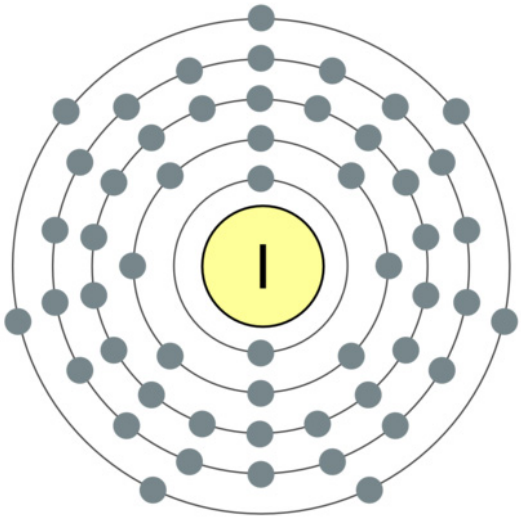
The influence of marine phytoplankton on iodine speciation in the Tropical and Southern Atlantic Ocean



Dissertation

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1. **Manuscript 1:** K. Bluhm, P. L. Croot, J. Schafstall, T. Steinhoff, and K. Lochte. „Speciation of Iodine in the Mauritanian upwelling system and the adjacent Tropical Atlantic Ocean", *manuscript*, 2009.
   Contribution: Katrin Bluhm performed the calculations, evaluated the data and wrote the paper. Peter L. Croot and Karin Lochte assisted with input to the manuscript and revision. Jens Schafstall provided the CTD data and assisted with the hydrography of the study area. Tobias Steinhoff did the flow velocity calculations of the water masses.

2. **Manuscript 2:** K. Bluhm, P. L. Croot, G. Rohardt, and K. Lochte. "Distribution of Iodide and Iodate in the Atlantic sector of the Southern Ocean during austral summer", *Deep Sea Research II*, in revision, 2009.
   Contribution: Katrin Bluhm performed the calculations, evaluated the data and wrote the paper. Peter L. Croot and Karin Lochte assisted with input to the manuscript and revision. Gerd Rohardt provided the CTD data and assisted with the hydrography of the study area.

3. **Manuscript 3:** K. Bluhm, P. L. Croot, K. Wuttig, and K. Lochte. "Transformation of Iodate to Iodide in marine phytoplankton driven by cell senescence", *Marine Ecology Progress Series*, submitted, 2009.
   Contribution: Katrin Bluhm conducted the experiments, performed the calculations, evaluated the data and wrote the paper. Peter L. Croot and Karin Lochte assisted with input to the manuscript and revision. Kathrin Wuttig provided additional experimental data valuable for the manuscript outcome.

In addition I have contributed to the following publications and manuscripts in the EU 6th framework project OOMPH (Organics over the ocean modifying particles in both hemispheres):

1. Yassaa, N., Peeken, I., Zoellner, E., **Bluhm, K**., Arnold, S.R., Spracklen, D.V., Williams, J. (2008): "Evidence for marine production of monoterpenes." *Environmental Chemistry 5*: 391-401

2. Gros, V., Peeken, I., **Bluhm, K**., Zoellner, E., Sarda-Esteve, R., Bonsang, B. (2009): "Carbon monoxide emissions by phytoplankton: evidence from laboratory experiments." *Environmental Chemistry 6*: 369-379

3. Bonsang, B., Gros, V., Peeken, I., Yassaa, N., **Bluhm, K**., Zoellner, E., Sarda-Esteve, R., Williams, J.: "Isoprene emission from phytoplankton monocultures, relationship with chlorophyll, cell volume, and carbon content." *In preparation*

TABLE OF CONTENTS

I.

SUMMARY

I. SUMMARY

The role of halogene species like iodine in the ocean and how their speciation is affected by marine organisms is not well known. This lack of knowledge demands for more detailed field as well as experimental studies in order to unravel the role of iodine in marine ecosystems. My thesis comprises field work on the iodine speciation in polar and tropical marine environments complemented by a set of laboratory experiments on the role of phytoplankton species from the two regions studied for the iodine biogeochemical cycle. A large scale survey across the Atlantic sector of the Southern Ocean and three cruises to the Mauritanian upwelling region during both strong and weak upwelling seasons provide valuable information on iodine speciation over large spatial scales in case of the former survey, and on seasonal variability in case of the latter cruises. Furthermore, comparison of these two oceanic provinces will allow to decipher differences and conformities in iodine speciation between areas as far apart as the Southern Ocean and the Mauritanian upwelling region. In both provinces the total iodine (iodate + iodide) concentrations were in the same range between 450-480nmol L^{-1}, while surface iodide values in the euphotic zone varied considerably and showed a steep vertical concentration gradient of less than 20nmol L^{-1} for antarctic and over 200nmol L^{-1} for tropical waters.

In seawater the interconversion of the two inorganic forms of iodine, iodate and iodide, can be mediated by abiotic and/or biotic processes. The accumulation of iodide in the euphotic zone in both regions is suggested to be a more biologically mediated process and as observed in the experimental studies phytoplankton cells do influence the iodate reduction to iodide. However, highest iodide concentrations were not coupled to highest biological productivity instead we observed highest iodide values during post bloom periods in the respective regions indicating a strong relationship between iodide production and phytoplankton senescence during bloom collapse. Interestingly, productive regions with high phytoplankton biomass measured as chlorophyll-*a* show a decline in surface iodide and also the experimental study revealed an iodide decline in cultures with viable cells suggesting that an iodide oxidation or uptake mechanism is present when cells are in the exponential growth phase.

Upwelled water was lower in surface iodide compared to water from a weak-upwelling scenario, and could on one hand be traced by its lower iodide concentrations while in the Weddell Sea Basin we observed elevated iodide in the deep Weddell Sea Bottom Water (WSBW) which could be traced on the other hand by its elevated iodide concentrations. From these results it appears that iodide can be used as a tracer for upwelled water on continental shelves and for newly formed WSBW.

From the results gained in the laboratory we can say that iodide formation and senescence in phytoplankton cells are coupled. Iodide production was found to be species specific and not related to chlorophyll-a, cell size or cell numbers. Moreover iodide concentrations peaked in the stationary and/or senescence growth phase. A shift from senescence back to the exponential growth phase resulted in a decline in iodide concentrations indicating that phytoplankton-mediated oxidation of iodide to iodate was triggering this shift.

In summary, the results of my thesis show that the combined effects of abiotic and biotic processes resulting in iodate reduction are coupled via phytoplankton senescence. These findings challenge the conventional view, as described in other studies, that iodate reduction in the ocean is directly coupled to nutrient uptake and biological production.

I.

ZUSAMMENFASSUNG

II. ZUSAMMENFASSUNG

Die Bedeutung von Halogen-Verbindungen wie Jod im Stoffkreislauf der Ozeane und die Rolle mariner Organismen für die Steuerung dieser Kreisläufe ist noch weit gehend unerforscht. Diese Arbeit leistet einen wichtigen Beitrag zum besseren Verständnis der Bedeutung von Jod in marinen Ökosystemen durch eingehende Feld- und Laborstudien. Meine Arbeit enthält Felddaten von jodhaltigen Verbindungen aus polaren und tropischen Meeresgebieten die durch Laborexperimente mit verschiedenen Phytoplankton-Arten aus den jeweiligen Meeresgebieten vervollständigt wurden. Die Laborexperimente haben gezeigt, dass alle untersuchten Phytoplankton-Arten an der Umwandlung von Jodat zu Jodid beteiligt sind und somit Phytoplankton-Blüten eine maßgebliche Bedeutung für den Jodkreislauf im Ozean haben. Die großflächigen Messungen im atlantischen Sektor des Südpolarmeeres erlaubten einen umfassenden Überblick über die Verteilung von Jod-Verbindungen in diesem Gebiet wohingegen drei Expeditionen ins Mauretanische Auftriebsgebiet wichtige Erkenntnisse über die saisonale Variabilität von Jod lieferten. Durch den Vergleich dieser beiden Meeresgebiete konnten sowohl die Gemeinsamkeiten als auch die Unterschiede in der Verteilung und relativen Zusammensetzung der Jod Verbindungen aufgezeigt werden.

Die gegenseitige Umwandlung der beiden inorganischen Formen von Jod im Seewasser, Jodat und Jodid, kann über biotische oder abiotische Prozesse erfolgen. Eine Gemeinsamkeit der beiden oben genannten Meeresgebiete ist die Jod-Gesamtkonzentration (Jodat + Jodid) von 450-480nmol L^{-1}, wohingegen große Unterschiede in der Oberflächenkonzentration von Jodid von weniger als 20nmol L^{-1} im Südpolarmeer und mehr als 200nmol L^{-1} in tropischen Gewässern bestehen. Die Akkumulation von Jodid in der euphotischen Zone wird in erster Linie durch biologische Prozesse angetrieben. Wir können dieses anhand unserer Laborexperimente bestätigen in denen ersichtlich wird, dass Phytoplankton die Umwandlung von Jodat zu Jodid stark begünstigt. Allerdings, konnten wir nicht feststellen, dass erhöhte Jodid-Werte an hohe Primärproduktionsraten gekoppelt sind. Vielmehr wurden die höchsten Jodid-Konzentrationen in beiden Meeresgebieten gegen Ende der Blüte gemessen. Diese Beobachtung deutet auf einen Zusammenhang zwischen der Jodid-Produktion und absterbenden Phytoplanktonzellen während des Zusammenbruchs einer Blüte hin. Interessanterweise zeigen Regionen in denen die höchste biologische Produktion stattfindet einen Rückgang in der Konzentration von Jodid-Ionen an der Meeresoberfläche. Diese Feldbeobachtungen konnten durch Laborexperimente bestätigt werden, bei denen die Jodid-Konzentration in wachsenden und gesunden Zellkulturen abnahm. Dies legt die Vermutung nahe, dass Zellen die sich in der exponentiellen Wachstumsphase befinden Jodid oxidieren können.

Während Auftriebsereignissen vor Mauretanien wird mit Jodid angereichertes Wasser aus der Tiefe an die Oberfläche transportiert. Außerhalb der Auftriebssaison sind die Jodid-Konzentrationen im Oberflächenwasser hingegen angereichert. Die niedrigeren Jodid-Konzentrationen während Auftriebsereignissen können daher als „Tracer“ bestimmter Wassermassen verwendet werden. Das gleiche gilt für die erhöhten Jodid-Konzentrationen im Tiefenwasser des Weddellmeeres, wobei Jodid hier anhand seiner erhöhten Konzentrationen verfolgt werden kann. Aufgrund dieser Beobachtungen liegt die Vermutung nahe, dass Jodid als „Tracer“ für Auftriebsereignisse aber auch für die Entstehung von Bodenwasser im Weddellmeer verwendet werden kann.

Die Laborexperimente haben gezeigt, dass die Entstehung von Jodid an den Zelltod von Phytoplankton gekoppelt ist, wobei die Entstehung abhängig von der Art ist und nicht in Zusammenhang mit Chlorophyll-*a*-Gehalt, Zellzahlen oder Zellgröße steht. Die höchsten Jodid-Werte wurden immer in der stationären Wachstumsphase bzw. während des Absterbens der Zellen beobachtet. Versetzt man Zellen aus der absterbenden Phase zurück in die exponentielle Phase kann man einen Rückgang in den Jodid-Konzentrationen feststellen, was auf einen Jodid-Oxidationsprozess hindeutet.

Zusammenfassend deuten die Ergebnisse alle darauf hin, dass die biotischen und abiotischen Prozesse der Jodat-Reduktion miteinander über den Zusammenbruch von Phytoplankton-Blüten verknüpft sind. Bisher hat man angenommen, dass die Jodat-Reduktion direkt mit der Nährstoffaufnahme und der biologischen Produktion gekoppelt ist, welches durch unsere Entdeckungen nun in Frage gestellt ist.

III.

General Introduction

III. GENERAL INTRODUCTION

Understanding the distribution of iodine in the environment is directly important for human health for two key reasons. Firstly, iodine plays an essential role in the human diet and functions of the thyroid glands as iodine deficiency leads to goitre and myxedema. Secondly, radioactive isotopes of iodine (e.g. I^{129}) produced during nuclear fission can accumulate in the thyroid as this organ is very sensitive to iodine concentrations. In the environment the ocean is the major source for iodine with average dissolved concentrations of 450-480nmol L^{-1} (Salinity 35) for all iodine species present (Wong 1991). Rainwater, rivers and lakes only show low levels of iodine (Figure 1; Whitehead 1984). Due to its great abundance in seawater iodine is mainly found in seafood and sea salt for which reason the sea salt was already used as a treatment of goitre in the early 19th century (Rosenfeld 2000).

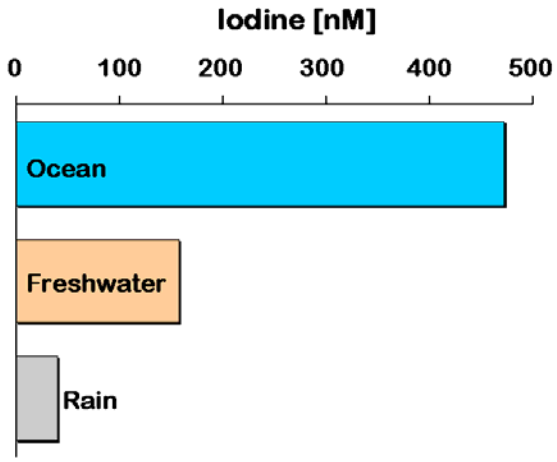

Figure 1: Iodine sources in the hydrosphere

Iodine is a non metal solid chemical element belonging to the halogens in Group 17 of the periodic table. This group comprises fluorine, (F); chlorine (Cl); bromine, (Br); iodine, (I); and astatine, (At). Due to their high reactivity, the halogens are likely to form complexes with other elements of the periodic table and are only found in the environment as either compounds or as ions. Halogen literally means "salt producers" as they react with metals to form salts like potassium iodate. Halide ions such as iodide (I^-) and oxyanions such as iodate (IO_3^-) can be found in many minerals and in seawater. In its elemental form, iodine exists as a diatomic molecule (I_2), which has only a fleeting existence in nature due to its reactivity (Mortimer 1975).

Iodine from the sea is transferred to the atmosphere where it can be transported over land and fall as precipitation onto soils and finally incorporated into plants and animals where it provides the main source of natural iodine for the human population. More recently new aspects of the iodine cycle have been identified that affect human health and quality of life indirectly via connections to climate change and O_3 loss. Therefore it is clear that studying the pathways of iodine in the environment is of great interest for human and animal health.

1. The biogeochemical cycle of iodine in the environment

Iodine has recently been identified as a potentially key element involved in climate change, as iodine emissions from the ocean can influence the formation of new aerosol particles with impacts on cloud formation and radiative balances. The source and mechanism of iodine emissions from the ocean are poorly understood as are other more fundamental aspects of iodine biogeochemistry in seawater such as the cycling between the major iodine species; iodate (IO_3^-) and iodide (I^-).

1.1. Iodine in the atmosphere

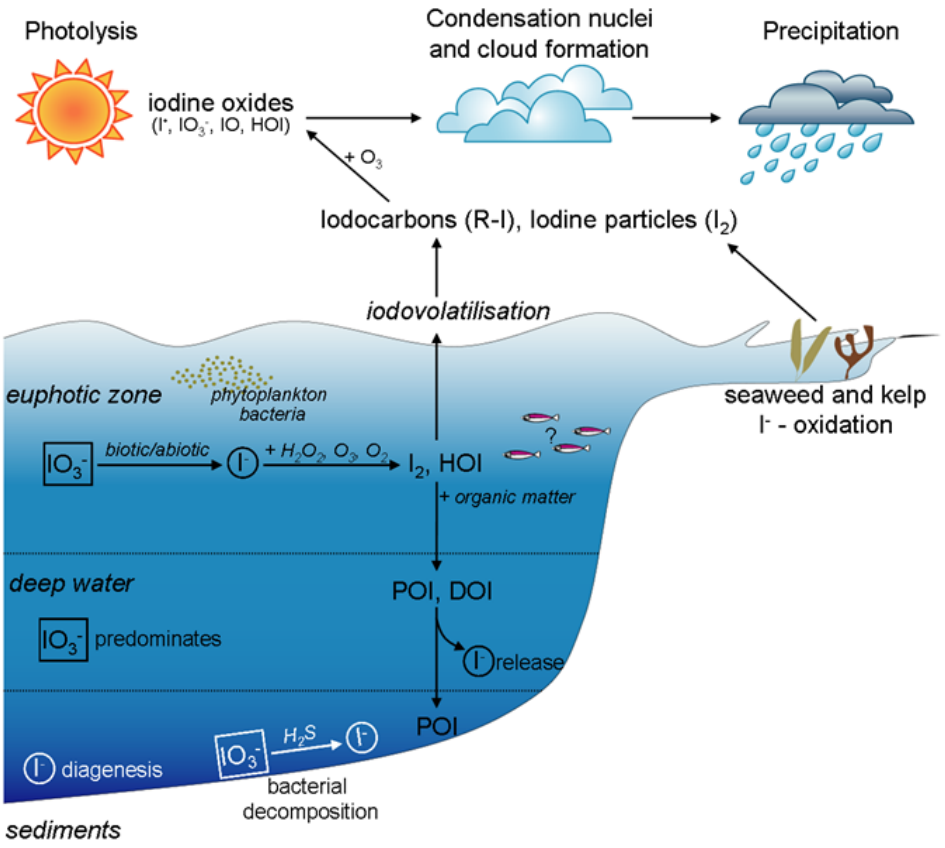

Figure 2: Iodine biogeochemical cycling in the marine environment and the atmosphere (modified after Leblanc et al. (2006)).

Iodine chemistry in the atmosphere is important as iodine released from the ocean is believed to be a source of new particles to the atmosphere (O'Dowd et al. 2002). The main flux from the ocean to the atmosphere is dominated by marine emissions of volatile organoiodine compounds (VOI's = R-I in Figure 2) such as methyl iodide (CH_3I) or diiodomethane (CH_2I_2; Carpenter et al. 2007). In seawater these VOI's are formed by reactions between dissolved organic compounds and iodine species via photolysis reactions

(Moore & Zafiriou 1994, Richter & Wallace 2004, Martino et al. 2009) or bacterial action (Amachi et al. 2001, Manley 2002). Gases such as CH_3I and CH_2I_2 are relatively short-lived in the atmosphere as sunlight and reactions with ozone (O_3) readily break the C-I bond producing iodine radicals ($I^{\bullet}$, IO, HOI, Figure 2; Garland & Curtis 1981, Martino et al. 2006) which form particulate aerosol iodine species (Hoffmann et al. 2001, von Glasow 2005). Aerosol particles act as cloud condensation nuclei (CCN) later followed by precipitation which brings the iodine back onto the earth's surface. The radiative reflectance of clouds (cloud albedo), and thus the cooling of the earth's surface, is sensitive to the CCN density which influences the radiation budget and climate (Charlson et al. 1987).

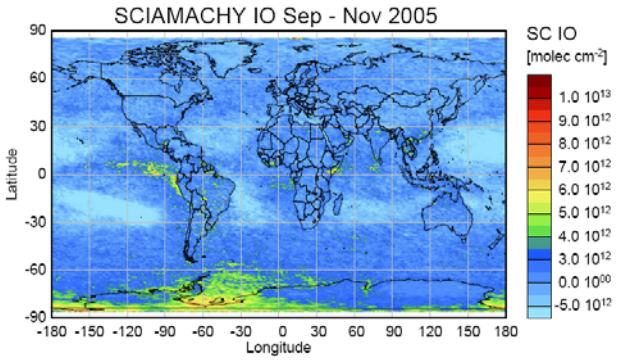

Figure 3: Iodine oxide concentrations as retrieved from SCIAMACHY satellite measurements averaged over three months (September to November 2005). Schonhardt et al. 2008

Satellite observations over the globe indicate high concentrations of IO in the Antarctic atmosphere with the Weddell Sea identified as one of the key source regions (Figure 3; Schonhardt et al. 2008).

1.2. Iodine in seawater

In fully oxygenated seawater (pH 8.0, pЄ 12.5) dissolved inorganic iodine is present as iodide and iodate while iodate is more stable and, at thermodynamic equilibrium, should be the only detectable form of iodine (Luther et al. 1995). However, iodide is often accumulating in surface waters and oceanic depth profiles tend toward a mirror image profile for iodate and iodide, where iodate has its minimum and iodide its maximum at the sea surface (Figure 4; Wong 1991). This phenomenon occurs to the greatest extent in tropical and subtropical waters (Tsunogai & Henmi 1971, Jickells et al. 1988, Campos et al. 1996, Truesdale et al. 2000). The accumulation of iodide in surface waters is still somewhat mysterious; neither its sources nor its sinks are well understood.

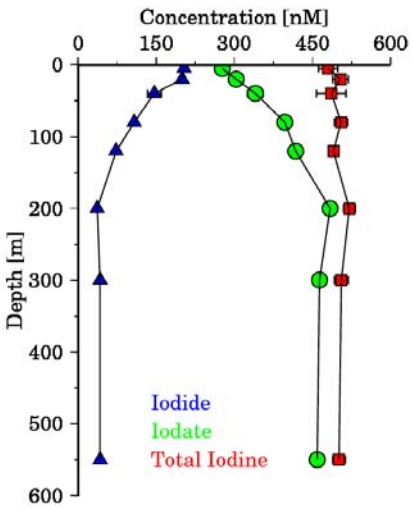

Figure 4: Typical vertical profiles of iodide, iodate, and total iodine in seawater from the Tropical Atlantic Ocean (own data).

It has been suggested that the relatively high concentrations of iodide in surface waters are related to primary productivity (Tsunogai & Henmi 1971, Elderfield & Truesdale 1980, Jickells et al. 1988, Moisan et al. 1994, Campos et al. 1996, Truesdale et al. 2000). In deeper waters, below the euphotic zone, iodide decreases to low levels (<5nmol L^{-1}), while iodate increases to a relatively constant level of about 450nmol L^{-1}. Molecular iodine is only a transient species due to its fast reactivity with organic matter (Truesdale 1974, Wong 1991) and loss to the atmosphere (O'Dowd et al. 2002).

1.2.1 Chemical pathways

The cycling between the two inorganic forms of iodine, iodate and iodide, in seawater can be driven by chemical processes. They include the reduction of iodate to iodide and the reverse oxidation of iodide to iodate. For a better understanding of the iodine species and their cycling in seawater the standard reduction potentials are listed in Figure 5.

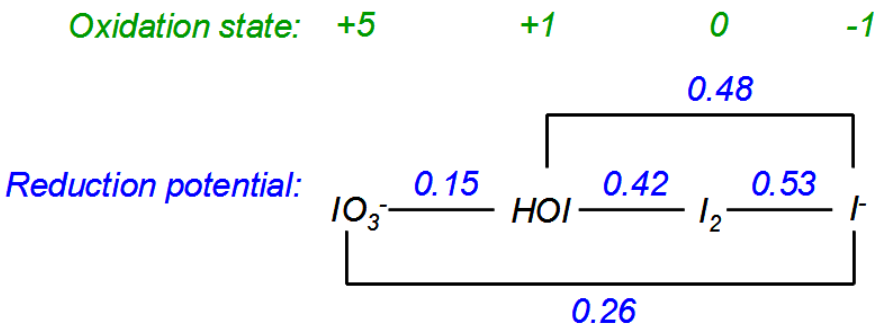

Figure 5: Standard iodine reduction potentials in seawater. In basic aqueous solutions the reduction potential, given in volts (V), is a measure of the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species affinity for electrons and tendency to be reduced.

1.2.1.1. Iodate reduction

In the past, several possible abiotic mechanisms have been suggested to reduce iodate to iodide and are listed in Table 1. These reactions include the direct chemical reduction of iodate by bisulphides under anoxic conditions (Jiazhong & Whitfield 1986), by Mn(II) which has been suggested to reduce iodate in sediments (Anschutz et al. 2000), and by other reduced sulphur species (thiols) like glutathione (GHS) (Hird & Yates 1961). GSH, an antioxidant, helps to protect cells from reactive oxygen species such as free radicals and peroxides and functions as a reducing agent (Eq.1).

$$IO_3^- + 6GSH \rightarrow 3GSSG + 3H_2O + I^- \quad (1)$$

Photochemical reactions which lead to photoreduction (reduction reactions that takes place in the presence of light) may also be important. Photoreduction of iodate catalyzed by reactions with dissolved organic matter (DOM) was suggested in experiments by Spokes and Liss (1996), where they observed photochemically induced iodide production dependent on the concentration of DOM. However, a 2h time lag between the start of UV-irradiation and significant iodide production suggests that it is not a direct photochemical reaction but the result of a subsequent secondary reaction.

Table 1: Possible mechanisms for the reduction of iodate to iodide in seawater identified in published studies. At seawater pH bisulphide (HS^-) and manganese (Mn(II)) directly reduce iodate to iodide under anoxic conditions. Glutathione, an antioxidant in living cells, was also found to directly reduce iodate to iodide within minutes. For the photoreduction (reduction reaction that takes place in the presence of light) organic matter is essential to reduce iodate to iodide. During photoinhibition (inhibition of algal photosynthesis by high light intensities) iodate might be used to mop up electrons which are present in excess of photosynthetic needs.

Process	Biotic/Abiotic	Rate	Reference
Photoreduction	abiotic	5nM h^{-1}	Spokes and Liss 1996
Bisulphide	abiotic	pM-nM d^{-1}	Jiazhong & Whitfield 1986
Glutathione	abiotic	unknown	Hird & Yates 1961
Mn(II)	abiotic	unknown	Anschutz et al. 2000
Photoinhibition	biotic	unknown	Waite & Truesdale 2003
Bacterial reduction	biotic	unknown	Farrenkopf et al. 1997
			Amachi et al. 2007
Nitrate reductase	biotic	--	Tsunogai & Sase 1969
		8-19pM (µg chl-*a*)$^{-1}$ d^{-1}	Hung et al. 2005
Zooplankton activity	biotic	unknown	Brandao et al. 1994

1.2.1.2. Iodide oxidation

The mechanisms of iodide oxidation in the environment are even more unclear. Under conditions prevailing in marine waters the complete oxidation of iodide to iodate is an extremely slow chemical process, since iodide seems to be inert under these conditions, with residence times of years (Wong 1991, Luther et al. 1995, Truesdale 2007). Direct

photochemical oxidation of iodide may only occur at the air-sea interface with the help of strong UV-radiation (Eq. 2) or strong oxidants like hydrogen peroxide (Eq. 3), ozone (Eq. 4) and molecular oxygen (Eq. 2); initially I_2 and HOI are formed. The reaction with hydrogen peroxide is the slowest among the reactions at seawater conditions (Wong & Zhang 2008).

$$2I^- + 0.5O_2 + H_2O \xrightarrow{h\nu} I_2 \uparrow + 2OH^- \quad (2)$$

$$I^- + H_2O_2 \longrightarrow HOI + OH^- \quad (3)$$

$$2I^- + O_3 + 2H^+ \longrightarrow I_2 \uparrow + O_2 + H_2O \quad (4)$$

An equilibrium is rapidly established between I_2 and HOI in aqueous solutions and at seawater pH this equilibrium favours HOI over I_2.

$$I_2 + OH^- \longrightarrow HOI + I^- \quad (5)$$

The two intermediates, I_2 and HOI, can on one hand be volatized back to the atmosphere but can also react further with dissolved organic matter (DOM) in seawater (Truesdale et al. 1995) and form dissolved or particulate organic iodine (DOI and POI), the latter sinking out of the water column to the seafloor taking the bound iodine with it (Figure 2). However, the oxidation of I_2 and HOI to iodate is surprisingly poorly understood and under seawater conditions most common abiotic processes are too slow to be important; it is suggested that this process must also be biologically mediated (Luther et al. 1995).

1.2.2. Biological pathways

Although abiotic mechanisms have been proposed for the cycling of iodine species the presence of iodide in the surface waters and the occasionally appearance of a sub surface drawdown in iodide is ascribed to biological activity due to the inertness of the two inorganic iodine species under seawater conditions (Tsunogai & Henmi 1971, Truesdale 1978, Wong 1991, Luther et al. 1995, Campos et al. 1996).

1.2.2.1 Iodate reduction

There is evidence that biological processes and in particular the phytoplankton community play an important role in the reduction of iodate to iodide (Eq. 6 and Table 1).

$$IO_3^- + 6H^+ + 6e^- \xrightarrow{abiotic/biotic} I^- + 3H_2O \quad (6)$$

A number of laboratory experiments (Sugawara & Terada 1967, Moisan et al. 1994, Wong et al. 2002, Chance et al. 2007) have shown that marine phytoplankton are able to reduce iodate to iodide to varying degrees. A comprehensive study examining the reduction of

iodate to iodide was carried out by Wong et al. (2002). In this work the six different phytoplankton species tested were able to reduce iodate to iodide and the rates of iodate depletion were noticeably faster than the rates of iodide formation, suggesting that also other iodine species had formed apart from iodide. A further set of experiments by Chance et al. (2007), examined changes in the speciation of inorganic dissolved iodine in nutrient-enriched seawater mediated by cold water diatoms. A *Nitzschia* species removed nearly 100% of the iodate from the growth media during the exponential growth phase and produced iodide at rates of 0.03 and 3nmol L^{-1} µg chl-*a*$^{-1}$ day^{-1}, depending on the iodate concentrations present. They believed that an iodide removal mechanism began to operate in the stationary growth phase as the iodide levels peaked during that phase of growth. Contrastingly, Butler et al. (1981) observed little or no conversion of iodate to iodide during the exponential phase of growth and iodate was transferred to iodide only in senescent cultures of the diatom *Skeletonema costatum*. These authors concluded that the reaction might be carried out by bacteria present in the senescent cultures as marine bacteria are likewise able to perform this reduction reaction (Amachi et al. 2007a).

In the field areas with high biomass generally do not correspond to regions with the highest iodide concentrations (Elderfield & Truesdale 1980). Thus, additional reduction mechanisms must occur including abiotic reduction as proposed in several works named above (Jickells et al. 1988, Spokes & Liss 1996, Truesdale 2007). Tian (1996) observed during a study over an annual cycle in the Mediterranean Sea that iodide concentrations varied considerably throughout the year and that the transformation from iodate to iodide was apparently linked to the regenerated production of phytoplankton. Primary production decreased in late spring continuing until a low level of production was reached towards winter while iodide concentrations began to increase in late spring and reached a maximum in late autumn.

1.2.2.2. Iodide oxidation

Biologically mediated iodide oxidation is still poorly understood although it has been considered that microorganisms such as *Pseudomonas iodooxidans* participate in the oxidation of iodide to I_2 (Gozlan & Margalith 1973, 1974). Amachi et al (2005) demonstrated that the iodide-oxidizing process is mediated by the extracellular enzyme iodide oxidase in marine *Proteobacteria*. Until now it is not clear whether biological processes can accelerate the iodide oxidation rates in seawater or if other processes control the iodate load in deeper water like vertical mixing.

Finally, at present no mechanism for iodide oxidation through to iodate has been identified although iodate's preponderance in deep ocean waters is strong proof that such a mechanism must exist (Luther et al. 1995, Edwards & Truesdale 1997).

2. Iodine metabolism

Iodine is a biophilic element and accumulates in various organisms including algae, shellfish and vertebrates. The first measurements of iodine accumulation in marine phytoplankton have been described by Sugawara and Terada (1967). The diatom *Navicula sp*. assimilated both, iodate and iodide, although iodide was the preferred form. Until now, iodine uptake has been characterized for the thyroid glands of mammals, in brown algae and marine phytoplankton but also in marine bacteria (Sugawara & Terada 1967, Gozlan & Margalith 1974, Küpper et al. 1998, Smyth & Dwyer 2002, Amachi et al. 2007b, de la Cuesta & Manley 2009).

2.1. Cellular pathways

In mammals iodide ions are taken up by the thyroid, mediated via the sodium/iodide symporter, so-called because it co-transports sodium (Na^+) with iodide (I^-) into the thyroid against the concentration gradient. The driving force for this process is the electrochemical gradient of sodium ions across the cell membrane. Possession of such a symporter enables the thyroid to concentrate iodide 20-40-fold (Smyth & Dwyer 2002). Küpper et al. (1998) proposed that iodide accumulation in brown algae like *Laminaria spp*. starts at the cell wall with the help of the enzyme haloperoxidase. Haloperoxidases are known to catalyze the oxidation of halides (e.g. I^-) to hypohalides (e.g. HOI) by hydrogen peroxide (Eq. 3). The evolved HOI (hypoiodous acid) can then freely penetrate algal cell walls by facilitated diffusion (Figure 6). However, the physiological functions and chemical form of iodine inside the algal cells, presumably iodide, are still unclear. Recently, de la Cuesta and Manley (2009) showed that iodide accumulation is present in various marine phytoplankton. Diatoms exhibited the highest accumulation rates and iodide was the preferred chemical species of iodine for uptake under nitrate-replete conditions. A schematic picture of a phytoplankton cell and the iodine pathways are shown in Figure 6.

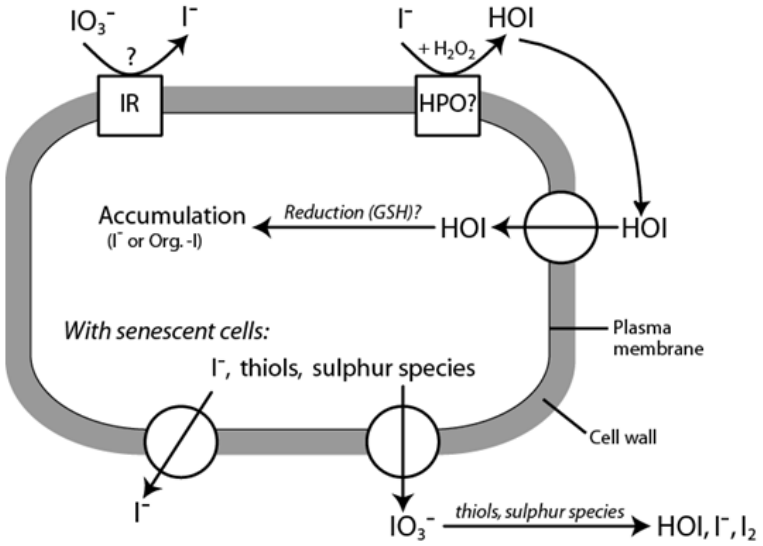

Figure 6: Schematic picture of a phytoplankton cell showing the mechanisms of iodine uptake and release of cellular components with senescent cells. IR: Iodate reductase; HPO: Haloperoxidase; GSH: Glutathione. Other abbreviations are explained in the text. (modified after Amachi et al.(2008)).

First, iodate is reduced to iodide by a membrane bound iodate reductase. Second, the iodide ion is oxidized to HOI by hydrogen peroxide and a haloperoxidase. The required hydrogen peroxide originates through leakage of internal produced hydrogen peroxide via the Mehler reaction (Mehler 1951) and from extracellular production by an enzymatic reduction of oxygen at the cell surface (Palenik et al. 1987). The HOI being an uncharged molecule can freely pass through the cell wall and once inside the cell it is believed to be reduced back to iodide by reactions with cellular components like glutathione (GSH) and bound intracellular (Shaw 1959, Gutknecht 1965).

Upon cell senescence and death cells lyse and release cellular metabolites especially reduced sulphur compounds such as sulphide and glutathione (GSH) into the surrounding medium. Sulphur is essential for all organisms as it is required for protein synthesis. GSH is often the most abundant amino acid and intracellular thiol in all eukaryotes and some prokaryotes. A major role of GSH is the detoxification of ROS (reactive oxygen species) in the chloroplast, where it acts as an intermediate for the removal of superoxide radicals which can occur during photosynthesis (Polle & Rennenberg 1992). The release of these cellular metabolites which are present in high concentrations inside phytoplankton cells are able to reduce iodate to iodide under typical seawater conditions (Hird & Yates 1961).

2.1.1. Iodate reduction by nitrate reductase

One possible explanation for the active reduction of iodate in phytoplankton and bacteria was first postulated by Tsunogai and Sase (1969). They accused the enzyme nitrate reductase, possibly due to the chemical similarity of iodate and nitrate, and showed that marine bacterial nitrate reductase reduced iodate to iodide when nitrate is limiting. A hypothesis which had grown out of earlier findings by Egami and Sato (1947) who had shown that chlorate was reduced to chlorite by nitrate reductase because of the similarity of the chlorate ion to the nitrate ion. The reduction of iodate to iodide is slower than the chlorate reduction but faster than the nitrate reduction hence nitrate reductase is capable to reduce iodate to iodide. Later field observations appeared to support this linkage between iodate reduction and nitrate uptake in general, which lead to the idea of using iodide concentrations as an indicator for nitrate uptake by phytoplankton (Elderfield & Truesdale 1980, Tian & Nicolas 1995, Wong & Hung 2001). More recently though, Waite and Truesdale (2003) discovered that the reduction of iodate to iodide was independent of the presence of nitrate reductase activity in cultures of the microalgae *Isochrysis galbana*, a marine prymnesiophyte. The enzyme was de-activated by growing the algae with tungsten instead of molybdenum and supplying ammonium instead of nitrate as a nitrogen source. Nevertheless, iodide was produced but the production pathway, while not nitrate reductase, was not determined. This conflicts with other studies using radiotracers (Hung et al. 2005) which apparently demonstrates a relationship between iodate reduction and nitrate reduction. At present, the possible role of nitrate reductase in reducing iodate to iodide is still unclear.

3. Species used in the experiments

In **Manuscript 3** the influence of phytoplankton on the chemical cycle of iodine in seawater was examined. The species used (four Antarctic diatoms, one coccolithophore and one dinoflagellate), represented coastal and oceanic species from cold to temperate waters. The following brief description highlight the variety of shapes and sizes represented by the five phytoplankton species used in the experiments and indicate their role for pelagic ecosystems and biogeochemical cycles.

3.1. Southern Ocean Diatoms

Diatom blooms are a common phenomenon during periods of new production. They drive the biological carbon pump (BCP) and hence play a major role in the oceans carbon

cycle (Falkowski et al. 1998). Furthermore the silica cycle of the ocean is largely dominated by diatoms that incorporate silicic acid into their frustules (Ragueneau et al. 2000).

The pennate diatom ***Fragilariopsis kerguelensis*** is characterized by its heavy silicified ribbed frustules that are joined along their valve faces in curved ribbon-like chains that can be over 100 cells long under favourable conditions (Figure 7a). The shape of the frustule and the cell size can be quite variable (10 to 90 µm in apical length) and empty cells are frequent within chains of this species (Tomas et al. 1997). *F.kerguelensis* is endemic to the Southern Ocean and among the most abundant diatom species in this area. It abounds mainly in the ice-free, open Antarctic Circumpolar Current (ACC). Because of its high abundance and heavily silicified cell walls which are very resistant to dissolution the frustules of *F.kerguelensis* are among the main contributors of the diatom ooze accumulating under the ACC (Zielinski & Gersonde 1997, Smetacek 2000). Thus, *F.kerguelensis* constitutes a major silica-sinker in an otherwise iron-limited ecosystem due to its morphological and ecological properties and makes it by far the most important diatom species in the global silicon cycle.

Within the centric genus *Chaetoceros* most bloom-forming species belong to the subgenus *Hyalochaete*. Many of these species display a cosmopolitan distribution with some species also penetrating into the Antarctic Zone. Due to their weak silification the vegetative cells of these species usually dissolve before reaching the sediment. However, the bloom-forming species are capable of converting vegetative cells into thick-walled resting spores that overwinter (Smetacek et al. 2004). The *Hyalochaete* species ***Chaetoceros debilis*** forms chains that are connected by thin and hyaline spines (Tomas et al. 1997). Usually, in the field, the spines are bent in one direction so that the algae form spiralling chains. However, in culture the chains do not curve and are somewhat shorter (Figure 7f).

The genus *Pseudo-nitzschia* shows a widespread distribution throughout the world ocean with ***Pseudo-nitzschia turgiduloides*** being almost exclusively observed in the Antarctic zone with greatest abundances near the ice-edge. This species is likely to be one of the endemic species to the Antarctic Ocean (Medlin & Hasle 1990). A characteristic feature of these pennate diatoms is the chain formation by overlapping of the cell ends, i.e. stepped colonies (Medlin & Hasle 1990). Lately this group has gained more and more attention due to the production of the toxin domoic acid in various *Pseudo-nitzschia* species although *P.turgiduloides* was not among them (Figure 7c).

The centric diatom ***Eucampia antarctica*** grows in long vegetative chains spiralling in broad girdle view under favourable conditions (Figure 7b) This conspicuous species is confined to southern cold water regions and its cells are lightly silicified although heavy silicified winter stages have also been observed (Fryxell 1989). In some parts of the

Southern Ocean this species has been reported as a dominant constituent of the phytoplankton assemblage (Froneman et al. 1997, Ward et al. 2006).

3.2 Temperate species

The two temperate species used in the experiments were both isolated from the North Sea. The dinoflagellate ***Scrippsiella trochoidea***, like most dinoflagellates forms cell walls of polysaccharide plates (cellulose) that are arranged in a species-specific pattern (called Kofoidian plate tabulation). Small-celled dinoflagellates (~10-20µm) like *Prorocentrum*, *Heterocapsa* and *Scrippsiella* commonly form blooms subsequent to the spring diatom bloom in coastal and shelf areas. The solitary pear shaped cells of *S.trochoidea* (Figure 7d) have a mixotrophic nutritional mode and are able to perform phagotrophy. *S.trochoidea* is a cosmopolite found in the neritic and estuarine environment and is the most commonly recorded planktonic scrippsielloid dinoflagellate (Tomas et al. 1997).

The calcareous coccolithophore ***Emiliania huxleyi*** belongs to the group of haptophytes (prymnesiophyres) and forms blooms in both coastal and open-ocean regions (Figure 7e). The small single cells are usually covered with calcareous plates or coccoliths consisting of calcium carbonate (Tomas et al. 1997). Coccolithophores can form extensive oceanic blooms normally after the diatom dominated spring bloom and are second in importance to the diatoms. Blooms of *E.huxleyi* are regularly terminated by the spread of viral infection within the population (Wilson et al. 2002). *E.huxleyi* contributes only a minor fraction to the total calcareous material accumulating in the deep North Atlantic despite its enormous abundance. Other species like *Calcidiscus leptoporus* are more heavily calcified and are therefore the main contributor to the calcareous sediments although being less abundant. A common characteristic of this group is the production of dimethylsulfoniopropionate (DMSP), which is split by an enzyme inside the cell to form volatile dimethylsulfide (DMS) and noxious acrylic acid (Malin et al. 1993, Matrai & Keller 1993).

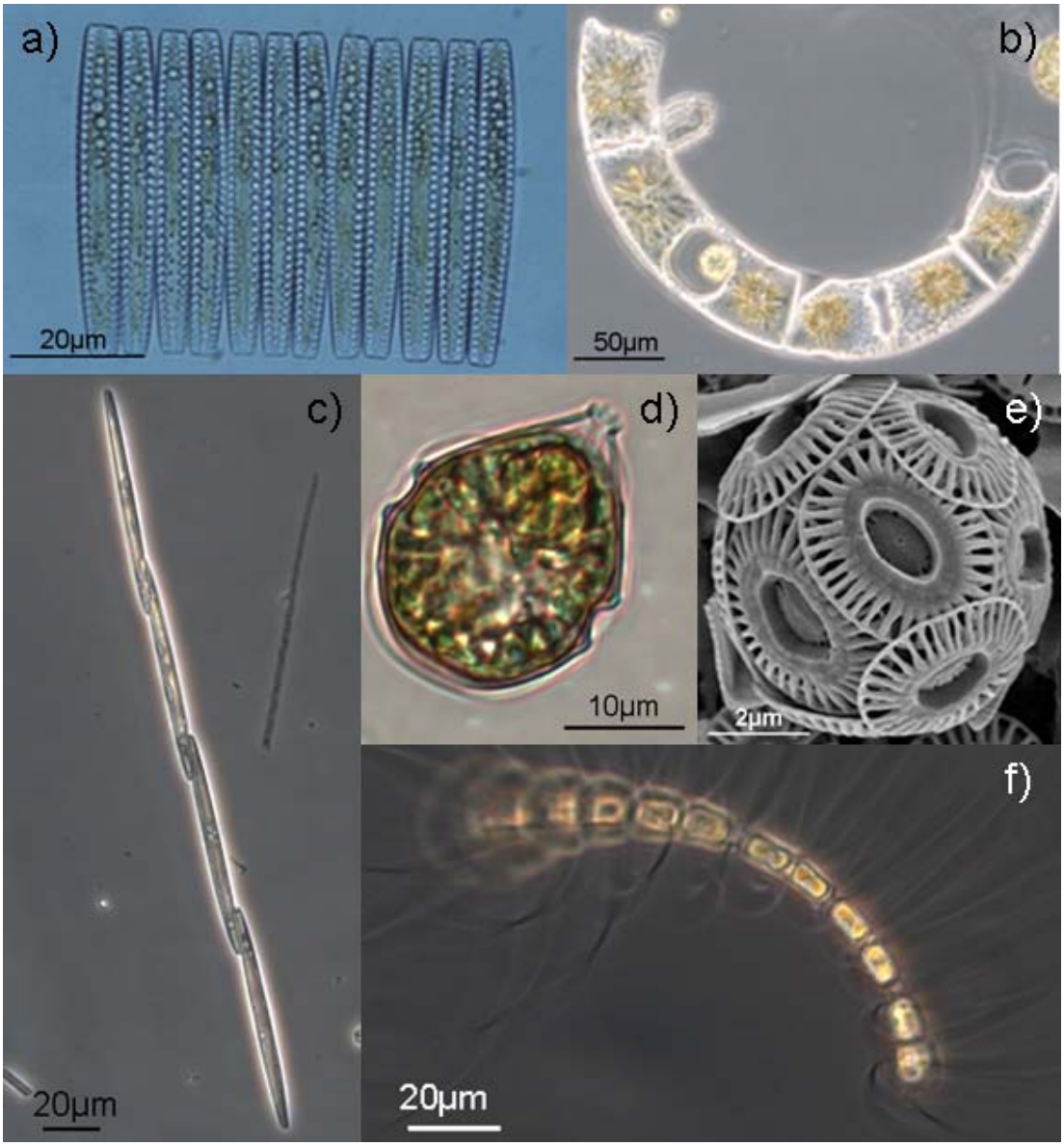

Figure 7: Pictures of a) a chain of *Fragilariopsis kerguelensis*, b) a chain of *Eucampia antarctica*, c) stepped colonies of *Pseudo-nitzschia turgiduloides*, d) a solitary cell of *Scrippsiella trochoidea*, e) a single cell of *Emiliania huxleyi* and f) a chain of *Chaetoceros debilis*. Light micrographs a), b), c) and f) have been kindly provided by P. Assmy. Light micrograph d) was kindly provided by M. Montresor. Scanning electron micrograph e) was taken by M. Müller.

4. Study areas

In the following work two oceanic regions were examined for iodine speciation. First, the Atlantic sector of the Southern Ocean during *RV* Polarstern cruise ANTXXIV-3 and second in the Mauritanian upwelling and the adjacent Tropical Atlantic Ocean during three cruises with *RV* Meteor (M68-3), *RV* Poseidon (P348) and *RV* L'Atalante (L'ATAIII; Figure 8)

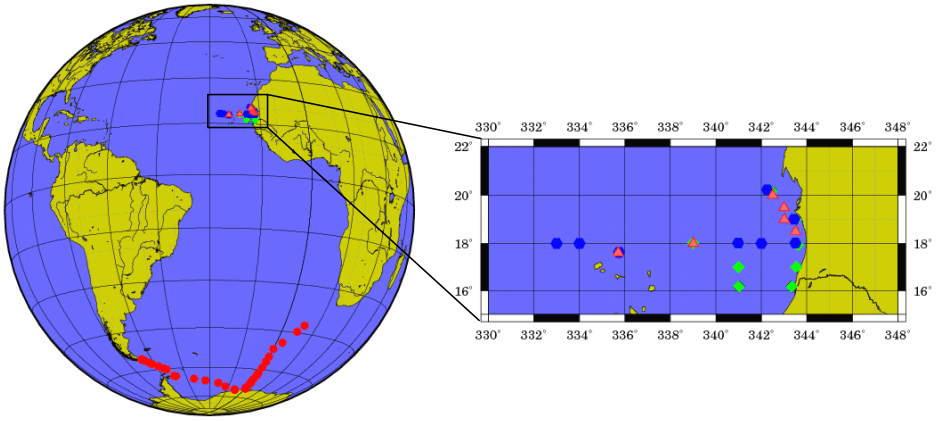

Figure 8 Areas studied in the course of this thesis showing the station locations of ANTXXIV-3 (red circles), M68-3 (blue circles), P348 (red triangles) and L'ATAIII (green diamonds).

4.1. Southern Ocean

The iodide concentrations in cold Antarctic surface water are generally low but the biogeochemistry of iodine in high latitude areas and particular in the Southern Ocean is relatively unknown at present with only two published studies (Tsunogai & Henmi 1971, Campos et al. 1999). Tsunogai and Henmi (1971) reported high surface iodide values of ~100nmol L^{-1} at a single vertical profile from 60°00S, 169°55W in the Pacific. In the more southern stations iodide concentrations were low in surface waters. Campos et al. (1999) undertook a section which ran along the WOCE A23 transect from the Weddell Sea at 75ºS to about 25ºS in March-May 1995. In this work they found a systematic increase in iodide in surface waters (0-100m) from south to north with lowest iodide values of ~20nmol L^{-1} in the Weddell Sea increasing to >100nmol L^{-1} towards the north. At depth greater than 100m iodide concentrations dropped below the detection limit of 0.15nmol L^{-1}. They also suggested that the cycling of iodine was different in the various sectors of the Southern Ocean resulting in different nitrate: iodide ratios in the surface waters. Unfortunately, Campos et al. (1999) had no supporting productivity or chlorophyll-*a* data for their work.

4.2. Tropical Ocean

Most iodine studies have been confined to temperate and tropical regions (Tsunogai & Henmi 1971, Jickells et al. 1988, Tian & Nicolas 1995, Campos et al. 1996, Truesdale et al. 2000, Truesdale & Bailey 2002) where iodide was found to accumulate in the surface while iodate values declined. The biophilic nature of iodine and the appearance of iodide in the euphotic zone gave rise to the idea that iodate reduction is influenced by biological activities. This was further supported by field observations where iodate and nutrient concentrations correlated well (Wong et al. 1976, Elderfield & Truesdale 1980, Truesdale et al. 2000) and surface iodate decreased towards the more productive equatorial regions (Tsunogai & Henmi 1971, Jickells et al. 1988, Campos et al. 1996, Truesdale et al. 2000). Up to now, these productive oceanic areas with marked nutrient loss have shown greater iodate reduction although in highly productive upwelling regions this could not be observed (Truesdale & Bailey 2000, 2002, in preparation). However, all these observations were particularly evident in the tropical and subtropical ocean and could not be re-observed in temperate (Truesdale & Jones 2000) or Polar regions (Tsunogai & Henmi 1971).

5. Aims and outline

Currently little is known about iodine speciation in the oceans and what controls iodate reduction and iodide oxidation there. This includes the central question in iodine oceanic research at present of whether iodate reduction is driven by primary production, via direct biologically mediated uptake, or alternatively it is mainly from chemical redox reactions which in part may be connected to the release of substances from the decay of biological materials. The ocean is a great natural laboratory with which to address some fundamental questions regarding iodine biogeochemistry. By undertaking a combined laboratory and field work program we tested the validity of the hypothesis that links primary production to iodate reduction and examined alternative hypothesis concerning potential chemical reduction pathways. This dissertation is based on three individual manuscripts that examined the following topics:

Manuscript 1 presents results on the biogeochemistry of iodine in the Mauritanian upwelling region and the adjacent Tropical Ocean during two different seasons. Iodine data were collected on three cruises: one in summer, while there was only weak upwelling present and two in winter during the upwelling season. Iodide had been proposed as a complimentary tracer for upwelling on continental shelves (Wong et al. 2004). Therefore, one aim of this study was to compare sea surface iodide concentrations at different upwelling seasons. A further aim was to distinguish between a productive (strong upwelling) and a

less-productive (weak upwelling) season and determine how iodine chemistry is connected to biological processes in the euphotic zone.

Manuscript 2 focuses on the speciation and distribution of iodine in the waters of the Atlantic sector of the Southern Ocean. Several vertical profiles were obtained along the Zero Meridian, in the Weddell Sea and Drake Passage. High latitude areas and particular the Southern Ocean are relatively unstudied areas for iodine and iodine research is still in its infancy here. Satellite data for iodine monoxide (IO; section 1.1.) suggest that the Weddell Sea is a major source region to the atmosphere (Figure 3). The aim of this study was to improve our understanding of the Southern Ocean biogeochemistry of iodine and whether iodine speciation is changing due to different physicochemical characteristics of this region compared to the tropical study in manuscript 1.

Manuscript 3 describes the transformation of iodate to iodide by marine phytoplankton. Iodine changes in the euphotic zone in the tropical and southern Atlantic Ocean lead to the suggestion that phytoplankton play an important role in iodine speciation. Cold water and species from the oceanic areas studied in manuscripts 1 and 2 were tested for their capability to reduce iodate to iodide under nitrate replete conditions. The aim of this study was to examine if all species tested are able to perform iodate reduction and under which environmental conditions this reduction takes place. Another issue was to detect whether the reduction mechanism is actively done by the phytoplankton present or if the reaction is more a subsequent passive production via the reaction with organic compounds.

This thesis will be completed by a comprehensive Synthesis, discussing the results and embedding them into current knowledge of iodine speciation, as well as by a personal outlook on important future perspectives emerging from this work.

IV.

MANUSCRIPTS

MANUSCRIPT 1

Speciation of iodine in the Mauritanian upwelling system and the adjacent Tropical Atlantic Ocean

Speciation of Iodine in the Mauritanian Upwelling system and the adjacent Tropical Atlantic Ocean

by

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Keywords: Iodine speciation, iodide, iodate, nutrients, tracer, Mauritanian upwelling

ABSTRACT

Iodide, iodate and total iodine concentrations have been measured along the coast of NW Africa, between Cape Blanc in the north and Cap Vert in the south (16°-19.5°N) during two strong and one weak upwelling seasons. Total iodine values lay within the range of previous studies (451nmol L^{-1} in average) and iodate reduction was greatest during the low upwelling season in the boreal summer. Thus iodide concentrations correlated positively with temperature; higher iodide came along with higher temperatures. Upwelled water was characterized by cold (<19°C), nitrate-rich (> 4µmol L^{-1}) and iodide-poor (<83nmol L^{-1}) water which could be traced farthest away from its source by the lower iodide concentrations. Highest iodide concentrations were not coupled to highest biological productivity. Instead in the upwelling area with a constant nutrient supply and high chlorophyll-*a* concentrations an iodide oxidation mechanism seems to be present as iodide is declining. During weak upwelling when stratification is present in the water column, high UV-radiation at the sea surface is suspected to cause iodide production through reactions with dissolved organic matter. These findings challenge the conventional view, gained from other tropical and subtropical studies, that iodate reduction in the ocean is coupled to nutrient uptake and biological production.

1. INTRODUCTION

The overall biogeochemical cycle of iodine in the ocean consists mainly of the cycling between the two inorganic forms, iodate and iodide, through planktonic organisms in the euphotic zone (Vinogradov 1953, Wong et al. 1976) followed by regeneration, sedimentation and diagenesis (Price & Calvert 1973, Kennedy & Elderfield 1987). Total dissolved inorganic iodine is found at concentrations between 0.43-0.48µmol L^{-1} in the open ocean and exists predominantly in two stable forms, iodate (IO_3^-) and iodide (I^-). The former is suggested to be the dominant form of inorganic iodine present at seawater conditions (pH 8.1 and pϵ 12.5). However, it often gets reduced to iodide and is found in oxic surface waters (Wong 1991, Luther et al. 1995), oxygen minimum zones (Farrenkopf & Luther 2002) and anoxic basins (Jiazhong & Whitfield 1986). The presence of iodate reduction and the subsequent iodide maxima within the euphotic zone has been commonly attributed to biological activity (Elderfield & Truesdale 1980, Jickells et al. 1988, Campos et al. 1996). This hypothesis had grown from field observations where iodate and nutrient concentrations correlated well (Wong et al. 1976, Elderfield & Truesdale 1980, Truesdale et al. 2000) and surface iodate concentrations decreased towards the more productive equatorial regions (Tsunogai & Henmi 1971, Jickells et al. 1988, Campos et al. 1996, Truesdale et al. 2000). However, all these observations were only evident in the tropical ocean and could not be re-observed in temperate (Truesdale & Jones 2000) or polar regions (Campos et al. 1999, Truesdale et al. 2003, Bluhm et al. 2009 in revision). There have been discrepancies about the iodate reduction process in surface waters and several authors argue that phytoplankton and bacteria actively reduce iodate to iodide (Tsunogai & Sase 1969, Moisan et al. 1994, Wong et al. 2002, Amachi et al. 2007, Chance et al. 2007) while others address more passive, chemical reactions (Taurog et al. 1966, Jiazhong & Whitfield 1986, Spokes & Liss 1996, Truesdale 2007). Spokes and Liss (1996) discovered that the photochemically induced iodate reduction is dependent on the concentrations of dissolved organic matter (DOM). Additional abiotic reductions of iodate are reactions with bisulphides (Jiazhong & Whitfield 1986) and thiols such as glutathione (Hird & Yates 1961). The latter one can take place upon cell death due to a release of these cellular metabolites into the surrounding seawater where they react with oxidizing agents including iodate. The reaction with bisulphides only takes place under anoxic conditions and is mainly found in sediments.

Under conditions prevailing in marine waters the complete oxidation of iodide to iodate is an extremely slow chemical process, since iodide seems to be inert under these conditions, with residence times of years (Wong 1991, Luther et al. 1995, Truesdale 2007). Direct photochemical oxidation of iodide only occurs at the sea-air interface with the help of strong UV-radiation or strong oxidants which results in the formation of molecular iodine (I_2) and hypoiodous acid (HOI).

The two intermediates, I_2 and HOI, can on one hand be volatized back to the atmosphere but can also react further with dissolved organic matter (DOM) in seawater (Truesdale et al. 1995) and form dissolved or particulate organic iodine (DOI and POI), the latter sinking out of the water column to the seafloor taking the bound iodine with it.

Low concentrations of iodide and the accumulation of iodate at greater depth indicate that most iodide oxidation must be completed there. The mechanisms for the return of iodide to iodate in seawater are still poorly understood since iodide seems to be inert under these conditions, with lifetimes of years (Wong 1991, Luther et al. 1995, Truesdale 2007). The most common abiotic processes such as photochemistry are too slow to be important, therefore biological mediated processes have also been suggested. There is not much information about the biological oxidation of iodide back to iodate with only one single study showing the complete oxidation where a fungus *Caldariomyces fumago* oxidises iodide to iodate via the enzyme chloroperoxidase (Thomas & Hager 1968). However, all other studies concerning this reaction did not find an oxidation through to iodate (Gozlan & Margalith 1973, 1974, Amachi et al. 2005). Due to the slow kinetics of oxidizing iodide to iodate and the apparent long lifetime of iodate in deep waters some authors came up with the idea to use iodide as a complimentary tracer for upwelling water on continental shelves (Wong & Zhang 2003, Wong et al. 2004).

The Mauritanian upwelling region off NW Africa in the tropical NE Atlantic Ocean is characterized by atmospheric deposition of Saharan dust over the tropical Atlantic and coastal upwelling of nutrient rich deep waters due to the prevailing trade winds. Upwelling regions in major dust deposition areas can thus be viewed as biogeochemical hotspots which are fuelled simultaneously by vertical supply of macro- and micronutrients from mesopelagic depths below and the atmosphere above, with major consequences for biogeochemical cycles and the ocean-atmosphere gas exchange. The offshore waters of Mauritania, receive little precipitation and also rain contains little iodine (Baker et al. 2001), similarly Saharan dust is also a poor source of iodine resulting in a minimal flux of iodine from the atmosphere to the sea. However the flux of iodo-organic compounds from the ocean is suggested to be an important source of iodine to the atmosphere (Chuck et al. 2005, Smythe-Wright et al. 2006) The formation of volatile iodine compounds including molecular iodine (I_2) and iodo-organic species in the surface microlayer (SML) (Garland & Curtis 1981, Martino et al. 2009) and euphotic zone can lead to a flux of volatile iodine out of the seawater and into the atmosphere. In the atmosphere photochemical processes break the C-I bond and release iodine which can be oxidized to the reactive transient species iodooxide (IO) (Schonhardt et al. 2008) which has been identified as a precursor to the formation of new particles in the atmosphere (McFiggans et al. 2004).

The dry deposition of Ozone (O_3) to the surface ocean is a principal loss term for this important trace gas and the reaction of iodide with O_3 in the SML has been identified as the most likely mechanism (Garland et al. 1980, Thompson & Zafiriou 1983, Chang et al. 2004). The importance of iodine chemistry processes to the global atmospheric O_3 has recently been assessed in global climate models (Oh et al. 2008, Ganzeveld et al. 2009) and in chemical models (Simpson et al. 2007). Previously, this reaction had only been examined briefly from the point of view of iodide cycling and its oxidation by O_3 to high oxidation states (Thompson & Zafiriou 1983). However a recent paper by Martino et al. (2009) has examined this formation of iodo-organics resulting from this process. An alternative pathway for ozone loss has recently been suggested from laboratory studies examining the reaction between chlorophyll-*a* and ozone at the ocean surface (Clifford et al. 2008, Reeser et al. 2008). Though, in the context of the present work in the oligotrophic waters of the eastern tropical Atlantic, where chlorophyll is low, it appears that iodide is the major sink for O_3.

The reaction of O_3 with iodide is rapid (rate constant = $1.2 \pm 0.1 \times 10^9$ M^{-1} s^{-1}) (Liu et al. 2001) and so the reaction is limited to the SML producing hypoiodous acid (HOI) and I_2 which can be volatilized to the atmosphere (Garland & Curtis 1981). O_3 can further oxidize HOI /I_2 to iodate (Parry & Hern 1973) but it is believed that this is a minor pathway in the SML as most of the O_3 flux to the surface reacts with iodide and not HOI (Bichsel & von Gunten 1999). The abundance of organic compounds in the SML (Zhou & Mopper 1997, Calace et al. 2007) suggest that HOI/I_2 can react to form iodo-organics which can also be volatilized to the atmosphere (Carpenter et al. 2007), or destroyed by UV-irradiation (Martino et al. 2006) or mixed deeper into the water column (Carpenter et al. 2007). Biologically mediated or photochemical production of iodo-organics is also likely to occur throughout the euphotic zone (Moore & Zafiriou 1994, Richter & Wallace 2004, Smythe-Wright et al. 2006).

In the present work we describe the distribution of dissolved inorganic iodate and iodide observed in the Mauritanian upwelling region and the adjacent oligotrophic Atlantic Ocean. We compare the results of a weak upwelling scenario with results gained from two strong upwelling scenarios to determine differences in iodine speciation due to biological processes on one hand and due to the upwelling intensity on the other hand.

2. HYDROGRAPHY OF THE STUDY AREA

Three cruises were carried out in the tropical Northeast Atlantic Ocean on the research vessels a) Meteor (M68-3) in July/August 2006, b) Poseidon (P348) in February 2007 and c) L'Atalante in February 2008. All cruises were part of the German contribution to SOLAS (Surface Ocean Lower Atmosphere Studies), via the BMBF sponsored project SOPRAN (Surface Ocean PRocesses in the ANthropocene), which is investigating the interactions between the ocean and the atmosphere. The area studied extends along the Mauritanian coast from Cap Blanc in the north to Cap Vert in the south (16°-19.5°N). The Mauritanian upwelling region is characterized by an approximately 30km wide shelf with depths of less than 100m whereas the shelf of the Banc D'Arguin region (19.5°–21.5°N) is approximately 130km wide and very shallow with depth usually not exceeding 50m. Initially both shelves are gently sloping away from the coast while further offshore the continental slope rapidly drops off to water depths exceeding 3000m (Figure 1). The period of major upwelling in the Mauritanian region is during late winter and early spring, induced by the North East trade winds (Hagen 2001). Wind, atmospheric pressure and air temperature exhibit typical diurnal and semi-diurnal variations. This upwelling system is probably the most complex of all coastal upwelling systems, particularly near Cape Blanc (20°N) where the frontal zone between the salty (>35) North Atlantic Central Water (NACW) and less salty (<35), nutrient-rich South Atlantic Central Water (SACW) reaches the African coast (Zenk et al. 1991). The largest proportion of the upwelling waters between 16°N and 19.5°N is provided by South Atlantic Central Water (SACW) from 50-300m depth. This SACW is carried northwards by a poleward undercurrent referred by some authors as upwelling undercurrent (Hagen 2001).

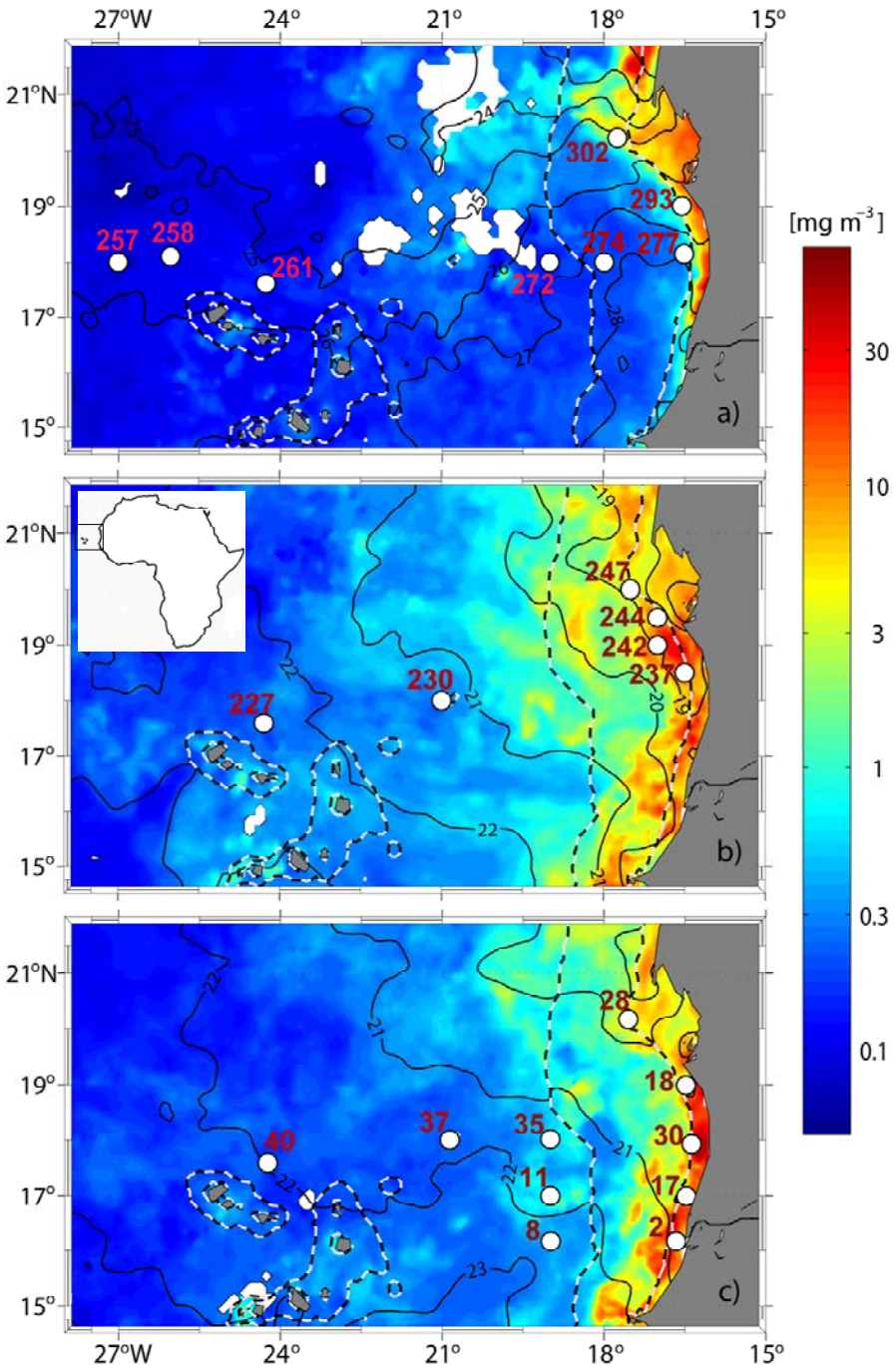


Figure 1: Chlorophyll-*a* concentration maps of the three areas studied, showing station locations and numbers during a) M68-3 from 10th July to 6th August 2006, b) P348 from 8th February until 26th February 2007 and c) L'Atalante from 4th February to 19th February 2008. Contour lines indicate sea surface temperature (SST), dashed lines indicate the 100m and 3000m isobaths. (Chlorophyll-*a* data from Seawifs)

3. MATERIAL AND METHODS

Iodine depth profiles were gained on three expeditions to the Mauritanian upwelling region: (1) RV Meteor in August/July 2006 (M68-3), (2) RV Poseidon in February 2007 (P348) and (3) RV L'Atalante in February 2008. Water samples were taken at discrete depths between 17°-27°W and 16°-19.5°N at stations shown in Figure 2. Stations sampled were divided in three groups. First, the group of open ocean stations as characterized by a water depth exceeding 100m depth. Second, the group of shelf stations with water depths below 100m depths. One key station, forming the third group, was at the TENATSO (Tropical Eastern North Atlantic Time-Series Observatory) Ocean site: www.tenatso.com. Station 261 during M68-3, station 227 during P348 and station 40 during L'Atalante (Figure 2 and Table 1). This station is situated at 17.35°N; 24.15°W and lies directly upwind of the island of Sao Vicente in the Cape Verde archipelago.

3.1. Sampling

A 9 plus CTD-(Seabird Electronics Inc., USA), was used in conjunction with a CTD rosette, equipped with a pressure sensor and two independent sets of temperature, conductivity and oxygen sensors. In addition, a fluorescence sensor (Chlorophyll-*a*), an altimeter and a Chelsea Instruments Alphatracka 25cm 660nm Transmissometer were attached to the rosette. For the final calibrated datasets the data from the primary set of sensors were used.

Dissolved inorganic phosphate, nitrate and nitrite were analysed on a TrAAcs 800 Auto-analyser from Bran & Luebbe (Norderstedt) by standard methods described in Grasshoff et al. (1999)

3.1.1. Iodine Speciation

Iodine samples were filtered over 0.2µm cellulose acetate filters immediately after collection and the filtrate was stored frozen at -20°C (Campos 1997) until analysis in the home laboratory. Iodide was determined by cathodic stripping square wave voltammetry according to the method of Luther et al. (1988), modified by Campos (1997) with a detection limit of 0.1-0.2nM and a precision of 5%. Iodate was determined spectrophotometrically by its conversion to the I_3^--ion with sulphamic acid and potassium iodide after the method of Truesdale (1978a). With this method the sulphamic acid eliminates interference by nitrite. Samples were measured in a 5cm cuvette on a "Unicam" spectrophotometer (UV300, Thermo-Forma) at a wavelength of 350nm. The detection limit of the method is ~20nmol L^{-1} with a precision of 5%. Samples were measured in triplicate for both iodide and iodate and

standard deviations were gained from the three triplicates measured. Total iodine was calculated by the sum of the two inorganic forms (iodate + iodide).

3.2. Satellite data

Satellite chlorophyll-*a* and sea surface temperature (SST) data were obtained from OBPG MODIS-Aqua Monthly Global 9-km Products via GIOVANNI using the Ocean Colour Time-Series Online Visualization and Analysis platform: ftp://oceans.gsfc.nasa.gov/MODISA/. Data for M68-3 were averaged over three months (July-September) due to cloudiness during the time of the cruise. Data for P348 and L'Atalante were obtained from February 2007 and 2008, respectively. All satellite images were finally displayed as postscript images using MATLAB.

4. RESULTS

Iodate values ranged between 320 to 420nmol L^{-1} in the surface and slightly increased to 400-450nmol L^{-1} at depth below 200m. Due to the higher detection limit of the iodate method it is often difficult to balance the complete conversion of iodate into iodide. In our dataset, on the level of an individual station, no clear 1:1 relationship was seen between the iodate and iodide levels. For this reason we will focus mainly on iodide values as these are more precise. It is easier to detect nanomolar changes in iodide but difficult to see equivalent concentration changes in iodate. Iodate values are shown in the depth profiles as additional information but will not be discussed here.

4.1 Temperature, chlorophyll-a and nutrients

Low sea surface temperatures (SST) and high nutrient concentrations reveal the influence of recent upwelling. Average SST and nitrate concentrations for all stations are listed in Table 1. Despite great fluctuations in the variability it is clearly seen that SST are lower and nitrate concentrations are higher in the shelf stations during upwelling due to the constant supply of cooler and nutrient rich water from the deep to the surface (Table 1). This also enhances phytoplankton growth and chlorophyll-*a* concentrations were greatest during P348 and L'Atalante (Figure 2). Low chlorophyll-*a* concentrations (<1mg m^{-3}) and higher SST (>24°C) were indicative of reduced upwelling in that area during summer cruise M68-3 (Figure 2a).

Table 1: Average values for sea surface temperatures (SST), nitrate and iodide concentrations during M68-3, P348 and L'Atalante in the upper 20m of the water column. Avg.: average.

Cruise	Avg. SST [°C]	Avg. nitrate [µM]	Avg. iodide [nM]
M68-3			
All stations	25.3 ± 0.9	0.2 ± 0.4	148.7 ± 39.9
Open ocean stations	25.1 ± 0.9	0.2 ± 0.4	124.8 ± 31.2
Shelf stations	25.6 ± 0.9	0.3 ± 0.5	179.5 ± 22.2
TENATSO	24.7 ± 0.0	0.1 ± 0.1	138.3 ± 3.3
P348			
All stations	18.8 ± 2.3	9.4 ± 6.7	94.6 ± 40.4
Open ocean stations	22.3 ± 0.4	0.0 ± 0.0	146.7 ± 37.1
Shelf stations	17.4 ± 0.5	12.8 ± 3.6	79.0 ± 26.4
TENATSO	22.6 ± 0.1	0.0 ± 0.0	136.4 ± 46.0
L'Atalante			
All stations	20.0 ± 1.4	3.2 ± 3.3	88.2 ± 23.7
Open ocean stations	21.5 ± 1.0	0.1 ± 0.1	97.8 ± 18.1
Shelf stations	19.2 ± 0.7	4.6 ± 2.7	82.2 ± 25.3
TENATSO	21.8 ± 0.0	0.0 ± 0.0	80.7 ± 18.7

4.2. Iodine in the area studied

Total mean iodine (iodate + iodide) concentrations (RI) were 451 ± 65nmol L^{-1}. The RI concentrations measured during P348 and L'Atalante were in the same range and thus comparable. In the following we mainly focus on the results of the L'Atalante cruise, as sampling was more frequent compared to P348 and therefore changes in iodide concentrations more significant.

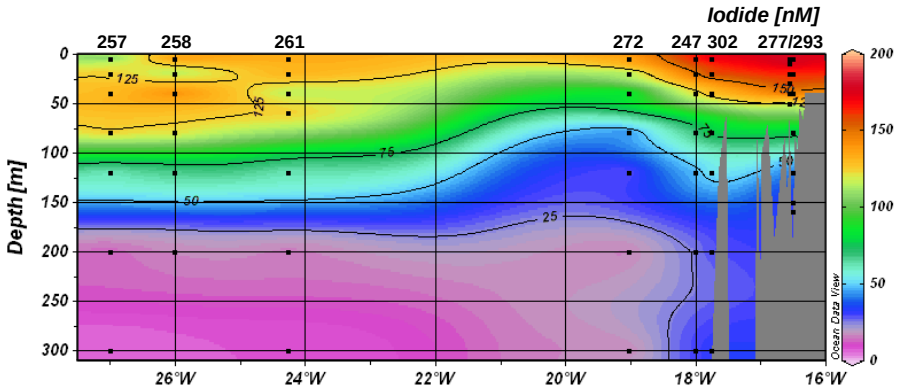
4.2.1. Section from Cape Verde Island to the Mauritanian shelf

Our dataset shows great differences in surface (5-50m) iodide concentrations between the weak upwelling summer cruise M68-3, and the two strong upwelling winter cruises P348 and L'Atalante. In general higher surface iodide concentrations were observed in all stations sampled during M68-3, compared to the other two cruises. This is even more pronounced when we only focus on the shelf stations where the upwelling is at its greatest intensity (Table 1). A paired t-test comparing M68-3 and P348 as well as M68-3 and

L'Atalante rejects the hypothesis that both samples originate from distributions with an equal mean at the 95% significance level.

During M68-3 surface iodide concentrations of more than 200nmol L^{-1} were observed at stations on the Mauritanian shelf slightly decreasing offshore and reaching a minimum of 74.4nmol L^{-1} at the open ocean station 257 (Figure 2a and 3a.). Over the period of the L'Atalante cruise iodide values were somewhat lower with highest surface concentrations of 131.7nmol L^{-1} and more homogenous throughout the study area. Lowest surface values of less than 68nmol L^{-1} were found at shelf station 17 but also at the open ocean TENATSO station 40 (Figure 2b. and 3b). For all stations a decline in iodide towards depth applies, usually reaching a minimum of less than 5nmol L^{-1} below 200-300m depths.

(a) M68-3 July/August 2006



(b) L'Atalante February 2008

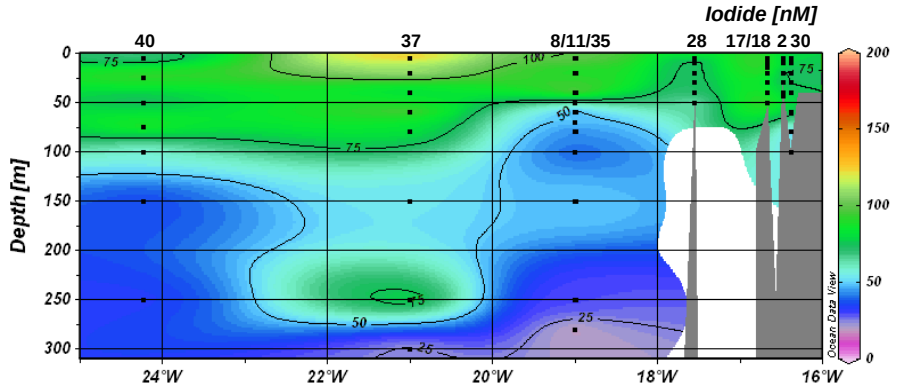


Figure 3: Iodide concentrations [nM] in the upper 300m during (a) M68-3 in July/August 2006 and (b) L'Atalante in February 2008. Iodide concentrations in the surface waters were lower during L'Atalante (~132nmol L^{-1}) compared to M68-3 (~203nmol L^{-1}). The section extends from the Cape Verde Islands in the west to the Mauritanian upwelling shelf in the east. Numbers at the top indicate station numbers on that transect (compare with Figure 2).

4.2.2. Vertical profiles

At the **TENATSO time series station** surface iodide concentrations ranged from ~68nmol L^{-1} during L'Atalante to ~140nmol L^{-1} for M68-3 (Figure 4). The vertical profiles of iodide at this station display a patchy distribution in the surface mixed layer (SML, 0-80m) followed by a constant decline towards depth. M68-3 and L'Atalante, both show a peak in iodide between 60 and 80m depth which had moved up closer to the surface (~20m) in the P348 profile (Figure 4). For the M68-3 and P348 station a decline in iodide towards depth applies, reaching less than 10nmol L^{-1} below the euphotic zone (>80m), whereas iodide in the L'Atalante station was still high (~25nmol L^{-1}) at depths exceeding 300m.

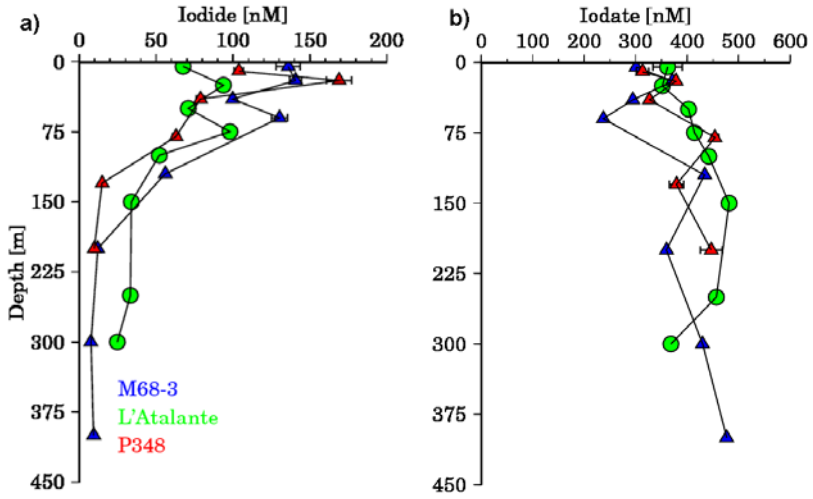


Figure 4: Iodine depth profiles at the TENATSO Times Series station during M68-3, P348 and L'Atalante, a) iodide and b) iodate. The L'Atalante station (St. 40) shows low surface iodide concentrations of less than 68nmol L^{-1} compared to M68-3 (St.261) were concentrations reached ~140nmol L^{-1}. Note that some error bars are smaller than the symbols size.

Comparing the vertical profiles of two **shelf stations** at the same location (Figure 5), clearly show the differences in surface iodide between summer (Figure 3a; St. 293) and winter (Figure 3b, St. 18). In summer surface iodide concentrations reached values close to 200nmol L^{-1} compared to values measured in winter (<80nmol L^{-1}; Figure 5a).

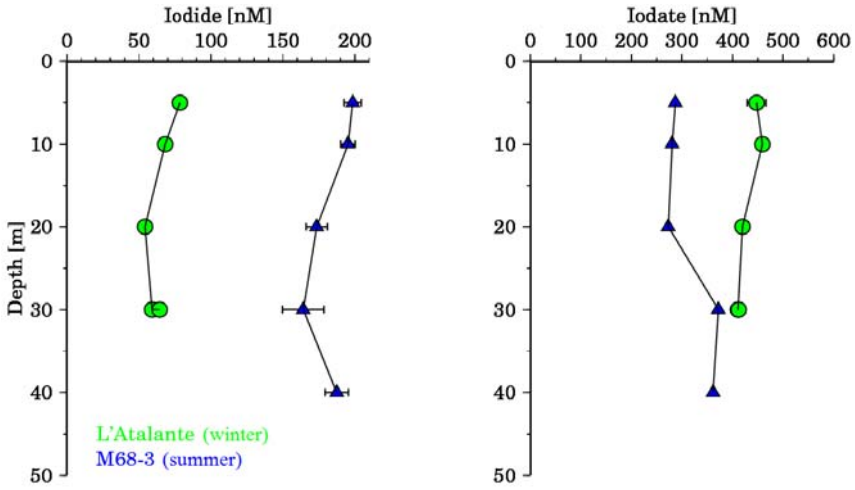


Figure 5: Typical iodine depth profiles from a shelf station in summer (M68-3, St. 293) and winter (L'Atalante, St.18), a) iodide and b) iodate. Surface iodide is less than half during the upwelling cruise. Note that some error bars are smaller than the symbols size.

4.3. Temperature and Iodide

In general a linear relationship between iodide and temperature existed in the upper 500m of the water column (Figure 6). Highest iodide concentrations coincided with higher temperatures. The gradient and intercept can be expressed as follows:

$$T = 0.073 * I^{-} + 12.604$$

The correlation coefficient (R^2) for this fit was 0.72.

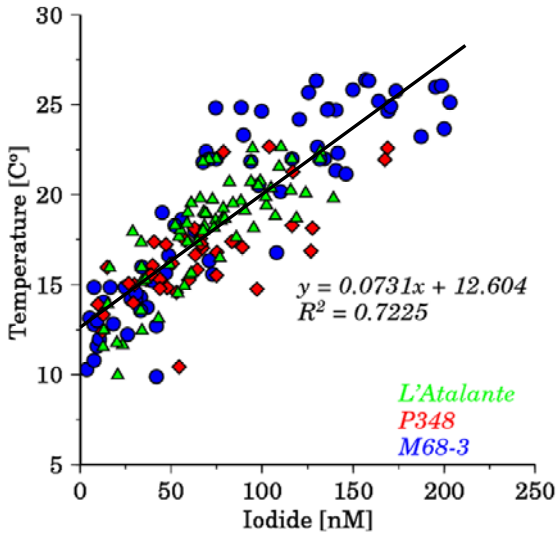


Figure 6: The relationship between iodide and temperature at all cruises in the upper 500m depth. The linear regression line and correlation coefficient (R^2) are named in the graph.

4.4. Phosphate and Iodide

Negative correlations where observed between phosphate and iodide during all cruises where phosphate declined towards the surface while iodide values were steadily increasing. However, differences in the phosphate correlation between strong and low upwelling episodes appeared in surface waters (Figure 7). During M68-3 the phosphate correlation with iodide breaks down at the surface as iodide is further increasing while phosphate is depleted (Figure 7a). Whereas the upwelling samples showed a drawdown in iodide in the surface waters while phosphate is depleted (Figure 7b).

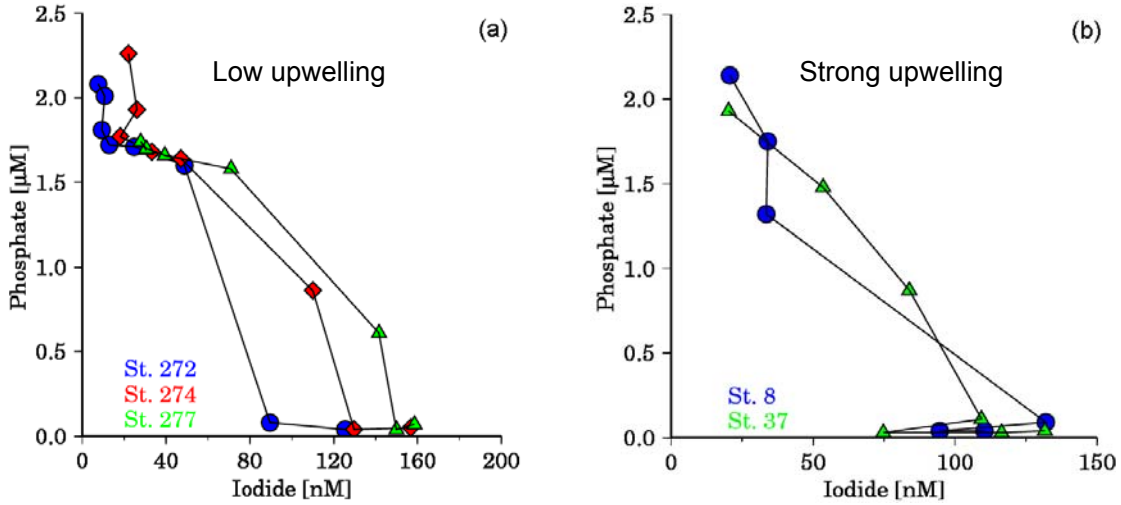


Figure 7: Correlation between phosphate and iodide during (a) M68-3 and (b) L'Atalante.

5. DISCUSSION

The mean total iodine concentration of 451nmol L^{-1} found in this study agrees well with previous studies from oceanic waters elsewhere (Jickells et al. 1988, Truesdale 1995, Truesdale et al. 2000, Truesdale & Bailey 2002). Significant amounts of iodide were only found in the euphotic zone and the intensity of iodide accumulation varied considerably between cruises. Abiotic and biotic iodate reduction processes prevailing in the surface layer of the ocean seem to be responsible for the iodide accumulation in the euphotic zone.

5.1. Chemical reduction of iodate to iodide

In the surface layer of the ocean iodate can be reduced through reactions with dissolved organic material (DOM) (Truesdale et al. 1995, Spokes & Liss 1996) In particular sulphur containing metabolites and thiols such as glutathione (GSH) which are able to reduce the iodate present in the surrounding medium to iodide (Hird & Yates 1961). GSH, an

antioxidant, helps to protect cells from reactive oxygen species such as free radicals and peroxides and functions as a reducing agent (Eq.1).

$$IO_3^- + 6GSH \rightarrow 3GSSG + 3H_2O + I^- \quad (1)$$

In the case of DOM reactions with UV-light are necessary to reduce oxidizing agents like iodate to iodide (Eq. 2 and 3).

$$DOM + h\nu \rightarrow DOM^* \quad (2)$$

$$DOM^* + IO_3^- \rightarrow I^- \quad (3)$$

It is known that the accumulation of DOM peaks during the senescent growth phase of a phytoplankton bloom (Fogg 1977, Sharp 1977, Engel et al. 2004) suggesting that the degree of iodate reduction is strongly dependent on the DOM concentrations present. The summer cruise M68-3 was carried out after the major upwelling episodes and extensive phytoplankton blooms had declined by the time we reached the sampling area (Figure 2a). The decomposition of these phytoplankton blooms might have resulted in elevated concentrations of DOM in the water column which reduced the prevailing iodate to iodide in the euphotic zone. High solar radiation and lower upwelling and vertical mixing causes high senescence in the phytoplankton cells releasing exudates like DOM. In winter and during times of strong upwelling we have lower solar radiation and higher vertical mixing. Cell senescence and necrosis are limited during this time of the year and reactions with UV-light and DOM are less resulting in lower surface iodide.

5.2. Biological reduction of iodate to iodide

Some laboratory experiments claim to have shown that marine phytoplankton can facilitate the reduction of iodate to iodide (Wong et al. 2002, Waite & Truesdale 2003, Chance et al. 2007), while others address abiotic mechanisms (Hird & Yates 1961, Jickells et al. 1988, Spokes & Liss 1996, Truesdale 2007). However, highest chlorophyll-*a* concentrations do not always correspond to highest iodide concentrations. Our results show that these are found during the low productive season in summer, representing a mismatch between biological productivity and iodide concentrations (Figure 2 and 4). Tian et al. (1996) demonstrated that the transformation from iodate to iodide in surface waters is linked to the regenerated production of primary productivity (PP). Our observations are coincident with the regenerated production explanation from Tian et al. (1996) since we observed less iodate reduction during strong upwelling episodes accompanied by new production. Over a period of strong upwelling regenerated production could only become significant in the euphotic zone when iodate is reduced by phytoplankton. Deeper phytoplankton cells grow on nutrients at the nutricline and would represent new production. We did not observe significant changes

in iodide at the nutricline. We also agree with an explanation posed by Truesdale et al. (2000) involving cell senescence and necrosis being responsible for the iodate reduction and formation of iodide since we found highest iodide concentrations during the post upwelling cruise M68-3. Truesdale and Jones (2000) suggested that diatoms are not able to reduce iodate to iodide. This would explain findings from temperate waters where no iodate reduction was found during the diatom dominated spring bloom (Truesdale 1978b, Truesdale & Jones 2000). Likewise in the Mediterranean, Tian (1996) found iodate to be reduced after the spring bloom when the non-diatom community is dominating. Comparing their findings to our results we must agree at first that iodate reduction is less during the productive upwelling seasons dominated by diatoms. However, several other workers examined iodide production in phytoplankton cultures including diatoms (Sugawara & Terada 1967, Moisan et al. 1994, Wong & Cheng 2001, Chance et al. 2007, Bluhm et al. 2009 submitted). We think the intensity of iodate reduction is indeed species specific but more connected to cell senescence and the release of metabolites.

Cycling of iodine in the ocean takes place through biological fixation and our observations argue that remineralization of biogenic matter might be the major force driving the iodate-iodide conversion. The iodate reduction is a coupling between biotic and abiotic processes although we think the actual reduction is best explained through secondary abiotic mechanisms caused by reactions with iodate and metabolites released by the algae.

5.3. Nutrients and Iodide

Several workers proposed that with high nitrate concentrations less iodate reduction takes place as nitrate suppresses this reaction (Wong & Brewer 1974, Elderfield & Truesdale 1980, Truesdale & Bailey 2002). We also observed less iodate reduction to iodide in the strong upwelling samples during our study. Although, it is not clear whether (1) the reduction is hampered by the simple presence of nitrate, (2) surface iodide is diluted through mixing with low iodide water from the deep or (3) nitrate replete and viable phytoplankton cells oxidize the surface iodide back to iodate. The latter one being observed in laboratory experiments with a *Chaetoceros debilis* culture grown under nitrate deplete conditions showed iodide production until nitrate was re-supplied. Accordingly, iodide values declined proposing that an iodide oxidation mechanism must prevail and that iodate reduction is coupled to cell senescence (Bluhm et al. 2009 submitted). The same could be applicable for the strong upwelling episodes in winter where iodide is oxidized back to iodate due to a constant supply of nutrients and therefore viable phytoplankton cells. This would suggest that biological processes can accelerate the iodide oxidation rates in seawater, although the process causing the iodide oxidation and the oxidation rates are still unknown and need to be further investigated.

The drawdown in phosphate towards the surface during M68-3 (Figure 7a) can be explained by phytoplankton growth since there is only low upwelling the production is regenerated and iodide is remineralized via the microbial loop. The continuous increase in iodide at the sea surface while phosphate is depleted is probably mainly influenced by reactions with UV-light and DOM released by senescent phytoplankton cells resulting in the production of iodide (eq. 2 and 3; Truesdale et al. 1995, Spokes & Liss 1996). During strong upwelling (Figure 7b) remineralization and cell senescence are less. The drawdown in iodide close to the surface while phosphate is depleted could be explained due to biological reasons. As mentioned earlier it seems that viable phytoplankton cells take up iodide and/or oxidize iodide back to iodate (Bluhm et al. 2009 submitted). However, the iodide oxidation mechanisms are still not clear and other biological organisms like bacteria as well as chemical oxidation, despite the fact that it might be too slow to be significant, needs to be considered as well.

5.3. Iodide as a complimentary tracer for upwelling

The linear relationship between iodide concentrations and sea surface temperatures (SST; Figure 6) indicates that iodide might be used as a tracer for upwelling on the shelf. It is well described that the upwelling in the Mauritanian region south of Cape Blanc is weak during summer and strong during winter/spring (Figure 8; Mittelstaedt 1983, Hagen 2001).

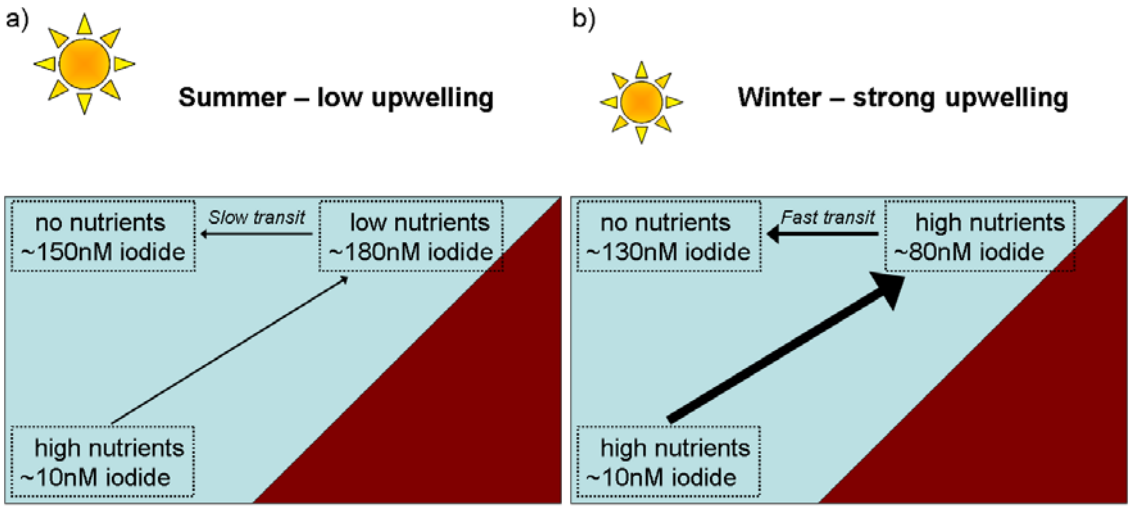


Figure 8: Schematic of the Mauritanian upwelling shelf and its nutrient and iodide distribution. a) A weak upwelling scenario during summer with low biological productivity and b) a strong upwelling scenario in winter/spring with high biological productivity.

In the season of low upwelling (Figure 8a) the transport of cold, nutrient and iodate rich, but iodide poor water to the surface is reduced. The relaxation of upwelling and stratification of the upper water column during the transition to the weak-upwelling phase will trigger bloom demise and subsequent senescence of phytoplankton cells. This in turn will result in a release of dissolved organic matter (DOM) into the water column (Fogg 1977, Sharp 1977, Engel et al. 2004) which catalyses the reduction of iodate to iodide. Iodide will thus accumulate unless low iodide water from the depth is brought up to the surface during upwelling where it displaces iodide rich water in the surface. During upwelling seasons colder and nutrient rich water is brought to the surface (Figure 8b) where it stimulates phytoplankton growth indicated by the chlorophyll-*a* field (Figure 2b and c). Most of these phytoplankton cells are viable, due to a constant supply of the required nutrients, and apparently do not produce iodide but oxidize it back to iodate (Bluhm et al. 2009 submitted) which would explain the lower iodide concentrations at the surface during this time. However, since iodide is accumulating in the surface in the upwelling season, as well there must also be iodate reduction mechanisms. One suggestion might be zooplankton grazing which causes a release of intracellular metabolites like glutathione and other sulphur species from the phytoplankton cells. These metabolites are able to reduce the iodate present (Hird & Yates 1961).

Once the upwelled water reaches the surface the prevailing currents transport it offshore due to the Earth's eastward rotation. Estimates of the transit time of water masses from the shelf to the offshore situated TENATSO Ocean Observatory lie between 10-20 days. During an upwelling episode the travel times are between 12-16 days as compared to 20 days during the low-upwelling season (Steinhoff et al. in preparation). What happens to this water? Is it subducted somewhere or diluted? To justify these explanations iodide oxidation rates in the surface waters of the Tropical Atlantic Ocean must be at least on the time scale of months as iodide values are still high at TENATSO and comparable to the concentrations on the shelf. Abiotic oxidation mechanisms of iodide are all kinetically slow (Luther et al. 1995) leading to long residence times for iodide of years which do not fit with the observed seasonal cycles in iodide (Campos et al. 1996, Tian et al. 1996). Estimates by Edwards and Truesdale (1997) on iodide oxidation in the field revealed an oxidation rate of 30 ± 10nmol L^{-1} yr^{-1} in the deep waters of a Scottish Loch. Biological issues are not taken into account here which might accelerate the iodide oxidation leading to shorter residence times in the surface. Campos et al. (1996) reported in a mass balance model that on an annual basis the *in situ* rate of iodide oxidation is relatively fast (70 days) at two Time Series station in the Tropical Ocean. They considered only the euphotic zone in their calculations where iodine cycling is most active and assumed that the rate of primary productivity is the controlling step which in turn led to a seasonal cycle in their iodine data. To declare the exact

half life and mechanism for the iodide to iodate conversion too little is known about the iodine cycle in seawater and needs further investigation.

The role of ocean mixing in controlling the iodide concentration in surface waters is much harder to constrain. In this region water mass transport and ventilation has been investigated using tritium-^{3}He ages (Jenkins 1988, Roether et al. 1988) and show that age estimates decrease from the southwest to the northeast in this region along the σ_0 = 26.5 contour consistent with upwelling along the eastern boundary, the Mauritanian coast, and with the entry of recently ventilated waters in the northeast corner of the gyre. The low tritium-^{3}He ages (2-6 years) observed along the upwelling pathway indicate the rapid turnover of surface water and the importance of subduction in supplying recently ventilated water into the thermocline. The interplay between ocean mixing and iodide concentrations is intriguing and worthy of inclusion into eddy resolving models of this region but in the present work without estimates for the rates of iodine oxidation or reduction any results would be too speculative.

5.5. Implication for Iodine fluxes to the atmosphere

The TENATSO atmospheric site on Sao Vicente, Cape Verde, is directly downwind of the associated ocean site which was sampled in the present work. Thus air masses measured at the atmospheric site have typically passed over the ocean site very recently. A strong diurnal signal for IO has been observed at the TENATSO atmospheric site during daytime and suggested that halogen chemistry was a major contributing factor to the tropospheric ozone loss found in this region (Read et al. 2008). These authors suggested that the source of iodine to the atmosphere was from biological release from the ocean around the atmospheric site. Previous measurements of iodo-carbons in the water and air in this region show a strong sea to air flux (Chuck et al. 2005, Smythe-Wright et al. 2006). The seasonal fluctuations in the iodide concentrations observed at TENATSO in the present work suggest that redox cycling of inorganic iodine is occurring throughout the year and this will result in the production of the transient volatile species HOI and I_2 which are necessary to form the iodo-organic species. Continuation of both the atmospheric and ocean times series at TENATSO should help to improve our understanding of this important link for iodine between air and sea.

6. CONCLUSIONS

In the eastern tropical Atlantic we have observed seasonal differences in iodide accumulation in the euphotic zone. Lower iodide concentrations in the Mauritanian upwelling

during the winter, the season with strongest upwelling and highest productivity, may be indicative of a biomass related reoxidation of iodide to iodate or simple dilution by the low iodide upwelled waters. The higher surface iodide concentrations observed during the summer, a period of reduced upwelling, are tentatively linked to a combination of reduced vertical mixing and increased photoreduction of iodate related to increased UV and DOM in the water column. Our data provide more support for the use of iodide as a tracer of recent upwelling. However information is still crucially lacking on the critical oxidation and reduction rates for inorganic iodine species in seawater and this must be the focus of future work on iodine biogeochemistry.

7. ACKNOWLEDGEMENTS

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MANUSCRIPT 2

Distribution of iodide and iodate in the Atlantic sector of the Southern Ocean during austral summer

Distribution of Iodide and Iodate in the Atlantic sector of the Southern Ocean during austral summer

by

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ABSTRACT

The biogeochemistry of iodine in the waters of the Atlantic sector of the Southern Ocean was investigated during the Polarstern cruise ANTXXIV-3 ZERO&DRAKE. The speciation and distribution of iodine (iodate and iodide) in seawater was examined across gradients of iron concentrations and phytoplankton abundance; ranging from an open ocean region along the Zero Meridian to the Weddell Sea and Drake Passage. Iodine cycling in high latitudes differs from that in low latitudes due to differences in the plankton community composition and the physicochemical characteristics. Iodate concentrations ranged between 400nmol^{-1}-450nmol^{-1} from the surface to the bottom. Surface concentrations of iodide (17nmol^{-1}- over 60nmol^{-1}) were about an order of magnitude higher than below the pycnocline. The peak values of iodide lay nearly always within the euphotic zone and showed a weak, positive correlation with nitrite concentrations in the upper 200m. In all vertical profiles a pronounced sub-surface maximum in iodide appears between 50m - 200m depth indicating an iodide drawdown at the near surface. Iodide distribution in the Weddell Sea showed elevated levels in Weddell Sea Bottom Water (WSBW) indicating slow oxidation kinetics and the potential for iodide as a tracer of WSBW formation.

1. INTRODUCTION

Iodine has recently been identified as a potential key element involved in climate change, as iodine emissions from the ocean can influence the formation of new aerosol particles with impacts on cloud formation and radiative balances. Iodine chemistry in the atmosphere is important as iodine released from the ocean is believed to be a major source of new particles to the atmosphere (O'Dowd et al. 2002). The main flux from the ocean to the atmosphere is dominated by marine emissions of volatile organoiodine compounds (VOI's) such as methyl iodide (CH_3I) or diiodomethane (CH_2I_2). In seawater, these VOI's may be formed by reactions between dissolved organic compounds and iodine species via photolysis reactions (Richter & Wallace 2004, Moore 2006, Martino et al. 2009) or bacterial action (Amachi et al. 2001, Manley 2002). Gases such as CH_3I and CH_2I_2 are relatively short-lived in the atmosphere as sunlight and reactions with ozone (O_3) readily breaks the C-I bond producing iodine radicals ($I^{\bullet}$, IO, HOI, Figure 2) (Garland & Curtis 1981, Martino et al. 2006) which form particulate aerosol iodine species (Hoffmann et al. 2001, von Glasow 2005). The source and mechanism of iodine emissions from the ocean are poorly understood as are other more fundamental aspects of iodine biogeochemistry in seawater such as the cycling between the major iodine species; iodate (IO_3^-) and iodide (I^-).

Dissolved iodine, as iodide and iodate, exists in open seawater at a total concentration of about 450nmol L^{-1}, with iodate predominating in the deep ocean (Elderfield & Truesdale 1980, Jickells et al. 1988, Campos et al. 1996, Farrenkopf et al. 1997). Iodide is mainly found in surface waters within the euphotic zone but can also appear at depth in anoxic basins (Kennedy & Elderfield 1987, Wong 1991, Luther et al. 1995). In a redox cycle, iodate and iodide are interconverted, and this is the most pronounced effect for iodine speciation in oxic seawater. Attempts to explain iodate reduction in oxic seawater have linked it to phytoplankton growth (Sugawara & Terada 1967, Tsunogai & Sase 1969, Moisan et al. 1994, Wong et al. 2002, Chance et al. 2007), microbial respiration (Amachi et al. 2007a, Amachi 2008) abiotic reactions (Hird & Yates 1961, Jiazhong & Whitfield 1986, Spokes & Liss 1996), and interactions at the sediment–water interface (Kennedy & Elderfield 1987). The uptake of iodate by phytoplankton has been shown by Moisan et al. (1994) where iodine is stored inside the cell presumably in the form of iodide which will be released upon cell death. The uptake and reduction of iodate to iodide may involve the enzyme nitrate reductase (NR) (Tsunogai & Sase 1969) which could be an assimilatory process inside the cell or a dissimilatory process at the cell wall.

Abiotic reduction are advanced by Spokes and Liss (1996) who discovered that the photochemically induced iodate reduction is dependent on the concentrations of dissolved organic matter (DOM). Additionally, reactions with bisulphides (Jiazhong & Whitfield 1986) and thiols such as glutathione (Hird & Yates 1961) are also important. The latter one can

take place upon cell death due to a release of these cellular metabolites into the surrounding seawater where they react with oxidizing agents including iodate. The reaction with bisulphide only takes place under anoxic conditions and is mainly constrained to sediments.

Most iodine studies have been confined to temperate and tropical regions (Elderfield & Truesdale 1980, Jickells et al. 1988, Tian & Nicolas 1995, Campos et al. 1996). The biogeochemistry of iodine in high latitude areas and particular in the Southern Ocean is relatively unknown at present with only two published studies (Tsunogai & Henmi 1971, Campos et al. 1999). Tsunogai and Henmi (1971) reported surface values from a north-south transect in the Pacific and a single vertical profile from 60°S, 169°55W which was high in iodide (~100nmol L-1) in surface waters. Campos et al. (1999) undertook a section from the Antarctic Peninsula across the Weddell Sea and towards the South American continent. Samples were collected and analysed in the upper 500m and only iodide values were presented. Here, surface iodide concentrations (0 - 100m) never exceeded 20nmol L^{-1} in the Weddell Gyre. The overall aim of the present study was to improve our understanding of the Southern Ocean biogeochemistry of iodine and related elements. The distribution of other potentially biolimiting elements along this transect can also be found in other papers accompanying this special issue (Fe: Klunder et al., Zn: Baars and Croot, Mn: Middag et al.).

Until now the mechanisms driving the major reduction of iodate are still unclear and no mechanism has yet been proposed for the return of iodide to iodate (Luther et al. 1995). The oxidation of iodide to iodate is an extremely slow chemical process under conditions prevailing in seawater, since iodide seems to have lifetimes of years (Wong 1991, Luther et al. 1995, Truesdale 2007). Studies of modelled data from time series stations (Campos et al. 1996, Edwards & Truesdale 1997) propose that biologically catalysed iodide oxidation must be operating when iodide oxidation rates are significantly faster than this. Information about biological iodide oxidation is limited indeed with only one published study where the fungus *Caldariomyces fumago* oxidises iodide to iodate via the enzyme chloroperoxidase (Thomas & Hager 1968). Other biological studies concerning this aspect could find iodide oxidation as well but never the complete oxidation through to iodate (Gozlan & Margalith 1973, 1974, Amachi et al. 2005). Due to the slow kinetics of oxidizing iodide to iodate and the apparent long residence time of iodate in the deep waters the idea to use iodide as a tracer for newly formed water masses like upwelling or bottom water formation emerge (Wong & Zhang 2003, Wong et al. 2004).

This work was a subsidiary contribution to the International GEOTRACES program and International Polar Year (IPY) research expedition ANTXXIV-3 undertaken in the Southern Ocean on the icebreaker Polarstern. The vessel departed Cape Town, South Africa on the 10th of February 2008, headed south along the Zero Meridian, through the Weddell Sea and across the Drake Passage before finally arriving in Punta Arenas, Chile on April 16,

2008. The major focus of this cruise was to examine the distribution and speciation of key trace elements and their isotopes in the Southern Ocean. This paper represents the first extensive study for iodine speciation of both surface and deep waters in the Atlantic sector of the Southern Ocean and provides constraints on the potential fluxes of iodine from the ocean to the atmosphere in this region. The aim was to improve our understanding of iodine biogeochemistry in the Southern Ocean a region that is under-sampled presently but could be critically important.

2. HYDROGRAPHIC DESCRIPTION OF THE STUDY AREA

The physical oceanography of the Atlantic sector of the Southern Ocean has been extensively reviewed (Whitworth & Nowlin 1987, Orsi et al. 1995, Veth et al. 1997) and the reader is referred to these works for more detailed information. Here we provide a short description of the relevant water masses and processes (Figure1).

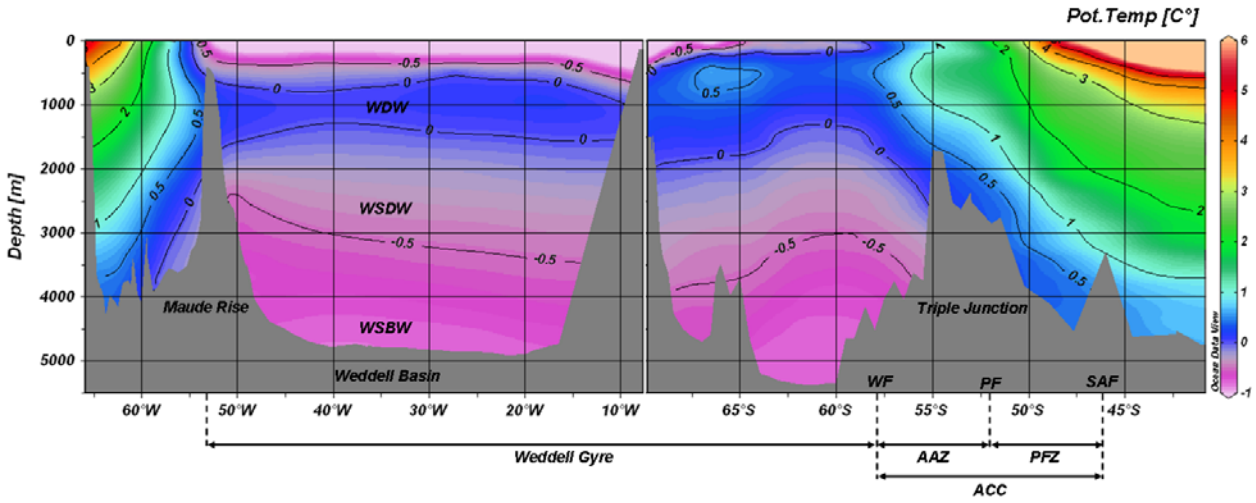

Figure 1: Potential temperature, relevant water masses and hydrography of the area studied. The section extents along the Zero Meridian, through the Weddell Sea and Drake Passage (see Figure 2). Abbreviations: WDW–Weddell Deep Water; WSDW-Weddell Sea Deep Water; WSBW–Weddell Sea Bottom Water; ASF–Antarctic Slope Front; WF–Weddell Front; PF–Polar Front; SAF-Subantarctic Front; AAZ–Antarctic Zone; PFZ–Polar Frontal Zone; ACC–Antarctic Circumpolar Current

2.1. Subantarctic Front

The Antarctic Circumpolar Current is dominated by two major fronts, the subantarctic front (SAF; S < 34,2 θ > 4-5°C) (Boyd et al. 2000) and the Polar Front (PF) (Whitworth & Nowlin 1987, Orsi et al. 1995). The SAF is an important biogeographical boundary

separating Antarctic and subantarctic/ subtropical groups of zooplankton (Pakhomov et al. 2000). The position of the SAF has been reported between 45°S and 48°S in this region (61°W–61°E; Lutjeharms & Valentine 1984, Pakhomov et al. 2000, Read et al. 2002).

2.2. Polar Front (PF)

Definitions of the PF range from subsurface or surface expressions for temperature (θ < 2°C) with the location of the PF varying between 49°S and 51.5°S in the region of the Zero Meridian (Lutjeharms & Valentine 1984, Lutjeharms 1985, Whitworth & Nowlin 1987, Orsi et al. 1995, Veth et al. 1997, Read et al. 2002, Turner et al. 2004) in this region biological production is not limited by the macronutrients, nitrate and phosphate but instead is iron limited (de Baar et al. 1995, Croot et al. 2004) as has been clearly shown in mesoscale iron enrichment experiments in this region (Gervais et al. 2002, Croot et al. 2005, Hoffmann et al. 2006).

2.3. Weddell Front (WF)

In the vicinity of the Zero Meridian a frontal feature separating the Antarctic Circumpolar Current and the Weddell Gyre (Veth et al. 1997) is called the Weddell Front (WF - S < 34.40, θ < 0.5°C) which is defined by Klatt et al. (2002) as the horizontal minimum of the mean geostrophic shear. The Antarctic Zone (AAZ) is the area between the PF and the WF, where salinity contributes most to the stratification of the surface layer (Pollard et al. 2002).

2.4. Antarctic Slope Front (ASF)

The southernmost circumpolar front is the Antarctic Slope Front (ASF), which is located on the continental slope boundary of the Antarctic continent and is identifiable by a subsurface zone of sharp horizontal gradients in temperature, salinity and chemical properties between shelf and deep waters (Jacobs 1991). The location of this front is controlled by the Antarctic shelf break and is an area of high biological activity in both sea ice and in the open ocean during the summer (Krell et al. 2005).

2.5. Deep Water masses in the Weddell Sea

Antarctic bottom water (AABW) is the coldest and most dense water mass in the world ocean with over 60% of it formed in the Weddell Sea (Orsi et al. 1999). It is formed in the southern and western margins of the Weddell Basin from Weddell Sea Deep (WSDW; -

0.7°C < θ < 0°C) and Bottom Water (WSBW; θ < -0.7°C) which are produced via interactions of warmer mid-depth and surface water masses with different shelf waters (Huhn et al. 2008). Warm Deep Water (WDW; θ > 0°C) is deep water from the southern east Atlantic advected into the Weddell Basin after splitting from the ACC and entering the Weddell Gyre at 20-30°E (Orsi et al. 1995, Hoppema et al. 1997, Klatt et al. 2002).

2.6. Drake Passage

Mesoscale eddy activity can be important in the Drake Passage and throughout the ACC (Glorioso et al. 2005, Kahru et al. 2007). The Drake Passage has also been identified as a 'hot-spot' for diapycnal mixing (Garabato et al. 2004) due to the influence of rough bottom topography on the strong current flows in this region.

3. MATERIAL AND METHODS

3.1. Sampling

Samples were collected during the Polarstern cruise ANTXXIV-3 along the Zero Meridian, in the Weddell Sea and Drake Passage (Figure 2) between February and April 2008.

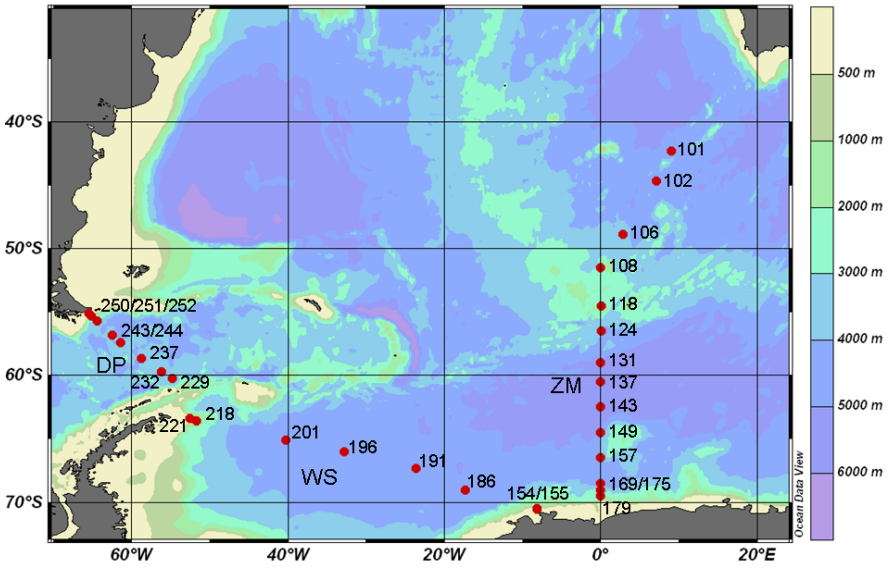

Figure 2: Station locations on transects along the Zero Meridian (ZM), in the Weddell Sea (WS) and Drake Passage (DP) during ANTXXIV-3 from 10 February until 16 April 2008 from Cape Town (South Africa) to Punta Arenas (Chile) on board RV Polarstern.

The standard Conductivity-Temperature-Depth (CTD)/water sampler consisted of a SBE911plus CTD system in combination with a carousel water sampler SBE32 with 24 12-L bottles. In addition to this a transmissometer from Wetlabs, a SBE43 oxygen sensor from Seabird Electronics and a Dr. Haardt Fluorometer were used. The CTD system was equipped with a CT sensor pair.
Dissolved inorganic nitrate and nitrite were analysed on a TrAAcs 800 Auto-analyser from Bran & Luebbe (Norderstedt) by standard methods described in Grasshoff et al. (1999).

3.2. Iodine Speciation

Unfiltered samples were analysed for iodide and iodate at sea within a few hours of collection. Iodide was determined by cathodic stripping square wave voltammetry according to the method of Luther (1988) and Campos (1997) with a detection limit of 0.1-0.2nmol L^{-1} and a precision of better than 5%. Iodate was determined spectrophotometrically by its conversion to the I_3^- ion with sulphamic acid, to remove interference by nitrite, and potassium iodide after the method of Truesdale (1978). Samples were measured using a 10 cm cuvette with an Ocean Optics USB 4000 spectrophotometer at a wavelength of 350nm. The accuracy of the method lies within 5% with a detection limit of around 20nmol L^{-1}. Samples were measured in triplicate for both iodide and iodate and standard deviations were gained from the three triplicates measured.

3.3. Satellite Data

Satellite Chlorophyll-*a* data was obtained from OBPG MODIS-Aqua Monthly Global 9-km Products via GIOVANNI (http://reason.gsfc.nasa.gov/Giovanni/) using the Ocean Color Time-Series Online Visualization and Analysis platform. Analyses and visualizations used in this paper were produced with the Giovanni online data system, developed and maintained by the NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC). Sea Ice concentration data were obtained from the NSIDC DMSP SSM/I daily gridded sea ice concentration data sets (Cavalieri et al. 1996 updated 2008. Jan - Apr 2008). Sea surface height anomaly (SSH) data (Leben et al. 2002) was kindly provided by the Colorado Center for Astrodynamics Research, University of Colorado, Boulder, and was produced from Jason, TOPEX/Poseidon(T/P), Geosat Follow-On(GFO), ERS-2 and Envisat altimeter data. All satellite images were finally displayed as postscript images using the Generic Mapping Tools (GMT) software (Wessel & Smith 1998).

4. RESULTS

4.1. Iodate

Iodate values ranged between 400-450nmol L^{-1} from the surface to the bottom. Some stations revealed a slight drawdown of iodate in surface waters compared to samples from deeper water. Due to considerable differences in the sensitivity of the iodate and iodide determination method it is difficult to detect the conversion of iodate into iodide. In this dataset no relation was seen between the iodate and iodide levels. For this reason we will focus mainly on iodide values as these are more precise. It is easy to detect nanomolar changes in iodide but difficult to see equivalent concentration changes in iodate. All values are shown in a station table in appendix I.

4.2 Iodide

The results are described in 4 parts (Figure 2). First, the transect to the Zero Meridian of three stations between station 101 (8.99°E; 42.34°S) and station 106 (2.8°E; 48.91°S). Second, the transect of 11 stations along the Zero Meridian between station 108 (0.0°E; 51.05°S) and station 179 (0.0°E; 69.52°S). Third, the transect of 8 stations in the Weddell Sea between station 154 (8.12°W; 70.57°S) and station 221 (52.53°W; 63.40°S) and fourth the transect of 8 stations through the Drake Passage between station 229 (54.80°W; 60.27°S) and station 252 (65.5°W; 55.12°S).

4.2.1. Transect to the Zero Meridian

There was no observable gradient in iodide surface concentrations along the transect south to the Zero Meridian with concentrations ~20nmol L^{-1} in the surface mixed layer (SML) and decreasing to below 6$nmol^{-1}$ below 400 m (data not shown). In the vicinity of the Sub Antarctic Front (see Figure 1) we found no indication of elevated iodide concentrations which differs from the results of Campos *et al.* (1999) along the A23 transect to the west of the Zero Meridian where they found an increasing concentration of iodide in the surface as they crossed the SAF. They also observed similar low iodide concentrations (~20nmol L^{-1}) as we did in the region of the PF.

4.2.2. Zero Meridian

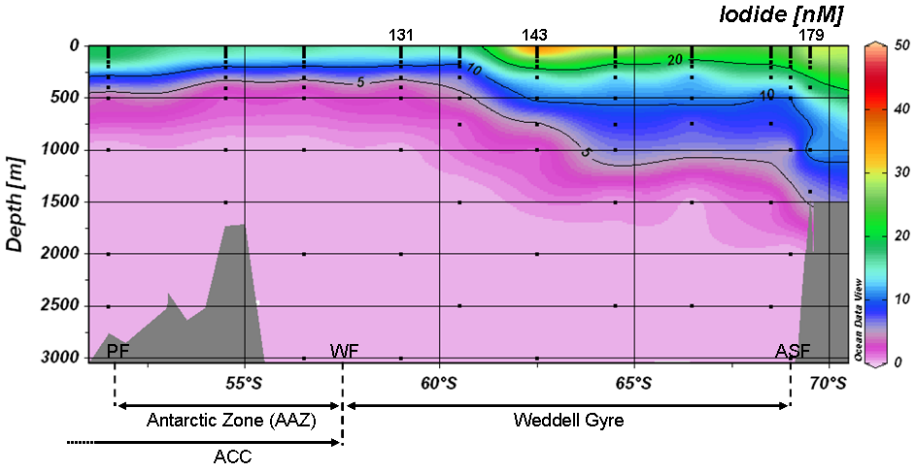

Figure 3: Iodide concentrations along the Zero Meridian during ANTXXIV-3. Numbers at the top indicate station numbers on that transect. Abbreviations in alphabetical order: ACC: Antarctic Circumpolar Current, ASF: Antarctic Slope Front, PF: Polar Front, WF: Weddell Front.

Our dataset shows a marked increase of surface iodide concentration from stations north of 62°S (below 20nmol L^{-1}) to stations south of 62°S (above 30nmol L^{-1}; Figure 3). Iodide concentrations north of 62ºS ranged from 17.3nmol L^{-1} in the SML, some of the lowest concentrations measured in surface waters, to undetectable concentrations in deep waters (>1000m). Water deeper than 500m showed low but detectable iodide concentrations of 1-2nmol^{-1}. Below 1500m depth, concentrations were below the detection limit (less than 0.1nmol L^{-1}) throughout the section. Bottom samples were not collected along the Zero Meridian. Highest iodide concentrations of ~40nmol L^{-1} were found in the SML south of 62ºS. Here, the 5nmol $L^{-1}$and 10nmol L^{-1} isopleth start to deepen markedly by more than 1200m towards the Antarctic continental shelf reaching its maximum at 70ºS and with increased concentrations (over 6nmol L^{-1}) down to 1500m depth (Figure 3).

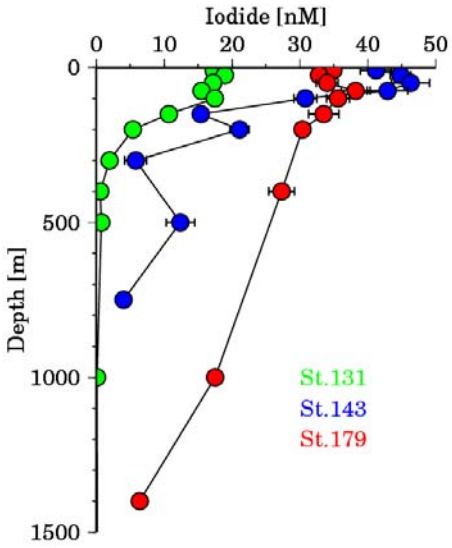

Figure 4: Iodide concentrations at three stations along the Zero Meridian during ANTXXIV-3.

The vertical profiles of iodide display a subsurface maximum between 25 and 75m depth (Figure 4). Four consecutive stations, from 60°S-67°S, showed a slight enrichment (~10nmol L^{-1}) of iodide at 500m depth (i.e. St.143) compared to other stations (i.e. St.131) along this transect (Figure 4).

The southernmost station (St. 179, 69°31`S) lay within the coastal current of the Antarctic continent. It revealed iodide concentrations between 20-40nmol L^{-1} from the surface down to 1000m depth (Figure 3 and 4).

4.2.3. Weddell Sea

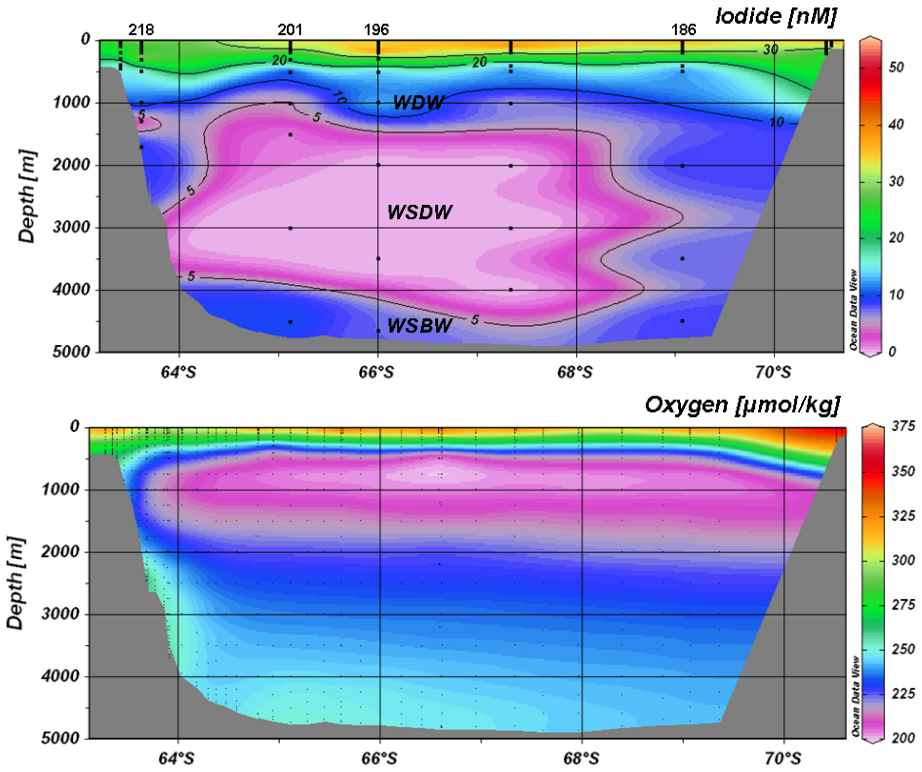

Figure 5: Iodide and oxygen in the Weddell Sea during ANTXXIV-3. The oxygen data was taken from the CTD sensor SBE 43. Numbers at the top indicate station numbers on that transect. Abbreviations: WDW: Warm Deep Water, WSDW: Weddell Sea Deep Water, WSBW: Weddell Sea Bottom Water.

Eight stations were sampled in the Weddell Sea so that sampling density was less compared to the other two transects as the main area of interest lay in the Drake Passage and along the Zero Meridian. In the Weddell Sea, the 10-30nmol L^{-1} isopleths showed a clear stratification in iodide throughout the section (Figure 5). Bottom water and deep water samples from along the shelves revealed a distinct iodide signal of close to 10nmol L^{-1} whereas samples from intermediate depths had undetectable concentrations. A similar pattern is seen in the dissolved oxygen data with high oxygen at the sea surface, a lower oxygen zone at intermediate depths and raised concentrations close to the bottom (Figure 6b) indicating the sinking of recently ventilated seawater.

The Weddell Sea receives glacial drainage from the East Antarctic Ice Sheet (EAIS) in the east, the West Antarctic Ice Sheet (WAIS) in the south, and ice caps in the Antarctic Peninsula region in the west (Bentley & Anderson 1998).

From the eight stations sampled in the Weddell Sea most of them were covered with an ice sheet (Figure 6).

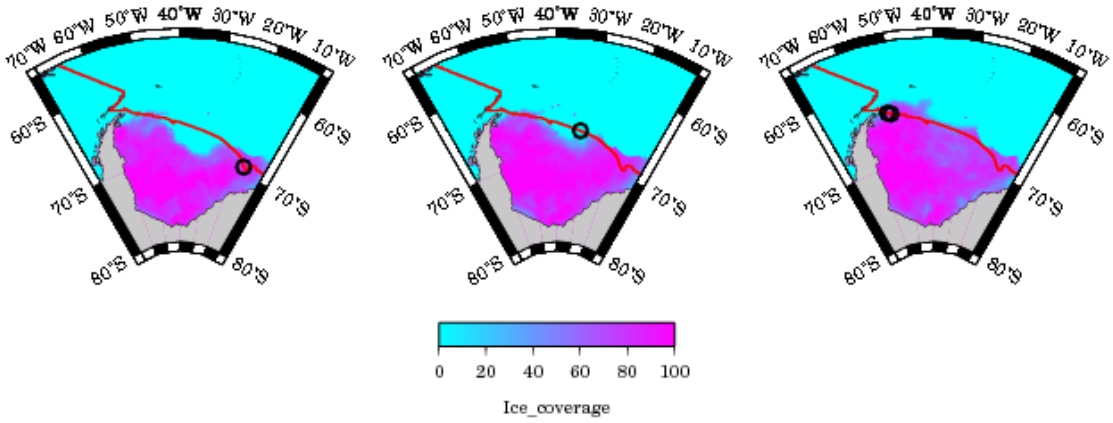

Figure 6: Sea Ice Coverage in the Weddell Sea during ANTXXIV-3. The thin red line indicates the cruise track and the red circles are the station locations on the day of sampling. 15th March 2008 (left, St. 186), 20th March 2008 (centre, St. 196) and 28th March 2008 (right, St. 218 and 221).

The vertical profiles of this section display high concentrations of ~30-60nmol L^{-1} in the upper 200m (Figure 7). Clearly indicated in these samples is a more pronounced and deeper (50-150m depth) subsurface maximum under the ice cover, with values between 40 to nearly 60nmol L^{-1}, compared to samples along the Zero Meridian.

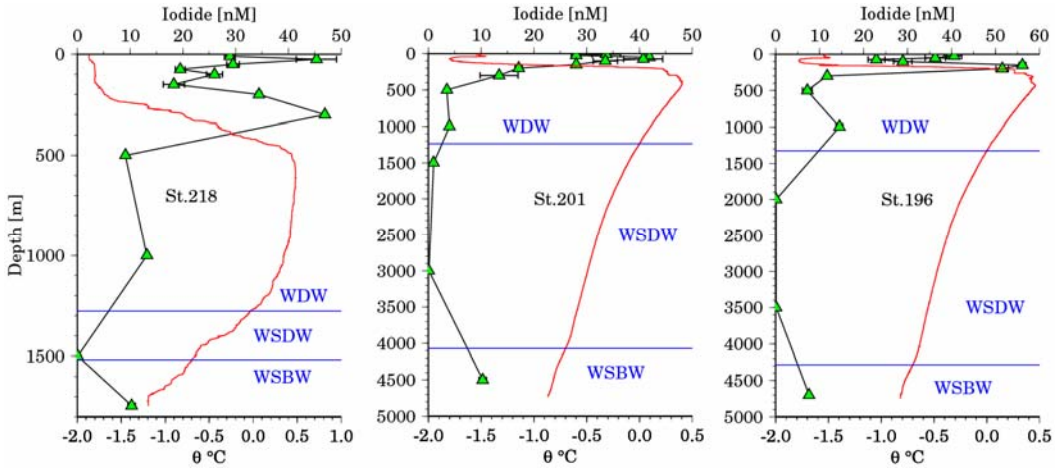

Figure 7: Iodide depth profiles of three stations in the Weddell Sea. Clearly seen is the disappearance of iodide in the WSDW and reappearance in the WSBW. Red line: potential temperature [°C]; triangles: iodide concentrations Abbreviations: WDW: Warm Deep Water, WSDW: Weddell Sea Deep Water, WSBW: Weddell Sea Bottom Water.

In terms of water masses the iodide distribution is clearly defined (Figure 5 and 7). The Weddell Sea deep water (WSDW) was always low in iodide or most of the time no iodide could be detected, whereas significant iodide concentrations recurred in the Weddell Sea Bottom Water (WSBW).

4.2.4. Drake Passage

Iodide depth profiles in the Drake Passage show a variable distribution with high values at the surface and low but measurable deep water iodide. In general higher surface iodide concentrations of 30-55nmol L^{-1} were observed. At each station iodide penetrated much deeper than on the Zero Meridian transect and concentrations were still high at 2000m depth (~10nmol L^{-1}). Highest surface iodide of over 55nmol L^{-1} was found in samples closest to Cape Horn and north of 56°S above the shelf of the South American continent (Figure 8).

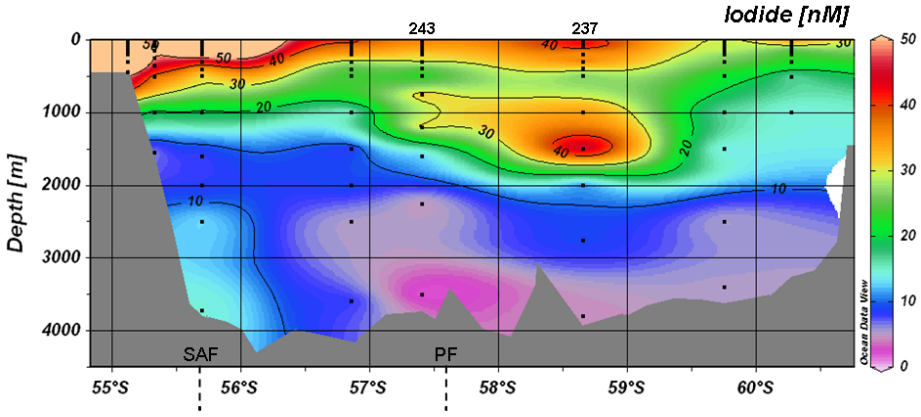

Figure 8: Iodide concentrations in the Drake Passage during ANTXXIV-3. Numbers at the top indicate station numbers on that transect. Abbreviations: PF: Polar Front, SAF: Sub Antarctic Front

The vertical profiles for St. 237 and 243 showed a distinct deep water iodide signal in two stations between 57º and 59ºS (>60nmol L^{-1}) between 750m and 1500m depth (Figure 8 and 9 bottom). Although, this feature is based on one sample it seems to be a real effect as iodate shows a corresponding minimum, which is seen despite fluctuations in the iodate measurements (data not shown).

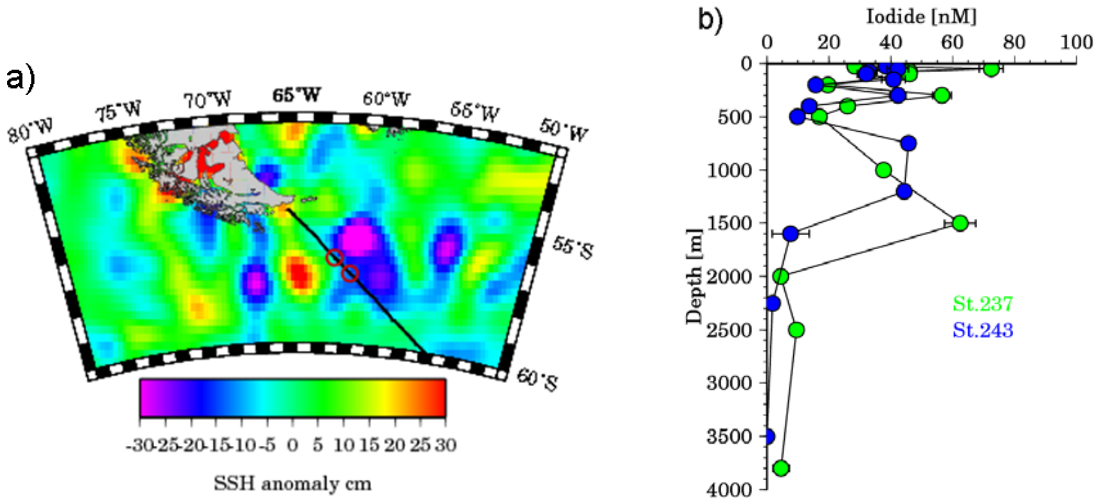

Figure 9: a) Sea Surface Height Anomaly Data. Red circles indicate the two stations (St. 237 and 243) on the edge of a large cyclonic eddy. b) Iodide depth profiles at station 237 and station 243 in the Drake Passage.

5. DISCUSSION

5.1 Iodide distribution in the three areas studied

Surface iodide concentrations are low in the Southern Ocean compared to lower latitudes where concentrations can reach up to 200nmol L^{-1}. This is most likely due to higher temperatures, higher biomasses and solar radiation on an annual basis in that region. The waters of the Southern Ocean are rich in macronutrients but often lack iron (Martin et al. 1990) so that primary productivity is limited. In summer however, iron is released into the water column through sea ice melting that accumulated iron during the winter via atmospheric particle deposition in higher quantities compared to seawater concentrations (Edwards & Sedwick 2001, Croot et al. 2004, Lannuzel et al. 2006). During the preceding cruise in austral summer (January 2008) the area between 61ºS and 64ºS along the Zero Meridian was rich in chlorophyll-*a* (Figure 10, left) and revealed a maximum biological productivity of 1.9µg chlorophyll-*a* L^{-1}, an intense phytoplankton bloom dominated by *Phaeocystis antarctica* (Personal correspondence: U Bathmann, Chief Scientist ANTXXIV-2). At the time of our sampling in this area this bloom had declined and biological production was limited again (Figure 10, center and right). For this region our results show that highest surface iodide values were found in the post bloom waters indicating towards a connection between iodide accumulation and phytoplankton senescence.

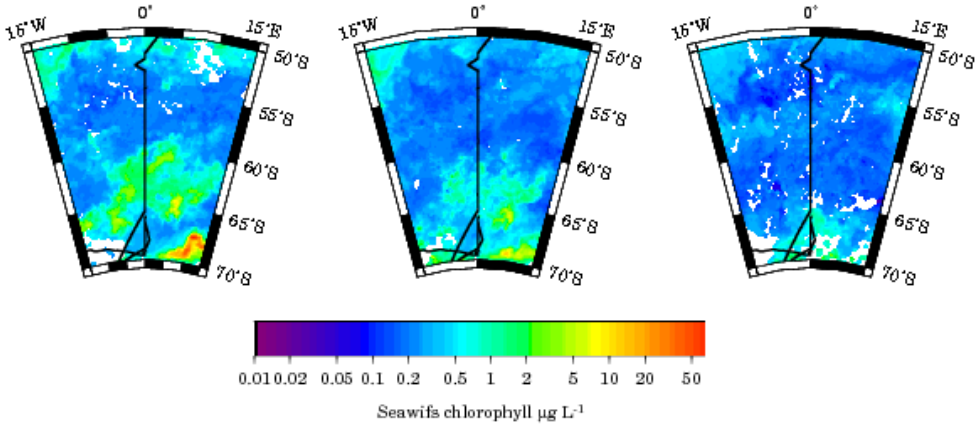

Figure 10: Monthly average chlorophyll-*a* distribution along the Zero Meridian. Jan 2008 (left); Feb 2008 (centre); March 2008 (right)

The deepening of the 10nmol L^{-1} iodide isopleth towards the Antarctic continent and within the Antarctic slope front is well pronounced (Figure 3). Whether this is mixing due to downwelling at the continent in the antarctic slope front (Klatt et al. 2002) which takes the iodide signal from the surface down deeper, similar to the CFC tracers, or simply because of a high iodide production within the euphotic zone and local production via sinking material is difficult to decide presently. The downwelling would presume longer iodide residence times of years than months as Campos et al. (1996) estimated for the Tropical Ocean. However, longer iodide lifetimes might be true for the cold waters of the Southern Ocean. The exact half life and mechanism for the iodide to iodate conversion, especially in surface waters where biological processes might be important, is still unknown (Wong 1991, Luther et al. 1995) and we develop some possible explanations in section 5.3.

In the Weddell Sea surface iodide were higher than previously reported for this region (Campos et al. 1999) although sampling was carried out in the same season. The elevated iodide concentrations in the Weddell Sea bottom and along the easterly slope of the Weddell Basin could be explained due to sediment releases and diagenesis. However these processes are mostly found in anoxic basins and are therefore considered unlikely as it was not observed elsewhere during this study and bottom waters are well oxygenated in the Weddell Basin (Figure 5 bottom). We come up with another possible hypothesis for this in section 5.4.

In the Drake Passage severe storms and wave actions lead to a thorough mixing of the water column taking surface water iodide down deep explaining the patchy distribution of iodide. Besides this high eddy activities are also known for these waters. During our cruise the two stations (St. 237 and 243, figure 8) with an iodide maximum at depth were situated right at the edge of a large cyclonic eddy which is associated with increased chlorophyll-*a* in the core (Figure 9a; Kahru et al. 2007) and might be an explanation for the deep iodide

signal. Biological material inside the eddy sinks out upon cell death and releases intracellular iodide as well as dissolved organic matter (DOM) due to bacterial remineralization (Luther et al. 1995). The released DOM such as sulphur containing metabolites are able to reduce the iodate present at depth. With the Drake Passage being a productive area throughout the year (Figure 11) higher amounts of particulate organic matter (POM) sink to the bottom and release iodide back to the water column through bacterial remineralization.

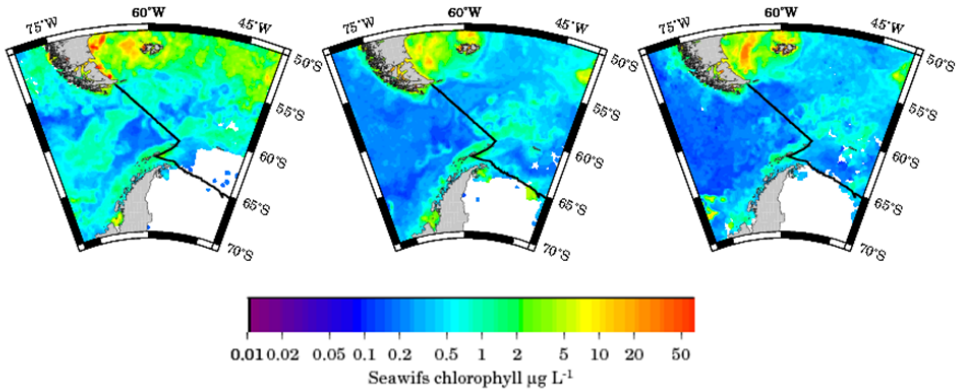

Figure 11: Monthly average chlorophyll-*a* distribution in the Drake Passage. Dec 2008 (left), Feb 2008 (centre), March 2008 (right).

5.1.1. Vertical profiles of iodide

In the vertical profiles we often observed an accumulation of iodide at depth which might be due to sinking algae material releasing small amounts of iodide through bacterial remineralization (Luther et al. 1995). This would imply that the accumulation of iodide is more a biological decomposition than a biological production mechanism. Additionally, iodide sub-surface maxima were observed in most of the stations sampled. Sub surface maxima point to a formation of iodide by non-photochemical processes involving zooplankton grazing and again bacterial remineralization (Luther et al. 1995). Therefore the iodide sub-surface maxima under the ice in the Weddell Sea can also be related to zooplankton grazing activity and bacterial remineralization resulting in a release of DOM back to the water column. Vertical distribution data of three different copepod species show that most of the adults and also younger life stages stay close to the ice cover at depth between 40m – 200m (Burghart et al. 1999) converging with the depths of the sub-surface maxima.

Two samples of the algal community were taken at station 152 along the Zero Meridian and station 241 in the Drake Passage. At both stations *Fragilariopsis kerguelensis* was the most abundant species with a percentage of 52% for station 152 and 27% for station 241. Additionally, *Pseudo-nitzschia turgiduloides* was also present in both stations but at lower quantities (11% in St. 152 and 3% in St. 243; P. Assmy unpublished data). *Pseudo-*

nitzschia turgiduloides has been found to exist predominantly in the neritic Weddell Sea zone south of the Antarctic slope front (Almandoz et al. 2008).

Complementary laboratory experiments concerning the reduction of iodate to iodide revealed that Antarctic diatoms can facilitate this reaction and and iodide levels peaked at the end of the stationary growth phase, suggesting that the iodide production mechanism is connected to cell senescence (Bluhm et al. 2009 submitted).

5.2. Nutrients and Iodide

Tsunogai and Sase proposed that bacterial nitrate reductases have a strong preference for nitrate over iodate (Tsunogai & Sase 1969). Usually in the open ocean the concentration of nitrate is low in the surface water and therefore the preference of nitrate over iodate might be reduced so that iodate is reduced instead. However, in the Southern Ocean surface nitrate concentrations are usually quite high as phytoplankton growth is limited due to the lack of iron (Martin et al. 1990, Boyd et al. 2000, Franck et al. 2000). Though, in areas with more chlorophyll-*a*, higher iodide concentrations could indicate that iodate might be reduced together with nitrate while excessive nitrate concentrations still prevail.

Campos et al. (1999) found an apparent relationship between iodide and nitrate concentrations during their study where iodide concentrations increased as nitrate concentrations decreased along their transect. Our field data did not reveal such a relationship but instead we found a slight positive correlation with nitrite concentrations in all three transects (data not shown). Nitrite is a waste–product and used as an indicator of senescence in phytoplankton cells which lead us to the assumption that the formation of iodide may be influenced by biological decay processes. Bacterial nitrification is responsible for the nitrite accumulation via organic matter remineralization and the subsequent oxidation of ammonia.

5.3 Oxidation of iodide to iodate

The several sub-surface maxima of iodide during ANTXXIV-3 could point either to an iodide production at that depth or an iodide oxidation in the surface layers above due to abiotic/biotic processes. Abiotic oxidation mechanisms of iodide are all kinetically slow (Luther et al. 1995) with only a few estimates of actual iodate formation in the field (Edwards & Truesdale 1997, Hou et al. 2007, Zic et al. 2008). Studies on the radiotracer ^{129}I in the North Sea showed that the overall oxidation rate from iodide back to iodate is extremely slow (Hou 2007). Edwards and Truesdale (1997) determined an oxidation rate of 30 ± 10nmol^{-1} y-1 in the deep waters of a Scottish Loch. While more recently Zic et al. (2008) found evidence

for oxidation back to iodate in a land locked cave pool with a subterranean connection to the ocean, called an anchialine pool, and suggested that this process was bacterially mediated. Anchialine pools are a feature of coastal aquifers which are density stratified, with the water near the surface being fresh or brackish, and saline water intruding from the coast below at some depth.

While the biological oxidation of iodide to hypoiodous acic (HOI) and molecular iodine (I_2) is reasonably well described via iodo-peroxidases (Amachi et al. 2005, Amachi et al. 2007b), the final oxidation step of HOI/I_2 to iodate is almost unreported in the literature. Indeed we can only find one instance with a chloroperoxidase containing fungus *Caldariomyces fumago* (Thomas & Hager 1968) and no information from the marine environment.

5.4 Iodide as a tracer

Following the iodide characteristics in the Weddell Sea basin could lead to the conclusion that iodide can be used as a tracer for recent deep water formation of 2-10 year old water masses as it is seen in the oxygen data (Figure 5). Here cold, dense water from the surface sinks to the bottom along the westerly slope of the Weddell Sea Basin and forms the Weddell Sea Bottom Water (WSBW; Figure 1). Iodide was only detected in these water masses and not in the older Weddell Sea Deep Water (WSDW) above, indicating that iodide oxidation is completed in the WSDW. Estimates of the transit time from the WSBW formation regions on the ice shelf are around 9 years for the northwestern part of our Weddell transect to 22 years for the central part (Huhn et al. 2008). Therefore the complete oxidation of iodide back to iodate in the Weddell Sea must be on the time scale of decades. Iodide oxidation should be very slow in the deep due to less biology and no photochemical reactions. Based on typical iodide shelf concentrations in the Antarctic of 40-80nmol L^{-1} (Chance et al. 2009 submitted and this study) would suggest an oxidation rate of 3-6nmol L^{-1} y^{-1}, assuming it is a linear process and mixing was negligible.

5.5 Iodine fluxes to the atmosphere

The dry deposition of Ozone (O_3) on to the ocean's surface causes reactions with iodide and is a principal loss term for this important trace gas (Garland et al. 1980). The importance of iodine chemistry processes to global atmospheric O_3 has recently been assessed in a global climate model (Oh et al. 2008) and in chemical models (Simpson et al. 2007) for the polar regions to explain the observations of the rapid formation of IO and depletion of O_3 in the marine boundary layer in both the Arctic (Hausmann & Platt 1994) and the Antarctic (Friess et al. 2004). The reaction of O_3 with iodide is rapid (Liu et al., 2001) and

limited to the sea surface microlayer (SML) where O_3 concentrations are high. During iodide oxidation with O_3 two intermediates, hypoiodous acid (HOI) and molecular iodine (I_2), are formed which can be volatilized to the atmosphere (Garland & Curtis 1981). O_3 can further oxidize HOI/I_2 to iodate (Parry & Hern 1973) but it is believed that this is a minor pathway in the SML as most of the O_3 flux to the surface reacts with iodide and not HOI (Bichsel & von Gunten 1999).

Further reactions with HOI/I_2 and dissolved organic matter (DOM) in the SML result in volatile organoiodine compounds (VOI's) formation such as methyl iodide (CH_3I) and diiodomethane (CH_2I_2) (Martino et al. 2009). Biologically mediated or photochemical production of VOI's is also likely to occur throughout the euphotic zone (Moore & Zafiriou 1994, Richter & Wallace 2004, Smythe-Wright et al. 2006). The VOI's can be volatilized to the atmosphere, destroyed by UV-irradiation or mixed deeper into the water column (Martino et al. 2006, Carpenter et al. 2007). In the Polar regions VOI's may be produced on the surfaces of sea ice (Swanson et al. 2007) and in frost flowers (Kaleschke et al. 2004) that form on sea ice. During the present work we made a limited set of measurements in sea ice collected close to shelf ice in the vicinity of the German Research station Neumayer. In only 1 of the 4 samples was iodide detectable (5nmol L^{-1}) while iodate appeared to be related to salinity. Unfortunately we were not able to analyze the brine water of the samples where models suggest that the iodide would be elevated (Saiz-Lopez & Boxe 2008) and this clearly remains a priority for future work in this region.

In the atmosphere photochemical processes break the C-I bond of the VOI's and release iodine which can then be oxidized to the reactive transient species iodine monoxide (IO). Satellite observations over the globe indicate high concentrations of IO in the Antarctic atmosphere with the Weddell Sea identified as one of the key source regions (Saiz-Lopez et al. 2007, Schonhardt et al. 2008). Our data indicate that the Weddell Sea has relatively low iodide in the surface waters and thus the source of the IO must lie in processes related with reactions on sea ice and not in the open water or under the cover of sea ice.

6. CONCLUSIONS

Elevated iodide in the post bloom waters along the Zero Meridian of the Eastern Weddell Gyre indicate towards a strong relationship between iodide production and primary production/decomposition but is presumably not connected to nitrate utilization in the water column. Furthermore, a correlation with nitrate was not observed during this study, but weak correlations with nitrite suggest that iodide production was partly related to bacterial remineralization of sinking organic matter. The oxidation of iodide is apparently slow in the

downwelling water close to the shelf at the Zero Meridian and in newly formed Weddell Sea bottom water (WSBW) and may be related to low biological activity in this cold and dense water mass. Alternatively the deep iodide could be released from the sediments but this is considered unlikely as it was not observed elsewhere during this study and bottom waters are well oxygenated. Thus iodide may have the potential as a short lived transient tracer for newly formed bottom waters along the Antarctic continent. The appearance of iodide in the WSBW and not in the Weddel Sea deep water (WSDW) indicate that iodide oxidation is complete in the older WSDW and that complete oxidation of iodide in the Weddell Sea must be on the time scale of decades.

The observations of high iodide concentrations in the Drake Passage are likely related to cyclonic eddy activity.

7. ACKNOWLEDGEMENTS

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MANUSCRIPT 3

Transformation of iodate to iodide in marine phytoplankton driven by cell senescence

Transformation of iodate to iodide in marine phytoplankton driven by cell senescence

by

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ABSTRACT

Previous studies have suggested that phytoplankton play an important role in the biogeochemical cycling of iodine. The reason for this lies in the appearance of iodide in the euphotic zone. During growth of a variety of phytoplankton taxa (diatoms, dinoflagellates and prymnesiophytes) changes in the speciation of iodine were examined over the course of the growth cycle. All species tested showed the apparent ability to reduce iodate to iodide, though production rates varied considerably between species (0.01-0.26nmol L^{-1} µg chl-*a*$^{-1}$ day^{-1}), with *Eucampia antarctica* the least efficient and *Pseudo-nitzschia turgiduloides* the most efficient iodide producer. Production was found to be species specific and was not related to parameters indicating biomass (i.e. cell size, cell volume or chlorophyll-*a* content). In all species, except for the mixotrophic dinoflagellate *Scrippsiella trochoidea*, iodide production commenced in the stationary- and peaked in the senescent growth phase of the algae indicating that iodide production is connected to cell senescence and suggesting that iodate reduction may occur due to increased cell permeability and subsequent reaction of iodate with reduced sulphur species exuded from the cell. A shift from the senescence back to the exponential growth phase resulted in a decline in iodide and indicated that phytoplankton mediated oxidation of iodide to iodate was likely occurring. Iodide production could not be observed in healthy cells kept in the dark for short periods. Bacterial processes appeared to play only a minor role in the reduction of iodate to iodide.

1. INTRODUCTION

Iodine exists principally in open seawater as the inorganic redox forms, iodate (IO_3^-) and iodide (I^-) with a total concentration of 400 – 500nmol L^{-1} in most oceanic regions. While iodate is predominating in the deep ocean (Tsunogai & Sase 1969, Elderfield & Truesdale 1980, Farrenkopf et al. 1997) significant amounts of iodide are found in surface and near bottom layers (Kennedy & Elderfield 1987, Wong 1991, Luther et al. 1995). The interconversion of the redox couple, iodate – iodide, within the euphotic zone, together with the biophilic nature of iodine has given rise to the idea that iodine speciation is linked to primary productivity (Sugawara & Terada 1967, Tsunogai & Henmi 1971, Elderfield & Truesdale 1980, Moisan et al. 1994, Campos et al. 1996, Truesdale et al. 2000). The evidence for iodate reduction by primary productivity has come from field observations where it has been observed that surface iodate decreases towards the productive equatorial regions (Tsunogai & Henmi 1971, Jickells et al. 1988, Campos et al. 1996, Truesdale et al. 2000) and additionally the distinct correlation between iodate and macronutrient concentrations at several stations (Elderfield & Truesdale 1980, Truesdale 1994, Campos et al. 1999). Although abiotic mechanisms have been proposed for the reduction of iodate and the consequent formation of iodide (Spokes & Liss 1996) the presence of iodide in the surface waters is typically ascribed to biological activity (Campos et al. 1996). Iodide reacts rapidly with O_3 and is believed to be a major sink for atmospheric O_3 at the sea surface (Garland et al. 1980). This reaction forms HOI and I_2 and has also been suggested as a source of organic halogens (RI) (Martino et al. 2009). RI released from the sea to the atmosphere will undergo photolysis and oxidation in the atmosphere to form IO (Saiz-Lopez et al. 2007, Schonhardt et al. 2008) which is the major source of new particles in the atmosphere (von Glasow 2005) with the potential to influence clouds properties and hence climate (O'Dowd & de Leeuw 2007). Thus information on the cycling of iodine species in the ocean is important in assessing the impact of iodine in tropospheric ozone chemistry and for climate dynamics. While clearly biology plays a role in the marine iodine cycle it is still not clear what the link between biological processes and the speciation of iodine in seawater is.

Laboratory experiments on the influence of phytoplankton on iodine speciation have led to varying results. In the first such work of this type, Sugawara and Terada (1967) examined iodide and iodate assimilation by a marine diatom, *Navicula sp.*, using radio tracers. In this work this diatom preferentially assimilated iodide over iodate and appeared to accomplish the conversion of iodide to iodate and vice versa. A recent radiotracer study into the accumulation rates of iodide and iodate by a number of phytoplankton batch culture experiments, confirmed this preference for iodide over iodate for uptake by phytoplankton but also showed large differences between species (de la Cuesta & Manley 2009). Other laboratory experiments with phytoplankton cultures have shown significant iodate uptake

rates (Moisan et al. 1994). The conversion of iodate to iodide has been shown in batch culture at close to ambient iodate concentrations (Wong et al. 2002, Chance et al. 2007). Throughout much of this work the driving force has been to test the hypothesis put forward by Tsunogai and Sase (1969) that nitrate reductase can reduce iodate to iodide in the ocean when nitrate is limiting. This hypothesis had grown out of the earlier finding by Egami and Sato (1947) that nitrate reductase is capable of reducing iodate under physiological conditions. Contrastingly a number of studies have found no relationship between iodine and biological activity or only observed iodide increases in phytoplankton cultures at iodate concentrations 10 times greater than naturally found (Truesdale 1978b, Butler et al. 1981, Waite & Truesdale 2003). A detailed study (Waite & Truesdale 2003) into the nitrate reductase hypothesis in which cells were either grown on ammonia or the enzyme was deactivated by the addition of tungsten showed that iodate reduction was relatively insensitive to the function of nitrate reductase.

Experiments examining changes in iodine speciation have been predominantly performed with temperate, tropical and to a lesser extent cold water species, with Antarctic species having been totally neglected. Surface iodide concentrations are low in the Southern Ocean although with some surface maxima which are possibly due to biological activity (Campos et al. 1999, Truesdale et al. 2000, Waite et al. 2006, Bluhm et al. 2009 in revision). During an Antarctic mesocosm experiment carried out by Truesdale et al. (2003) no changes in iodine speciation were observed. The authors suggested that the large, chain forming diatom *Thalassiosira antarctica*, which dominated the mesocosm blooms, is unable to perform the reduction of iodate to iodide. As phytoplankton blooms in polar regions typically exist over more than 30 days (Boyd 2004) the 25 day duration of their mesocosm experiment apparently did not catch the end of the bloom. The importance of this lies in the observation from an earlier field study conducted over a seasonal cycle in the Mediterranean by Tian et al. (1996) which indicated that iodate reduction was related to regenerated production and not primary production directly. Thus the mesocosm work of Truesdale et al. (2003) may not have run long enough to observe the critical phase of senescence. As most of all the earlier culture studies were focused on examining the purported link between iodate reduction and nitrate reductase this suggested to us that the differences and contradictions between these earlier experiments may have been related to the duration of the experiments and to the phase of culture growth of the cells during the experiments.

In the present work we tested whether the different growth phases exhibited different iodate reduction rates. We examined the iodate reduction over long term culture experiments where the cells pass through the 5 characteristic phases of growth in cultures (Fogg & Thake 1987): (1) lag phase, (2) exponential phase, (3) phase of declining relative growth rate, (4) stationary phase, and (5) senescent or declining phase. This work was performed in the

laboratory under nitrate replete conditions with six different species of phytoplankton (four Antarctic diatoms, one coccolithophore and one dinoflagellate), representing coastal and oceanic species from cold to temperate waters.

2. MATERIAL AND METHODS

2.1. Phytoplankton cultures

Three Antarctic diatom strains, *Fragilariopsis kerguelensis, Chaetoceros debilis* and *Pseudo-nitzschia turgiduloides*, were isolated from the Southern Ocean during the iron fertilization experiment EIFEX in February/March 2004 by P. Assmy (AWI-Bremerhaven). A fourth Antarctic diatom *Eucampia antarctica* [CCMP 1452] and the tropical strain of the cocclithophore *Emiliania huxleyi* [CCMP 371] were obtained from the Provasoli-Guillard Centre for the Culture of Marine Phytoplankton, Bigelow Laboratory, USA. The dinoflagellate *Scrippsiella trochoidea* was isolated from the southern North Sea in 2001 by U. Tillman (AWI-Bremerhaven). All species were non - axenic and their characteristics are listed in Table 1. *E. huxleyi*, although being isolated from the tropical ocean was cultured under temperate conditions and is referred to here as temperate species.

2.2. Experimental set-up

Several experiments were carried out to determine the iodide production mechanism and are listed in Table 2. In general all species examined were grown in seawater collected from their natural habitat, with nutrient concentrations of f/2 conditions, according to the method of Guillard and Ryther (Guillard & Ryther 1962, Guillard 1975) The final phosphate and silicate concentrations in the medium are 36µmol L^{-1} and 106µmol L^{-1}, respectively. Additionally all diatom species were supplied double the usual silicate concentrations (212µmol L^{-1}). In Experiment 1a nitrate concentrations were lowered to f/20 conditions with a final concentration of ~88µmol L^{-1}. Two sets of culture were run in parallel. One set was exposed to a Photosynthetically Active Photon Flux Density (PFD) of 50µmol quanta m^{-2} s^{-1} and the other to 100µmol quanta m^{-2} s^{-1}. Aliquots were sampled regularly to a total length of 55 days or until cells reached mortality. Growth conditions for each experiment are listed in Table 2.

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Table 1: Species characteristics of the two temperate strains *E.huxleyi* and *S.trochoidea* and four cold water diatoms *C.debilis*, *P.turgiduloides, E.antarctica* and *F.kerguelensis* used in the experiments and their natural distribution. Average values are quoted; n > 30. Coccol.: coccolithophorid; dino.: dinoflagellate.

Phytoplankton species	Algal group	Size [μm^2]	Volume [μm^3]	pg C $cell^{-1}$	Area $Volume^{-1}$	Distribution
Temperate species						
E.huxleyi	Coccol.	47	31	5	1.49	Cosmopol. oceanic, not polar regions
S.trochoidea	Dino.	1335	4045	581	0.33	Cosmopol. neritic/estuarine, not polar regions
Cold water species						
C.debilis	Diatom	90	63	8	1.42	Cosmopol., mainly cooler waters
P.turgiduloides	Diatom	1168	1388	102	0.84	southern cold water
F.kerguelensis	Diatom	1697	4677	200	0.36	southern cold water
E.antarctica	Diatom	2711	6741	276	0.40	southern cold water

Table 2: Overview of experiments conducted during this study. L:D: Light : Dark cycle given in hours.

Experiments	Species	Temperature [C°]	L:D [h]	PFD	Iodate added [µM]	Nitrate added [µM]	Nitrate depletion
Experiment 1							
(a) iodide production	Temperate	18	12:12	50 / 100	5	88	No
	Cold water	4	16:08	50 / 100	5	88	No
(b) iodide production	*C.debilis*	4	16:08	50	1	44	Yes
Experiment 2							
Metabolites and bacteria	*P.turgiduloides*	4	16:08	50	5	88	No
Experiment 3							
Dark production	*P.turgiduloides*	4	0:24	---	5	88	No

Experiment 1b was carried out with a *C.debilis* culture at lower initial iodate and nitrate concentrations of approximately 1µmol L^{-1} and 44µmol L^{-1}, respectively. After cells used up all nitrate and the photosynthetic efficiency (Fv/Fm; description see below) reached a value below 0.3, a second nitrate addition of f/20 conditions (~88µmol L^{-1}) was performed on day 24. Sampling frequency was the same as in Experiment 1a. Controls were run in parallel to each experiment (1a and 1b) with the same conditions but containing no phytoplankton cells.

An extra control was obtained for Experiment 2 by filtering a senescent *P.turgiduloides* culture over a 5µm mesh to discard phytoplankton cells but retain all dissolved organics and bacteria in the water. This was done to see whether these metabolites or bacteria have an effect on the conversion of iodate to iodide itself or if it is exclusively done by the phytoplankton. The filtrate was sampled over a period of 30 days.

Experiment 3 was conducted to ascertain whether the conversion of iodate to iodide is light dependent and connected to photosynthesis. Duplicates of *P.turgiduloides* and *C.debilis* were placed in the dark and sampled over a period of 31 days.

All cultures used were monoclonal and culture handling was done under a laminar flow hood to prevent any outside contamination. The sample bottles and lids were sterilized via autoclaving and sterile filtered (Sartobran 300 capsules with a filter combination of 0.45µm and 0.2µm) growth media was used.

2.3. Measured parameters and analytical methods

Nutrient samples were filtered over cellulose acetate filters (pore size 2µm) and the filtrate stored frozen (-20°C) until analysis. Measurements were performed using standard methods for macronutrient analysis after Grasshoff et al. (1999). Samples for chlorophyll-*a* measurements were filtered on glass fibre filters (GF/F-Whatman) and immediately stored at -20°C. The frozen filters were placed in polypropylene vials together with 11ml of 90% acetone and glass beads (2mm and 4mm). Thereafter, the closed vials were placed in a cell mill for at least 5 minutes until the filters were completely homogenized. The vials were then centrifuged at -5°C (10min at 5000rpm) and the supernatant was measured fluorometrically with a Turner fluorometer according to the method of Welschmeyer (1994).

The photosynthetic efficiency (Fv/Fm) (Suggett et al. 2003, Rottgers 2007) of the cells was assessed with a Phyto-PAM Phytoplankton Analyzer (WALZ, Effeltrich, Germany). In this work samples of phytoplankton culture were dark adapted for 30min before measurement. Optimal values of Fv/Fm lie around 0.4-0.6 for phytoplankton cultures, lower values indicate cells under stress from nutrient limitation or iron limitation (Maxwell & Johnson 2000).

For cell enumeration all cultures except *E.huxleyi* were preserved with LUGOL's solution at a final concentration of 4%. *E.huxleyi* was preserved with 0.2µm prefiltered formaldehyde at a final concentration of 1%. All samples were stored at 4°C in the dark for subsequent

counting. Cells were enumerated using inverted light microscopy (Axiovert 135, Zeiss, Oberkochen, Germany) according to Utermöhl (1958). Only viable cells which were still auto-fluorescing were counted. The cell size of the different species and groups was determined and their biovolume calculated from equivalent geometrical shapes (Hillebrand et al. 1999). The cell volume was then converted to cellular carbon content through carbon conversion equations using a carbon to volume relationship recommended by Menden-Deuer and Lessard (2000).

Bacterial abundances were determined by Flow Cytometry according to Gasol and Del Giorgio (2000). Samples were fixed with 0.2µm prefiltered formaldehyde (2% final concentration) in 5ml cryovials, deep-frozen in liquid nitrogen after a 30min dark incubation, and stored at -80°C. Before analysis, the thawed samples were stained with SYBR Green 1 (Molecular Probes, final concentration 5 µM, diluted in dimethyl sulfoxide (DMSO)) for 15min in the dark. Samples were run through a FACScalibur flow cytometer (Becton & Dickinson, San José, CA, USA). Bacterial biomass was calculated from abundance data using a conversion factor of 20fg C $cell^{-1}$ (Lee & Fuhrman 1987).

2.4. Iodine speciation

Samples were filtered over cellulose acetate filters (pore size 2µm) and if not measured immediately stored frozen (-20°C) until analysis. Iodide was determined by cathodic stripping square wave voltammetry according to the method of Luther and Swartz (1988), modified by Campos (1997) with a detection limit of 0.1-0.2nmol L^{-1} and a precision of better than 5%. Iodate was determined spectrophotometrically by its conversion to the I_3^- ion with sulphamic acid, to remove interference by nitrite, and potassium iodide after the method of Truesdale (1978a). Samples were measured in a 5 cm cuvette with a “Unicam” spectrophotometer (UV300, Thermo-Forma) at a wavelength of 350nm. The accuracy of the method lies within 5% with a detection limit of around 20nmol L^{-1}. Samples were measured in triplicate for both iodide and iodate and standard deviations were gained from the triplicates measured.

3. RESULTS

3.1. Chlorophyll-a, growth and bacterial carbon

The changes in chlorophyll-*a* concentration, cell numbers and bacterial carbon for all species tested are shown in Figure 1 - 4. As expected for all species, less chlorophyll-*a* per cell was observed in samples grown under the higher light intensity of 100 µmol quanta m^{-2}

s^{-1}. The exact time when cells entered a particular growth phase varied between species. The exponential phase, as indicated by a rapid increase in both chlorophyll-*a* and cell numbers until a maximum value is reached, lay within the first 8-18 days for most of the species except *Eucampia antarctica* and *Fragilariopsis kerguelensis*. Both these species are slow growing due to heavy silicification and a great cell size (Table 1) and their exponential phase continued until day 24 (Figure 1c).

The stationary growth phase was in general between 4 and 17 days long, whereas in *Emiliania huxleyi* and *Pseudo-nitzschia turgiduloides* a distinct stationary phase could not be observed. Their cell numbers increased exponentially and went straight into senescence after reaching a maximum. This might be due to the timing of sampling, so that we missed the stationary phase, or just their fast growing behaviour (Figure 1c – 4c). Throughout the experiment most of the cultures did not run into nutrient limitation. Nitrate, silicate and phosphate concentrations were still high when cells reached a senescent growth phase with over 30µmol L^{-1} for nitrate, over 60µmol L^{-1} for silicate and over 23µmol L^{-1} for phosphate. The only two exceptions, *Scrippsiella trochoidea* which used up all nitrate present within 10 days, and *Fragilariopsis kerguelensis* which used up all available silicate and phosphate before cells showed a rapid decline in cell numbers (data not shown).

Iodine (I_2) can be toxic to organisms and is used in LUGOL's solution for preserving phytoplankton cells (Stoecker et al. 1994). The behaviour and growth of the phytoplankton was not affected by the added iodate. Measured chlorophyll-*a* and cell densities appeared similar to untreated samples and species showed normal growth rates of 0.11-0.31 throughout the experiments suggesting that the added iodate neither enhanced nor inhibited cell growth.

Bacterial densities are expressed in bacterial carbon [µg C L^{-1}] and are related to the phytoplankton biomass also expressed in µg C L^{-1}. Bacterial numbers in the batch cultures varied between phytoplankton species but usually were the minor component. Numbers peaked at the end of the experiment and within the senescent growth phase of the phytoplankton (Figure 1b - 4b).

3.2. Depletion of iodate

Iodate depletion was only observed when iodide concentrations typically exceeded 60 nmol L^{-1} this was due to the combination of high iodate concentrations and the higher detection limit of this method (20 nmol L^{-1} for undiluted samples). Overall however a total mass balance was obtained for iodate and iodide throughout the experiments within experimental error, suggesting organic or particulate iodine species were less than 20nmol L^{-1} throughout the experiment. Thus for the remainder of the manuscript we concentrate solely on the iodide results.

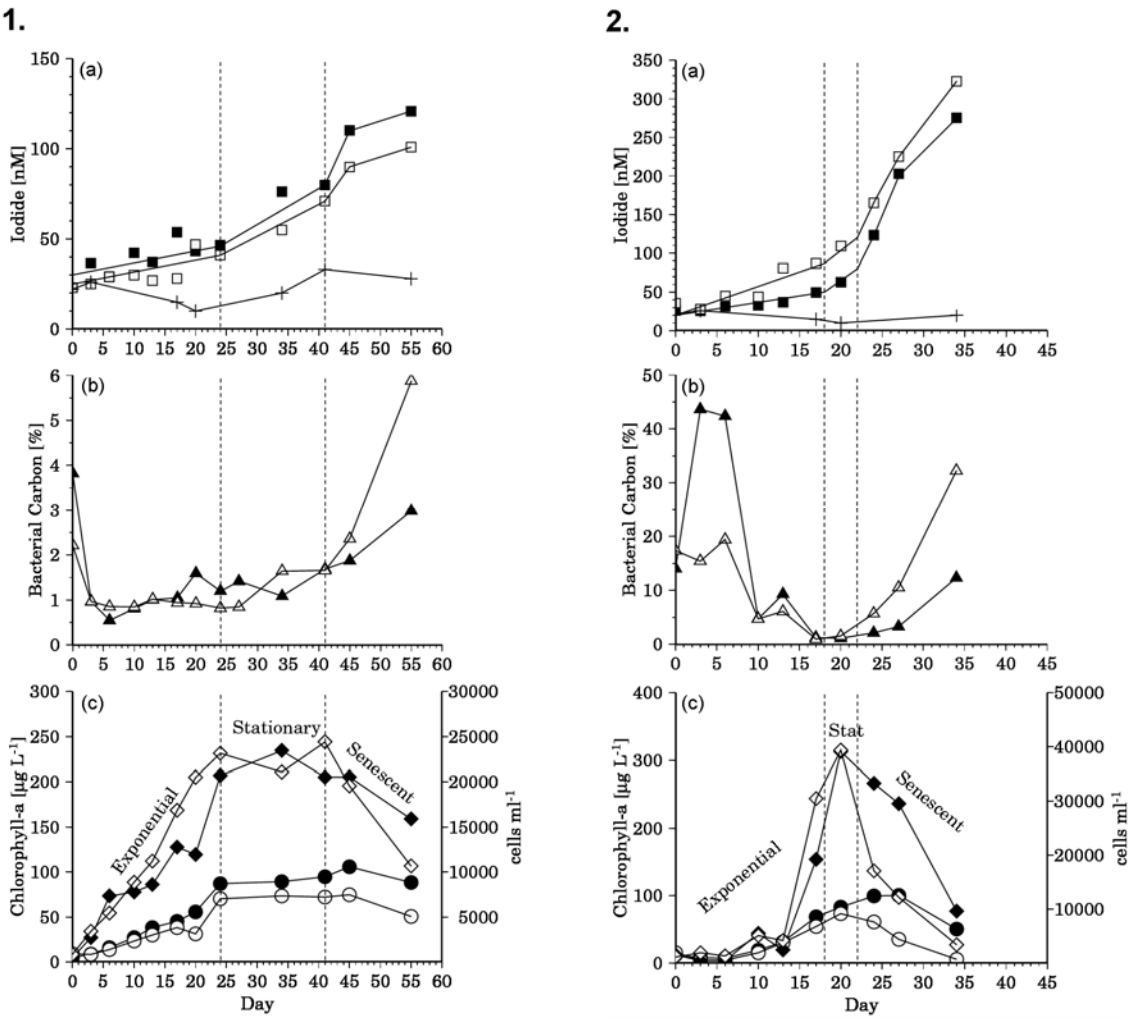

Figure 1 and 2: (a) Iodide production, (b) bacterial carbon, and (c) chlorophyll-*a* and cell numbers in cultures of 1. *Fragilariopsis kerguelensis* and 2. *Pseudo-nitzschia turgiduloides*. Dashed lines indicate the position of the different growth phases. Solid symbols represent samples grown at 50µmol quanta m^{-s} s^{-1}, open symbols represent samples grown at 100µmol quanta m^{-s} s^{-1}. Bacterial carbon is given as percentage of the total carbon present in the culture flask. (Circles: chlorophyll-*a*, diamonds: cell numbers, triangles: bacterial carbon, squares: iodide production, crosses: control without algal cells) Note that the scales for the y-axes are changing for each species.

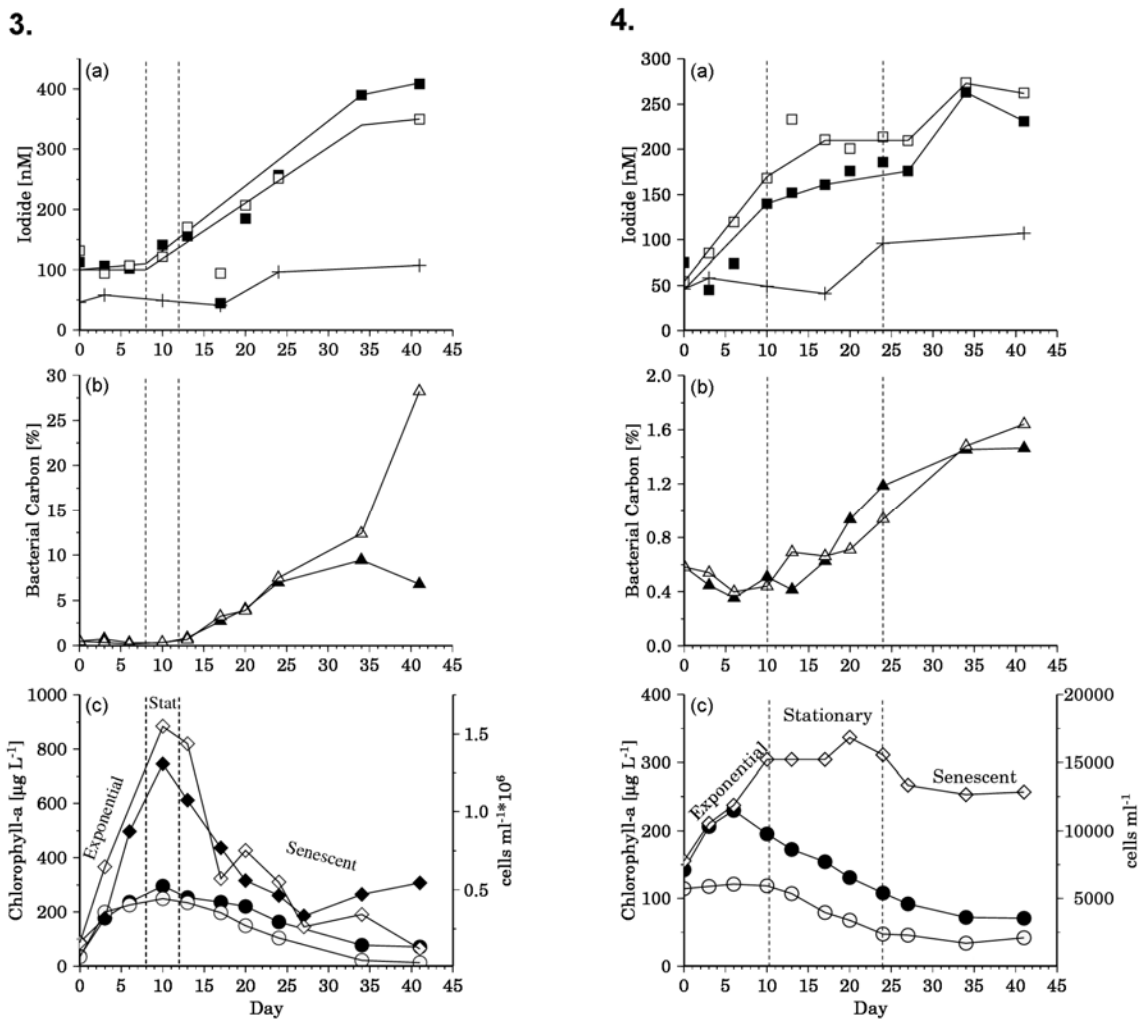

Figure 3 and 4: (a) Iodide production, (b) bacterial carbon, and (c) chlorophyll-*a* and cell numbers in cultures of 3. *Emiliania huxleyi* and 4. *Scrippsiella trochoidea*. Dashed lines indicate the position of the different growth rates. Solid symbols represent samples grown at 50µmol quanta m^{-s} s^{-1}, open symbols represent samples grown at 100µmol quanta m^{-s} s^{-1}. Bacterial carbon is given as percentage of the total carbon present in the culture flask. (Circles: chlorophyll-*a*, diamonds: cell numbers, triangles: bacterial carbon, squares: iodide production, crosses: control without algal cells) Note that the scales for the y-axes are changing for each parameter and species.

Table 3: Characteristics of the iodide production rates in cultures of marine phytoplankton. [a]initial iodate concentrations added; [b]total iodide produced over the course of the experiment; [c]time averaged chlorophyll-*a* gives an average chlorophyll-*a* value for each species; [d]rates were the slope of a linear regression analysis of iodide concentration vs. time; [e]is the rate k normalized to time averaged chlorophyll-*a*. avg: average; R^2 correlation coefficient

					Iodide production rates[d]			
Phytoplankton species	Iodate[a] [µM]	Iodide[b] [nM]	chl-*a*/cell [pg cell^{-1}]	avg. chl-*a*[c] [µg L^{-1}]	rate (*k*) [nM d^{-1}]	*k*/chl-*a* [nM µg^{-1} d^{-1}]	*k*/cell *10^{-4} [nM cell^{-1} d^{-1}]	R^2
Temperate species								
E.huxleyi 50	5	302	0.29	169.98	6.76	0.04	0.11	0.94
E.huxleyi 100		256	0.19	128.98	7.15	0.06	0.09	0.77
S.trochoidea 50	5	186	9.63	122.16	3.40	0.03	2.65	0.89
S.trochoidea 100		208	6.55	67.48	3.39	0.05	2.96	0.78
Cold water species								
C.debilis 50	5	166	0.47	110.70	4.19	0.04	0.16	0.95
C.debilis 100		142	0.29	60.96	3.83	0.06	0.14	0.87
P.turgiduloides 50	5	249	4.15	52.91	7.74	0.15	4.93	0.81
P.turgiduloides 100		295	3.03	31.24	7.97	0.26	6.43	0.87
F.kerguelensis 50	5	78	4.08	67.99	1.25	0.02	0.80	0.92
F.kerguelensis 100		98	2.91	50.88	1.51	0.03	0.93	0.92
E.antarctica 50	5	122	43.29	159.62	1.95	0.01	5.00	0.80
E.antarctica 100		152	37.07	111.30	2.75	0.02	8.53	0.96

3.3. Production of iodide

Iodide production was only observed in the presence of the algae with no production in the cell-free controls (Figure 1a - 4a). In Experiment 1 the production of iodide was observed in all species examined. The average iodide production rates per day (*k*) were estimated as the slope of a linear regression analysis and the results are listed in Table 3. The correlation coefficients R^2 were always between 0.77 and 0.96. The amount of total iodide produced over the length of the experiment varied within species from 78–302nmol L^{-1} and *k* ranged from 1.25 to a maximum of 7.97nmol L^{-1} day^{-1} (Table 3). *Emiliania huxleyi* and *Pseudo-nitzschia turgiduloides* had the highest rate *k* with the greatest amount of total iodide produced relative to the other species.

The rate *k* was additionally normalized to the so called "time-averaged chlorophyll-*a*" and this was done with the trapezoidal method. The trapezoidal method is used to approximate the area under a curve (the chlorophyll-*a* vs. time curve in this case) by circumscribing *n* number of trapezoids under this curve. The area of the trapezoids is then summed. This method is used to gain average chlorophyll-*a* values for the whole length of the experiment for each species. The same method was used to normalize *k* to cell densities and is named "time-averaged cell density" here. According to this method *P.turgiduloides* was by far the most efficient producer per chlorophyll-*a* with a maximum production rate of 0.26nmol L^{-1} µg chl-a^{-1} day^{-1}. All other species revealed lower rates between 0.01 and 0.06nmol L^{-1} µg chl-a^{-1} day^{-1} (Table 3). Production of iodide could be observed in cultures with higher iodate concentrations than naturally found in seawater (5µmol L^{-1}) but also at concentrations close to natural (1µmol L^{-1}; Figure 5).

3.3.2. Iodide production vs. growth phase

All species, except *Scrippsiella trochoidea*, showed the same behaviour when relating the production of iodide to the state of their growth phase (Figure 1 - 4, Table 4). During the exponential growth phase no or negligible amounts of iodide were produced, once cells reached the stationary phase iodide increased rapidly and peaked in the senescent phase. In contrast *S.trochoidea*, a mixotrophic dinoflagellate, showed an increase in iodide accompanying their exponential phase.

Table 4: Time period given in days for when the iodide production took place and iodide production during the different growth phase of each phytoplankton species.

Phytoplankton species	Time period [d] of iodide production	Exponential phase	Stationary phase	Senescent phase
Temperate species				
E.huxleyi	8-41	No	Yes	Yes
S.trochoidea	3-41	Yes	No	Yes
Antarctic diatoms				
C.debilis	10-41	No	Yes	Yes
P.turgiduloides	18-34	No	Yes	Yes
F.kerguelensis	24-55	No	Yes	Yes
E.antarctica	24-55	No	Yes	Yes

3.3.1. Influence of nitrate on iodide production

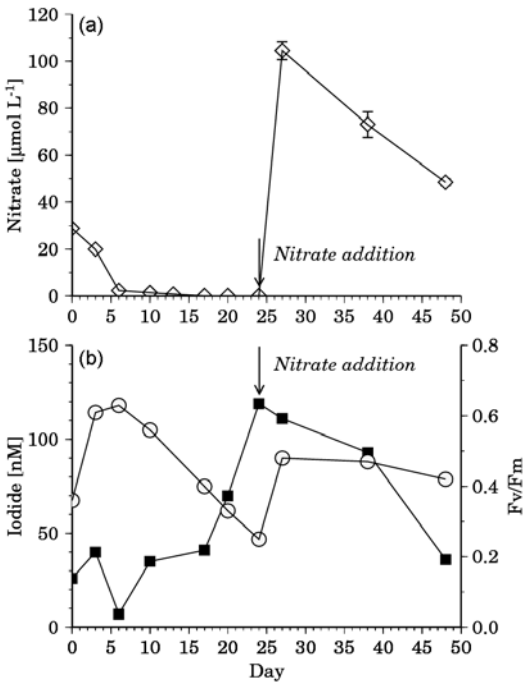

Figure 5: (a) Nitrate, (b) iodide and photosynthetic efficiency (Fv/Fm) in *C.debilis* during experiment 1b. (solid squares: iodide concentrations; open circles: Fv/Fm)

In Experiment 1b iodide production was observed in the *Chaetoceros* species tested. The *k* rates were comparable to Experiment 1a where we added 5 times more iodate. Additionally, the lower initial nitrate concentrations of ~44µmol L^{-1} used in this set-up caused a total nitrate consumption in the first six days (Figure 5a). Over the following 18 days cells showed a corresponding decline in Fv/Fm, whilst iodide concentrations increased with an iodide production rate of 0.05nmol L^{-1} µg chl-*a*$^{-1}$ day^{-1}. The re-supply of nitrate on day 24 led to a recovery in the Fv/Fm but a decline in iodide (Figure 5b).

3.4. Bacterial influences and dark incubation

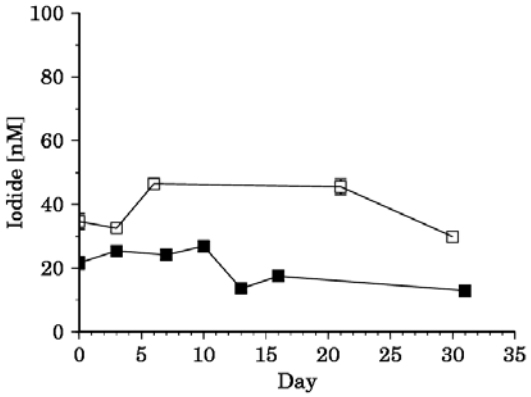

Figure 6: Dark and bacteria control for *Pseudo-nitzschia turgiduloides*. (solid squares: dark control, open squares: bacteria control)

Batch cultures were non-axenic and the bacterial influences to iodide production needed to be observed. This was examined in Experiment 2, where a algal-cell-free filtrate control, containing bacteria and phytoplankton exudates of a senescent *P.turgiduloides* culture, showed no notable iodide production (Figure 6) as did the dark incubation (Experiment 3). Cells showed healthy Fv/Fm values of 0.4-0.5 and were sufficiently supplied with macro- and micronutrients but did not show an increase in chlorophyll-*a* or cell numbers due to the lack of light.

4. DISCUSSION

4.1. Iodide production rates per day (k)

All species tested produced significant amounts of iodide through the conversion of iodate. Average production rates per day were in general agreement with those reported in previous studies (Wong et al. 2002, Chance et al. 2007) and are shown in Table 3. In all cultures, except *Scrippsiella trochoidea*, the iodide production began in the stationary growth phase (Figure 1-4). *S.trochoidea* is a mixotrophic dinoflagellate and able to perform phagotrophy. Phagotrophy is usually the primary nutritional mode in mixotrophic dinoflagellates as they are only able to reach maximum growth rates phagotrophically (Raven 1997). These species have a high nutrient demand especially when grown under autotrophic conditions which was reflected in our experiments by total nitrate consumption within 10 days. Consequently, for mixotrophs, photosynthetic carbon fixation has been interpreted as a survival strategy when food densities are low (Andersson et al. 1989, Sanders et al. 1990). Mixotrophs utilise digestive enzymes to consume organic matter and it has been demonstrated that this process can be used to assimilate colloidal iron (Maranger et al. 1998). A low pH environment is required to dissolve colloidal iron and under such conditions the redox equilibrium between iodide and iodate is shifted towards iodide once the

pH is below 5.7 (Sillen 1961). We then suggest that mixotrophs may passively reduce iodate to iodide via the ingestion of seawater when feeding. Interestingly this would also suggest that protozoans who have also been shown to dissolve iron colloids (Barbeau et al. 1996) may also contribute to iodate reduction in the ocean.

Pseudo-nitzschia turgiduloides showed the highest iodide production out of all species tested. During a Polarstern cruise ANTXXIV-3 in March 2008 we found elevated iodide values in the neritic Weddell Sea Zone compared to samples taken further north along the Zero Meridian (Bluhm et al. 2009 in revision). *P.turgiduloides* has been found to exist predominantly in this region of the southern Polar Ocean (Almandoz et al. 2008).

4.2. Iodide production rate k per cell

Interestingly, *Fragilariopsis kerguelensis* produced considerably less iodide per cell (0.86nmol L^{-1} $cell^{-1}$) compared to its remote relative *Pseudo-nitzschia turgiduloides* (5.37nmol L^{-1} $cell^{-1}$). The latter one being 1.5 times smaller with 3.5 times less cell volume (Table 1). Our initial hypothesis was that if it was purely a metabolic process by the cells then the production of iodide per cell should be proportional to some indicator of biomass (cell volume) or cell surface area. However, in the present work we did not observe any significant relationship between cell volume, or cell surface area, and the amount of iodide produced. We conclude from this that iodide production is species specific and related to some specific physiological process or processes that differ between the phytoplankton examined here.

4.3. Iodide production rate k per chlorophyll-a

The simple iodide production rates per day (*k*) were equal in both light regimes in basically all species but *k* normalized to chlorophyll-*a* was always higher at higher light intensities based on the decrease in chlorophyll-*a* per cell (Figure 1 - 4 and Table 3). Due to a greater light availability cells may photo-adapt leading to chloroplasts with less chlorophyll-*a* which however, produce the same amount of iodide per day compared to chloroplasts from cells grown under lower light. Highest rates per chlorophyll-*a* were observed in *Pseudo-nitzschia turgiduloides* (0.26nmol L^{-1} µg chl-a^{-1} day^{-1}) and the processes explained above are best expressed in this species (Table 3). *Emiliania huxleyi* produced iodide with a maximum rate of 0.06nmol L^{-1} µg chl-a^{-1} day^{-1} which is comparable to Wong et al. (2002) but 4 times lower than observed by Chance et al. (2007) during their studies. This might be due to divergent calculations of the average chlorophyll-*a* concentrations. In our study we used the trapezoidal method, like Wong et al. (2002), and obtained comparable values. Chance et al. (2007) normalized their values to the plain average chlorophyll-*a* concentration over the selected period. They observed an iodide production in *E.huxleyi* only in the exponential

growth phase of the algae and no production in the stationary phase with their cells apparently not reaching the senescent phase. This is in contrast to our results for the same species, although a different strain cultured under similar conditions (nutrients and light). However, we suggest that part of the difference may be due to their use of a coulter counter for cell enumeration, which does not distinguish between live and dead cells, unlike epi-fluorescence microscopy. Thus in their data the senescence phase does not appear as cells are still counted even though they may be lacking chloroplasts.

4.4. Why was nitrate not totally consumed?

Some of our cultures apparently did not run into macronutrient limitation (Experiment 1a) and thus we must look for an alternative reason for the passage into the senescent phase. Physiological death and subsequent lysis of phytoplankton cells has been shown to result from a number of factors apart from nutrient limitation:

1. Light limitation due to high cell densities in the batch cultures. Nitrate reduction in phytoplankton strongly depends on light energy and will be hampered under these conditions (Berges & Falkowski 1998).
2. Changes in alkalinity and pH. Uptake of inorganic carbon by phytoplankton during photosynthesis may increase pH and cells become carbon limited as CO_2 concentrations decrease under these conditions (Hansen 2002).
3. Viral lysis. Cells get infected by specific viruses which induce a loss in the viability of the algal cell and hence automortality (Suttle 1992, Bratbak et al. 1998, Nagasaki et al. 2004, Bettarel et al. 2005).
4. Apoptosis. Autocatalysed cell death which can be induced by pathogen exposure or through the production of superoxide radicals (oxidative stress) (Antunes et al. 2001, Segovia et al. 2003).

All possibilities mentioned result in cell death followed by a rapid release of cellular constituents to the surrounding medium which serves as a food supply for bacteria. Consequently, bacterial numbers increase rapidly in this growth phase of the phytoplankton. We suggest here that viral lysis was most likely the reason for cell senescence and cell lysis in our batch cultures as light limitation, as seen in the dark control experiments, apparently had little effect on cell mortality. Interestingly light is apparently required for viral replication in some marine phytoplankton and this may be the reason why the dark control cells remained intact (Baudoux & Brussaard 2008). Diatoms are relatively insensitive to light deprivation which is concordant with previous observations that non spore forming species such as *Thalassiosira weissflogii* survive several weeks in good condition (Peters & Thomas 1996). We did not measure pH or alkalinity in our cultures, so that we can not totally rule out that

cells might also have become carbon limited, although with the added nitrate concentrations of 88 µmol L^{-1}, cells would have rather become nitrate limited.

4.5. Iodate reduction by nitrate reductase (NR)

The enzyme nitrate reductase (NR) has been postulated to perform the reduction of iodate to iodide in phytoplankton and bacteria when nitrate is limiting in the ocean (Tsunogai & Sase 1969). Our work does not support that view and instead we believe the reaction is connected to cell viability and senescence. This also supports the findings of Waite & Truesdale (2003); who still found iodide production when NR was deactivated.

4.6. Iodide oxidation to Iodate by Diatoms

We did however see an interesting effect of nitrate with *Chaetoceros debilis* (Figure 5) when iodide production was initiated during cell senescence caused through nitrate limitation. However, upon re-supply of nitrate iodide production stopped and the concentration declined while cells resumed exponential growth. Thus an iodide oxidation mechanism must have been active during this time that oxidized 80nmol L^{-1} iodide over 25 days. Diatoms have been observed previously to oxidize iodide to iodate (Sugawara & Terada 1967) and other phytoplankton have been shown to possess iodoperoxidases (Murphy et al. 2000, Hill & Manley 2009) though these enzymes are normally not capable of oxidizing iodide to iodate. A review of the literature on this subject reveals only one reference to a chloroperoxidase in a fungus *Caldariomyces fumago* that can oxidise iodide to iodate (Thomas & Hager 1968). Iodo peroxidases are also present in marine bacteria (Gozlan & Margalith 1973, 1974, Amachi et al. 2005) though none of these studies found oxidation through to iodate.

4.7. The role of bacteria

Many phytoplankton cultures are often only available with their associated bacteria; especially diatoms mostly require the associated bacteria for normal growth (Fukami et al. 1997, Croft et al. 2005, Grossart & Simon 2007). Therefore it is difficult to separate phytoplankton responses from those of the surrounding bacteria. Bacteria were present in all cultures to varying amounts; highest numbers were observed in the cultures of *Pseudo-nitzschia turgiduloides* and *Emiliania huxleyi* towards the end of the experiment (over 30% of total carbon biomass, Figure 1b – 4b). The increase in bacteria goes hand in hand with the increase in iodide and we can not totally rule out that bacteria also reduce a certain amount of iodate to iodide as they are capable to do so (Tsunogai & Sase 1969, Amachi et al. 2007).

In all other cultures bacteria were minor constituents and can be neglected (Figure 1 - 4). These results are additionally accompanied by the bacteria control in Experiment 2, where no significant changes in iodide were observed (Figure 6).

4.8 Influence of light

No influence of light on the iodide production in the deployed range (50 and 100µmol quanta m^{-2} s^{-1}) was observed in Experiment 1a as samples showed similar *k* rates under both light regimes (Table 3). However cells that were kept in the dark for several days did not show any iodide production, indicating that light did have some effect. However as both, *P. turgiduloides* and *C. debilis*, went into a resting phase where they did not take up anymore nutrients it suggests that iodide production was not related to photosynthesis as the highest iodide production occurred when C fixation was minimal. Cells were still viable with Fv/Fm values never dropping below 0.4 which makes us believe that no cell lysis took place.

4.9. The role of cell permeability

From our experiments it is apparent that part of the high iodide production rates in the later growth phases are related to cell senescence. When cells become extremely permeable under stressful conditions like nutrient limitation or viral infections metabolites will be released back into the surrounding media and can react with the components of that media including iodate. The release of cellular material can be hastened during this time by direct cell lysis mediated either by viruses (Nagasaki et al. 2004, Bettarel et al. 2005) or apotosis (Antunes et al. 2001, Segovia et al. 2003). In the present work we can not determine which process caused the cells to lyse but the evidence that this process was occurring can be found in the decrease in cells containing intact chloroplasts as observed by microscopy and the subsequent increase in bacterial numbers presumably from the release of labile dissolved organic matter (DOM). The release of cellular metabolites especially reduced sulphur compounds such as sulphide and glutathione (GSH) which are present in high concentrations inside phytoplankton cells (Matrai & Keller 1994) and are able to reduce iodate to iodide under typical seawater conditions (Hird & Yates 1961, Jiazhong & Whitfield 1986) seems then the most likely cause for the increase in iodide at this time. Our finding is consistent with phytoplankton culture experiments investigating sulphide production (Walsh et al. 1994) where increases in the dissolved free sulphide concentration were observed during the senescence phase. Additionally field work on sulphide in the ocean suggests that metal complexation is important (Cutter et al. 1999) in reducing the extent of the reaction between sulphide and iodate, thus in phytoplankton cultures in which the metal speciation is

dominated by EDTA complexes we could infer that reduction rates of iodate would be maximal.

Our finding contradicts the work of Wong et al. (2002) who found no clear relationship between iodide production and the growth phase of the culture. Indeed they ruled out cell lysis as a possible cause, though this may have been because they did not measure cell numbers or any proxy of cell permeability. In the present work we can examine the potential of cell lysis by determining the rate of iodide increase as a function of cell mortality, for time points where both chlorophyll-*a* and cell numbers are decreasing, as a function of the estimated C content per cell, here used as a proxy for S content (Figure 7). Our results suggest that to a first approximation there is a relationship between C content and iodide production. Species specific variations in the S:C ratios (Matrai & Keller 1994) may be responsible for the variations in this relationship.

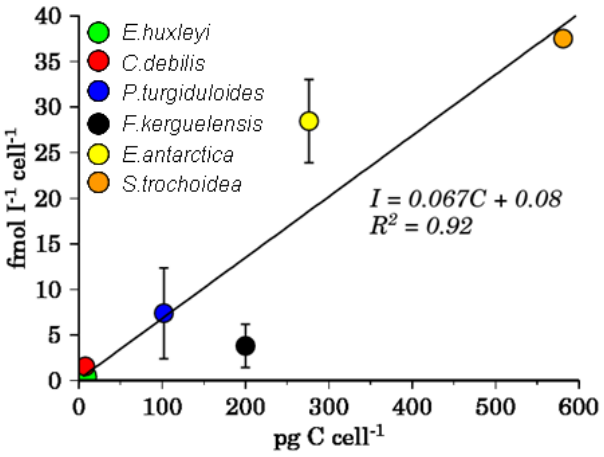

Figure 7: Calculated iodide production per dead cell (calculated as the difference in cell numbers between time points) as a function of the estimated C content per cell. Only data that showed both a decrease in chlorophyll-*a* and cell numbers after the maximum values were reached is used here.

4.10. Ecological relevance

In the open ocean the presence of iodide in the euphotic zone, and its oxidation back to iodate in deeper waters, are linked to biological activity controlling the cycling of micronutrients like iodine. The data obtained during this study suggest that production of iodide is a process connected to cell senescence and cell permeability and may be intimately linked to S species. If for example 10^5 diatom cells L^{-1}, these organism being present in a range of 10^4-10^6 cells L^{-1} in the Southern Ocean (Kopczynska et al. 1986, Kopczynska et al. 1998, Olguin et al. 2006), produced iodide at a rate we measured for our Antarctic species (average rate: $3.2*10^{-4}$nmol L^{-1} $cell^{-1}$), their total contribution would be 31.6nmol L^{-1}. Reported iodide concentrations of the Southern Ocean lie within this number for surface waters (Campos et al. 1999, Bluhm et al. 2009 in revision).

5. CONCLUSIONS

The influence of phytoplankton on the biogeochemical cycle of iodine was investigated in a set of experiments carried out with a variety of phytoplankton taxa. From the results we derive the following conclusions:

In batch cultures of marine phytoplankton the reduction of iodate to iodide is observed but principally in the late phases of cell growth. The production of iodide is only observable in the stationary and/or senescent growth phase of the algae with the only exception of the mixotrophic species *Scrippsiella trochoidea*. In this species the iodide production commenced right at the beginning of the experiment.

Cells were grown under nitrate replete conditions and it is clear, the reduction of iodate to iodide is not related to nitrate availability but more to the viability of the cells.

Iodine is assimilated by the phytoplankton cells preferentially as iodide but it remains still unclear whether phytoplankton has an essential metabolic need for iodine. Further investigations are needed to define the role of iodine for phytoplankton needs. The importance of light or nutrient limitation and the resulting senescence in phytoplankton should be observed further in terms of iodide production and the link to S species. A second step would be to examine the behaviour of natural assemblages instead of monoclonal batch cultures.

6. ACKNOWLEDGEMENTS

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V.

Final Conclusions & Future Perspectives

V. FINAL CONCLUSIONS AND FUTURE PERSPECTIVES

Iodine released to the atmosphere from the ocean may play a pivotal role in climate change due to the importance of iodine reactions with ozone in the atmosphere and the formation of new particles through iodine monoxide (IO). Despite this overarching importance the current knowledge about the processes involved in the marine biogeochemical cycle of iodine is still in its infancy. This thesis aims at elucidating the sources and mechanisms of iodine speciation in seawater such as the cycling between the major species; iodate (IO_3^-) and iodide (I^-). The **first two manuscripts** contain results of two field work campaigns exploring iodine speciation in the Atlantic sector of the Southern Ocean and the Mauritanian upwelling region in the Tropical Atlantic Ocean. The general distribution of iodine in seawater as well as a comparison between productive/upwelling and non-productive/weak-upwelling regions was accomplished. In the **third manuscript** the involvement of phytoplankton on iodine speciation was examined in batch cultures with critical observation on the timing of iodide production.

1. Iodine pathways in the environment

1.1. Iodate reduction to Iodide

It is a well known phenomenon that iodide accumulation occurs to the greatest extent in the euphotic zone and this has been examined previously by several researchers (Tsunogai & Henmi 1971, Elderfield & Truesdale 1980, Jickells et al. 1988, Wong 1991, Moisan et al. 1994, Campos et al. 1996, Truesdale et al. 2000). Therefore, the central question in iodine oceanic research at present is whether iodate reduction is driven by biological processes via active biologically mediated uptake, or alternatively if it is from chemical redox reactions which in part may be connected to the release of substances from the decay of biological materials.

We examined elevated iodide concentrations within the euphotic zone in the Southern Ocean and the Tropical Atlantic. However, highest iodide concentrations in the respective regions were observed in post bloom waters indicating towards a strong relationship between iodide production and the decline of a phytoplankton bloom. Noticeable was the steep concentration gradient between these two oceanic regions with lowest surface iodide values (<20nmol L^{-1}) in Antarctic waters and highest values in tropical waters (>200nmol L^{-1}). Since tropical oceans in upwelling regions are more productive over the long term, as phytoplankton blooms raise and decline faster due to the prevailing temperature, light and nutrient conditions, more iodide can accumulate in the surface. Blooms in the Southern Ocean can last over months without running into senescence (EIFEX–cruise report; Boyd 2004).

Additionally, solar radiation is greater in the tropical ocean so that photochemically driven iodate reduction in the surface layers is at its maximum there.

It appears that chemical iodate reduction rates alone do not explain the higher iodide within the euphotic zone, additional reduction mechanism must prevail which is suggested to be biologically mediated. The laboratory study in **Manuscript 3** was accomplished with phytoplankton species from the waters of the two oceanic regions studied. We discovered that phytoplankton reduced iodate to iodide principally in the stationary and/or senescent phase of cell growth while in the exponential phase an iodide oxidation mechanism seemed to be operating. Tian and Nicolas (1995) had earlier suggested that if iodate can be assimilated like nitrate that it must be reduced to ammonium (NH_4 (-III)) in order to be incorporated into cells. However, can one draw such analogous conclusions for iodine? Truesdale et al. (2000) suggested that it could also be a dissimilatory reduction i.e. at the cell surface with no precedent assimilation of iodate. A possible explanation for the iodate reduction and iodide oxidation mechanisms may be that during the **exponential phase** of growth cells continuously reduce iodate to iodide via an, as yet unidentified, enzyme that acts as an iodate reductase at the cell surface. Subsequently halo-peroxidases oxidize the iodide ion to HOI which passes into the cell, and further reacts there to form iodo-organics and inorganic iodide leading to an accumulation of iodine in the cell (Figure 6 chapter III.). This mechanism and iodine pathway was observed in brown algae such as *Laminaria spp.* by several authors where they found that the stored form of iodine is iodide and suggested that this was used as an inorganic antioxidant upon oxidative stress (Küpper et al. 1998, Leblanc et al. 2006, Küpper et al. 2008). The same might be applicable for the phytoplankton community so that we conclude and speculate that iodide is not detectable in the surrounding water during cell growth as it is immediately processed and stored inside the cell. Following this idea we can further speculate that during the **stationary growth phase** iodate is still reduced to iodide by cellular processes but this may be balanced by the re-oxidation of iodide to iodate leading to a slight increase, or sometimes even a decrease, of iodide in the surrounding medium. The biological oxidation of iodide to iodate is currently the biggest missing piece in the iodine puzzle but evidence in this thesis indicates that it does occur. Once in the **senescent phase** cells become more permeable and the accumulated iodide (de la Cuesta & Manley 2009) together with iodate reducing metabolites such as glutathione and other sulphur species (Hird & Yates 1961) will be released upon cell lysis and cell death (Figure 6, chapter III). These findings could be used as an explanation for why algae transfer iodate to iodide but it remains still unclear whether phytoplankton has an essential metabolic need for iodine. Further investigations are needed to define the role of iodine for phytoplankton requirements.

In general the experimental set-up showed that temperate and cold water species produced iodide at a similar rate whereas the Antarctic species *Pseudo-nitzschia turgiduloides* was the most efficient one amongst them. Therefore the amount of iodide appearance in the euphotic zone could be dependent on the species composition and presumably the amount of intracellular metabolites as well as the species abundances. In the future accompanying measurements of dissolved organic sulphur (DOS) and dissolved organic material in general should be made when sampling for iodine speciation in the field to analyze whether there is a connection between DOS concentrations and iodate reduction.

The experimental culture work performed in this thesis was undertaken to determine the iodate reduction mechanism and whether this is actively done by the phytoplankton present or if the reaction is more a subsequent secondary production via the reaction with organic compounds. Previously the enzyme nitrate reductase (NR), present in phytoplankton and bacteria, has been postulated to reduce iodate when nitrate is limiting in the ocean (Tsunogai & Sase 1969, Wong 1991). Our batch cultures were grown under nitrate replete conditions and it could be argued that iodate was reduced together with nitrate while adequate nitrate concentrations still prevailed. Since, enzymes are very specific for their substrates though NR would rather reduce the remaining nitrate preferentially over the iodate. However, there is a clear need to apply a test whether the enzyme shows a significantly higher affinity for nitrate over iodate which could be done in competition experiments with the isolated enzyme. We think the reduction of iodate to iodide is not related to nitrate availability nor to the activity of NR but instead to the viability and senescence of the cells, regardless of how the cells came into senescence. Recent results of an identical iodide production experiment with *Prochlorococcus sp.* [MED 4] showed production rates of 0.04nM µg chl-*a*$^{-1}$ day^{-1}. *Prochlorococcus* species lack the enzyme NR and cells were grown on ammonia instead of nitrate, nevertheless iodide was produced from iodate (K. Wuttig, in preparation).

From the results of my thesis it appears that both abiotic and biotic processes resulting in iodate reduction are coupled and that the actual reduction is best explained through secondary abiotic mechanisms caused by reactions with iodate and metabolites released by the algae. It is clear that more culture work is needed to determine the iodate/iodide reduction/oxidation mechanisms and to conduct these experiments with natural assemblages instead of monoclonal batch cultures in order to determine the kinetics of iodine speciation processes under ambient conditions. The importance of light or nutrient limitation followed by the resulting senescence and the link to iodate reduction by sulphur species in phytoplankton, needs also to be examined in terms of iodide production. In addition, it is also essential to improve the method of iodate measurements to a lower detection limit and better accuracy. Similarly the development of a corresponding method for

determining other iodine species such as hypoiodous acid (HOI) and volatile organoiodine compounds (VOI's) at seawater concentrations would be a major advance. Overall this would help to greatly improve our knowledge of iodine speciation and better determine mass balances particularly with regard to the critical aspect of matching iodate drawdown to iodide increases in surface waters. Concerning culture work a better accuracy of the iodate measurements will greatly influence the determination of the iodide oxidation process through to iodate. We would be capable to see whether iodate is formed upon iodide depletion or vice versa. Likewise, measurements of reduced sulphur species and detection of some physiological measure of cell senescence as well as determining viral numbers could greatly influence our understanding concerning iodine cycling.

1.2. Iodide oxidation

Iodide oxidation rates are important in order to balance the iodine cycle and they are a key to determining if iodide could be used as a tracer for newly upwelled water on continental shelves and for newly formed Weddell Sea Bottom Water (WSBW). Since iodate is the dominant form in the deep, iodide oxidation must be completed there. Hence, if iodide is found in oxygenated deep water masses such as the WSBW it must have been taken down from the surface. In the case of an upwelling scenario iodate rich but iodide poor water is brought up and displaces the iodide rich waters in the surface. Both hypotheses presume long residence times for iodide in oxygenated surface waters. Very little is known about the rate of oxidation of iodide through to iodate besides that abiotic oxidation mechanisms of iodide are all kinetically slow in seawater (Luther et al. 1995) leading to estimates of the residence time for iodide on the order of years. However, this might be only applicable for the deep ocean as there is evidence that iodide is oxidized back to iodate in surface waters due to biological processes (Sugawara & Terada 1967), accelerating the process. In case of the WSBW formation though, iodide oxidation by biological activity should be limited due to the coldness and density of sinking newly formed bottom waters. Thus iodide may have the potential as transient tracer for newly formed WSBW along the Antarctic continent.

Compared to temperature, which is also used as a tracer for water masses, iodide has the advantage of a longer lifetime. The question here is: Can you tell a previously upwelled filament only by its temperature? Especially in the tropics were surface waters heat to higher temperatures fairly quick and are then claimed as the same water mass, where iodide can still reveal differences due to its longer lifetime in the water.

In the case of the seasonally driven upwelling processes observed off the Mauritanian coast, the question arises whether the lower iodide concentrations observed in surface waters during periods of strong upwelling is due to faster iodide oxidation connected to the increased biomass existing in the winter, or if it is related to increased dilution via mixing with

iodide poor water from the deep. To eventually determine iodide as a transient tracer for upwelling water future research is needed. This hypothesis could be tested by a lagrangian tracer study where a patch of low iodide, upwelling water is marked with a tracer such as sulphur hexafluoride (SF_6). This tracer patch can then be followed to the surface to observe where it might get subducted or if it even stays at the surface for a long time. Simultaneous measurements of iodide will allow an evaluation of reduction and oxidation rates and test the hypothesis directly to see whether iodide is really acting as a natural tracer for upwelled waters.

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Ich versichere an Eides statt, dass ich die von mir vorgelegte Dissertation – abgesehen von der Beratung durch meinen Betreuer – selbstständig und ohne unerlaubte Hilfe angefertigt habe und alle benutzten Quellen und Hilfsmittel vollständig angegeben habe. Die Zusammenarbeit mit anderen Wissenschaftlern habe ich kenntlich gemacht. Die Arbeit ist unter Einhaltung der Regeln guter wissenschaftlicher Praxis der Deutschen Forschungsgemeinschaft entstanden. Ferner habe ich weder diese noch eine ähnliche Arbeit an einer anderen Abteilung oder Hochschule im Rahmen eines Prüfungsverfahrens vorgelegt, veröffentlicht oder zur Veröffentlichung vorgelegt.

Kiel, 11. Dezember 2009 _____

(Katrin Bluhm)