; Abdel-Moati, 1999) where it seems to be a bottom-effect. In this laboratory the need to identify an onshore, diffuse source for iodate reduction, with little seasonal variation, is so compelling as to even suggest that beach tidal-flushing should be considered.

The big seaweeds have been inextricably linked to iodine since 1811 when Courtois discovered the element in the ash of burnt *Laminaria digitata* after adding sodium nitrite, and seeing the purple I_2 vapours develop (Partington, 1953). Depending upon local conditions, including geographical position and sea-action, iodine can contribute up to about 1.2% of the dry weight in some seaweeds (Black, 1948; Young and Langille, 1958; Saenko et al., 1978). Shaw (1959) calculated an enrichment factor of about 3×10^4 for *L. digitata.* Ar Gall et al. (2004) reported finding contents as high as 4.7% and even 6.4% in *L. digitata* fronds grown in flowing seawater tanks. In older fronds of *L. digitata* Küpper et al. (1998) found that the younger, fast-growing tissue had lower iodine content than tissue of older parts. Using ^{131}I Baily and Kelly (1955) reported that *Ascophyllum nodosum* assimilates iodide but not iodate from seawater, and they hypothesised that an initial fast phase (minutes) was followed by a slower one of tens of hours. Küpper et al. (1998) also reported an efflux of iodine from *L. digitata*. Shaw (1959) provided a mechanism for iodide uptake by *L. digitata*, linking it to respiration in the seaweed such that I_2 and HOI are produced enzymatically at the seaweed surface, and the HOI is absorbed. The enzymes are now thought to be iodoperoxidases (Küpper et al., 1998; Ar Gall et al., 2004), and Küpper et al. (1998) showed that uptake of iodide by *Laminaria saccharina* and *L. digitata* followed Michaelis–Menten kinetics.

Although relatively few studies have been made (Roche and Lafon, 1949; Scott, 1954; Tong and Chaikoff, 1955; Fenical, 1975; Hou et al., 1997) seaweeds seem to contain iodine both as iodide and a variety of organic-I compounds such as mono and diiodotyrosine. Ar Gall et al. (2004) showed that in *Laminaria digitata* the greater accumulation of iodine in meristematic tissues, as compared to the central blade, probably results from the higher uptake rate of iodide there. The whole curiosity of iodine bio-concentration developed a much wider biological significance when it was proposed that it is part of a defence against herbivores (Fenical, 1975) and microbes (Wever et al., 1991; Küpper et al., 1998). Recently some of the big seaweeds have been found to release significant amounts of a spectrum of haloalkanes, e.g., CH_3I, C_2H_5I, etc., into the atmosphere (e.g., Manley and Dastoor, 1988; Carpenter et al., 2000), which may exert a significant biogeochemical role in forming particles for cloud nucleation (Klick, 1993; McFiggans et al., 2004; Saiz-Lopez et al., 2005). Finally, the uptake of airborne ^{131}I by the brown seaweed *Fucus* sp. was used to monitor the spread of radioactivity following the Chernobyl incident (Druchi et al., 1988).

The possibility has also been considered that excess I_2 from the iodoperoxidase facilitated oxidation of iodide at the weed surface is released to the atmosphere. Within a fraction of a second at 25 °C any biochemically produced I_2 or HOI would come into equilibrium with I_2OH^-, I_2Cl^- and IO^- (Truesdale et al., 1995, 2003b). The chemical kinetics of this iodine system can be modelled simply, using linear combinations of the oxidised species concentrations derived from a redox continuity equation (Truesdale et al., 1995, 2003b). So, provided the rate of biochemical production of I_2 or HOI was much greater than the rate of reduction back to iodide by organic matter (Truesdale et al., 1995), the appearance of I_2 in the atmosphere is feasible. The process would be accelerated if the seaweed surface dried, as I_2 and HOI would be volatilised, whence I_2Cl^- would also give up its I_2.

This paper describes some preliminary experiments conducted in 1969 on the biogeochemical significance of large seaweeds in relation to natural concentrations of dissolved iodide and iodate in seawater. A key difference between this and other work is that it was conducted with whole and undamaged weeds rather than discs cut from fronds. Given the high concentration factor for iodine between weed and water the deliberate laceration of fronds seemed likely to provoke a major loss of iodine which, while perhaps not problematic in a biochemical mechanism study, would invalidate a biogeochemical flux measurement. This investigation was therefore