

**Factors influencing  
methyl iodide production  
in the ocean  
and its flux to the atmosphere**

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## Abstract

Methyl iodide is an atmospheric trace gas and a major source of atmospheric iodine. Recent estimates of methyl iodide sources and sinks indicate that anthropogenic sources are neglectable. The major source of atmospheric methyl iodide are emissions from the ocean. The production pathways of methyl iodide in the ocean are, however, poorly understood. The known oceanic sources can only account for about 10 % of the ocean-atmosphere flux, whereas the sources for the remaining 90 % are not known.

In this work a measuring system, consisting of an equilibrator connected to a 2-dimensional gas chromatograph, equipped with two electron capture detectors, was developed. This system was used on four cruises in the tropical and North Atlantic to measure the seawater concentrations and the atmospheric dry gas mole fractions of methyl iodide, and the ocean-atmosphere flux was calculated. A mean flux of  $\sim 22 \text{ nmol m}^{-2} \text{ d}^{-1}$  was calculated from all cruises. A global annual flux of  $2.89 \text{ Gmol a}^{-1}$  was estimated using this flux. The limiting factor for the methyl iodide flux seems to be the production in the ocean, because the measured fluxes were relatively uniform and independent from observed changes in the surface water concentrations and wind speeds.

Incubation experiments were done in the tropical Atlantic to test the hypothesis that methyl iodide is produced in the surface water by a photochemical pathway, instead direct biological production by phytoplankton or bacteria. During the experiments untreated, filtered and poisoned seawater was incubated at ambient water temperature, either in the sunlight or in the dark. The production of methyl iodide observed in all incubations kept in the sunlight was five times higher than the production from incubations kept in the dark. No significant difference was observed between untreated, filtered and poisoned samples. This strongly indicates a photochemical production with no direct influence by biota. The mean photochemical production rate from all incubations was  $0.12 \text{ nmol m}^{-3} \text{ h}^{-1}$ . A layer of 14 m with this production rate is needed to balance the methyl iodide sinks from the halogen exchange reaction with chloride in the mixed layer and the flux to the atmosphere, based on model calculations. The global photochemical production of methyl iodide was estimated to be  $5.3 \text{ Gmol a}^{-1}$ , using the measured production rate and a the calculated layer depth of 14 m. From these results the photochemical production of methyl iodide is an important, and may be the dominant, source of methyl iodide for the ocean.

## Zusammenfassung

Iodmethan ist ein atmosphärisches Spurengas und eine wichtige Quelle für Iod in der Atmosphäre. Neuere Abschätzungen der Quellen und Senken von Iodmethan zeigen, dass anthropogene Quellen vernachlässigbar klein sind. Die Hauptquelle für atmosphärisches Iodmethan ist die Emission aus dem Ozean, wobei die Produktionswege in Ozean noch kaum bekannt sind. Die bekannten ozeanischen Quellen erreichen nur eine Produktion von etwa 10 % des Flusses vom Ozean in die Atmosphäre, die Quellen für die restlichen 90 % sind nicht bekannt.

In dieser Arbeit wurde ein Messsystem entwickelt, welches aus einem Equilibrator und einem zweidimensionalen Gaschromatografen mit zwei Elektronen-Einfang-Detektoren besteht. Mit diesem System wurden auf vier Fahrten im tropischen Atlantik und im Nordatlantik die Konzentrationen von Iodmethan im Seewasser und seine Molfraktion in der Atmosphäre gemessen, und der Fluss vom Ozean in die Atmosphäre abgeschätzt. Der mittlere Fluss von allen Fahrten wurde mit  $\sim 22 \text{ nmol m}^{-2} \text{ d}^{-1}$  berechnet, woraus sich ein globaler, jährlicher Fluss von  $2.89 \text{ Gmol a}^{-1}$  ergibt. Der limitierende Faktor für den Fluss scheint die Produktion von Iodmethan im Ozean zu sein, da die gemessenen Flüsse relativ gleichmässig verteilt sind und nicht von gemessenen Änderungen der Konzentration von Iodmethan im Oberflächenwasser oder Änderungen der Windgeschwindigkeit beeinflusst wurden.

Im tropischen Atlantik wurden Inkubationsexperimente durchgeführt, um die Hypothese zu testen, dass die Produktion von Iodmethan im Oberflächenwasser durch einen photochemischen Reaktionsweg erfolgt, im Gegensatz zu einer direkten Produktion durch Phytoplankton oder Bakterien. Während der Inkubationsexperimente wurden unbehandelte, gefilterte und vergiftete Seewasserproben entweder im vollen Sonnenlicht oder in Dunkelheit aufbewahrt, wobei die Temperatur der des umgebenden Seewassers angeglichen war. Die beobachtete Produktion von Iodmethan in den Inkubationen im Sonnenlicht war fünf Mal höher als die der Inkubationen im Dunkeln. Es wurden keine signifikanten Unterschiede zwischen den unbehandelten, filtrierten und vergifteten Proben beobachtet. Diese Tatsache weist stark auf eine photochemische Produktion von Iodmethan hin, ohne direkten Einfluss von Biota. Die mittlere photochemische Produktionsrate von allen Inkubationen war  $0.12 \text{ nmol m}^{-3} \text{ h}^{-1}$ . Um die Senken von Iodmethan durch die Reaktion mit Chloridionen und durch den Ozean-Atmosphäre-Fluss auszugleichen, wurde mittels einer Modellrechnung eine benötigte Schichtdicke photochemischer Produktion von 14 m mit dieser Produktionsrate berechnet. Eine Abschätzung der globalen photochemischen Produktion von Iodmethan, basierend auf der gemessenen photochemischen Produktionsrate und einer Dicke der Schicht photochemischer Produktion von 14 m, ergab einen Wert von 5.3 Gmol pro Jahr. Basierend auf diesen Ergebnissen ist die photochemische Produktion von Iodmethan eine wichtige, wenn nicht die dominierende Quelle von Iodmethan im Ozean.

# 1. Introduction

Methyl iodide is a major carrier of iodine to the atmosphere, which gained increasing interest because iodine is involved in many atmospheric reactions, some of them leading to the destruction of atmospheric ozone (*Solomon et al.*, 1994, *Vogt et al.*, 1999) and possibly to the formation of aerosol (*Kolb*, 2002, *O'Dowd et al.*, 2002). The understanding of sources, fluxes and sinks of methyl iodide will help to improve the overall understanding how halogens cycle between oceanic, atmospheric and terrestrial environments, and to assess the impact on natural cycles by human activity.

The focus of this study lies on the air-sea exchange of methyl iodide and the sources of methyl iodide in the ocean. The global air-sea flux has been attributed by several investigations, but the resulting flux estimates still show large differences between different authors (see chapter 1.2.1 for details). In this work a set of surface water and atmospheric measurements of methyl iodide from four cruises in the tropical Atlantic and the North Atlantic at different times of the year has been used to estimate an ocean atmosphere flux. The sources of methyl iodide in the ocean are not well understood and there is a big discrepancy between sources and sinks (see chapter 1.3.1 for details). Data from incubation experiments during one of the cruises have been used to investigate possible sources of methyl iodide in the ocean and estimate their strength.

The remainder of chapter 1 first provides a brief introduction in natural halocarbons, followed by a more detailed discussion of the role of methyl iodide in the atmosphere and the ocean, including the known sources and sinks. Chapter 2 describes the instruments and procedures used in this thesis. In chapter 3 the results from surface seawater and atmospheric measurements will be presented and discussed, together with the flux estimates derived from the data. In chapter 4 the incubation experiments, which were done to investigate the source of oceanic methyl iodide, will be described and the results will be discussed. Chapter 5 is devoted to the global flux estimates from our data and a discussion of the global methyl iodide budgets in the light of the results from the incubation experiments.

## 1.1 Natural halocarbons

The first halocarbon measurements have been done to test if the chlorofluorocarbons (also called CFC's or freons) released as propellants to the atmosphere can be used as inert tracers for mass transport processes in the atmosphere and the ocean. During a study of the global distribution of CFC 11 ( $\text{CCl}_3\text{F}$ ), *Lovelock et al.* (1973) detected methyl iodide both in the atmosphere and the surface water of the ocean. To their surprise the seawater was supersaturated with methyl iodide with respect to the atmosphere, indicating a natural



oceanic source. *Zafiriou* (1974) found evidence by the evaluation of reaction rates that halogen atoms may destroy ozone. Other studies inspired by these results found a variety of different halocarbons in the environment, including chloride containing substances like methyl chloride, dichloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene (e.g. *Koppmann et al.*, 1993, *Sturges*, 1993), bromine containing substances like methyl bromide, bromoform and dibromomethane (e.g. *Dyrssen and Fogelqvist*, 1981, *Krysell*, 1991, *Khalil et al.*, 1993, *Sturges*, 1993), and iodine containing substances like methyl iodide, ethyl iodide and diiodomethane (e.g. *Lovelock et al.*, 1973, *Fogelqvist and Tanhua*, 1995), next to others not mentioned here. Many of these compounds are produced naturally, either by marine organisms like algae (e.g. *Manley and Dastoor*, 1988, *Schall et al.*, 1994, *Sturges and Cota*, 1995, *Laternus*, 1995, *Giese et al.*, 1999, *Carpenter et al.*, 2000), and/or plankton (e.g. *Tokarczyk and Moore*, 1994, *Tait and Moore*, 1995, *Itoh et al.*, 1997, *Murphy et al.*, 2000, *Ballschmiter*, 2003), from plants (e.g. *Muramatsu and Yoshida*, 1995, *Saini et al.*, 1995, *Redeker et al.*, 2000, *Dimmer et al.*, 2001), from bacteria (e.g. *Manley and Dastoor*, 1988, *Amachi et al.*, 2001) or from geological sources like volcanoes (e.g. *Jordan et al.*, 2000). Another natural source, which is linked to human activities, is the release of halocarbons from biomass burning (e.g. *Crutzen and Andreae*, 1990, *Manö and Andreae*, 1994, *Blake et al.*, 1996).

Methyl iodide is the most abundant iodine containing halocarbon, and it is believed to be the primary source of iodine to the atmosphere (*Klick and Abrahamson*, 1992, *Schall et al.*, 1997). *Carpenter et al.* (1999) measured different iodine containing halocarbons in the atmosphere at Mace Head, Ireland. Albeit methyl iodide had the highest concentration of all iodinated compounds measured, they calculated that its contribution to the total organic iodine mixing ratio was about 57 %. The rest was contributed mainly from diiodomethane ( $\text{CH}_2\text{I}_2$ ), next to chloriodomethane ( $\text{CH}_2\text{ClI}$ ), bromiodomethane ( $\text{CH}_2\text{BrI}$ ) and iodoethane ( $\text{C}_2\text{H}_5\text{I}$ ). The atmospheric measurements close to the shore are influenced by coastal phenomena, especially the abundance of algae, thus the relative high concentration of  $\text{CH}_2\text{I}_2$  may be caused by algae. Another study (*Klick and Abrahamson*, 1992) found high concentrations of  $\text{CH}_2\text{I}_2$  in coastal waters and especially in an algae belt spring, but could not detect it in open ocean waters. Thus  $\text{CH}_2\text{I}_2$  may dominate the iodine flux to the atmosphere locally, since it undergoes photolysis faster than methyl iodide (*Rattigan et al.*, 1997, *Mossinger et al.*, 1998) and contains two iodine atoms per molecule.

The interest in the natural cycle of methyl iodide is further increased by the plan to replace methyl bromide, used for soil fumigation prior to agricultural use, with methyl iodide. Methyl bromide is used to fumigate fields before planting them, in order to control soil borne pests like parasitic nematodes, insects and bacteria (*Gan et al.*, 1997). Since the use of methyl bromide was banned under the Kyoto protocol, because of its potential to deplete stratospheric ozone, methyl iodide was proposed as a replacement (e.g. *Ohr et al.*, 1996). In order to assess the environmental risks caused by the fumigation with methyl iodide, it is necessary to know its natural cycle.

## 1.2 Methyl iodide in the atmosphere

Methyl iodide is an atmospheric trace gas which was first measured by *Lovelock et al.* (1973). The reported dry gas mole fractions mostly fall within the range of 1 to 2 pmol mol<sup>-1</sup> (e.g. *Rasmussen et al.*, 1982, *Singh et al.*, 1983, *Schall and Heumann*, 1993, *Yokouchi et al.*, 1994, *Groszko*, 1999, *Li et al.*, 2001, *Yokouchi et al.*, 2001, *Cohan et al.*, 2003), but single higher values have been reported. *Reifenhäuser and Heumann* (1992) measured atmospheric methyl iodide gas mole fractions between 0.6 and 7.9 pmol mol<sup>-1</sup> in the Antarctic and *Yokouchi et al.* (1997) reported dry gas mole fractions between 0.05 and 5.0 pmol mol<sup>-1</sup> in the western Pacific and between 0.24 and 2.0 pmol mol<sup>-1</sup> in the eastern and south-eastern Asian seas. Atmospheric dry gas mole fractions of methyl iodide concentrations over land have a similar range as reported by *Barletta et al.* (2002) with 0.5 to 4.5 pmol mol<sup>-1</sup> over Karachi, Pakistan. Exceptional high dry gas mole fractions up to 12 pmol mol<sup>-1</sup> were reported by *Carpenter et al.* (2003) at a coastal site in Ireland.

### 1.2.1 Sources for the atmosphere

The main source of methyl iodide for the atmosphere is thought to be the ocean. The first estimate of the global flux from the ocean to the atmosphere was made by *Liss and Slater* (1974) with 1.90 Gmol a<sup>-1</sup> (the units from the different authors have been converted to Gmol a<sup>-1</sup> for better comparison) with data from *Lovelock et al.* (1973) and their own gas exchange model. *Rasmussen et al.* (1982) calculated the global flux to be 9.16 Gmol a<sup>-1</sup>, based on their own concentration measurements and data from *Lovelock* (1975). Their high value is critically dependent on the high seawater concentrations from *Lovelock* (1975) for coastal waters with a high biomass productivity. They calculated that these areas alone contribute 7.05 Gmol a<sup>-1</sup> to the total flux, despite the fact that they account for only about 10 % of the total ocean area. Since other authors gave lower seawater concentrations for methyl iodide in such regions (e.g. *Manley et al.*, 1992, *Schall and Heumann*, 1993, *Carpenter et al.*, 2000), this high flux is likely to be an overestimate. Consequently, later estimates are lower with 2.11 – 3.52 Gmol a<sup>-1</sup> from *Singh et al.* (1983), 5.64 Gmol a<sup>-1</sup> from *Reifenhäuser and Heumann* (1992), 2.42 Gmol a<sup>-1</sup> from *Groszko* (1999) and 1.48 Gmol a<sup>-1</sup> from *Bell et al.* (2001). The differences between the reported flux estimates are quite large. This is mainly due to the different data sets of methyl iodide seawater concentrations, which cover only a small part of the ocean area. Most data sets in these estimates did not include concentrations from both cold and warm waters and from coastal and open ocean regions with high and low productivity. Another problem is the calculation of the transfer velocity, for which several different models exist, yielding different values for identical conditions (this point will be discussed in more detail in chapter 3.4.1 and chapter 5.1.2). Despite the variance in the estimated fluxes all authors agree, that the ocean is the main source of methyl iodide to the atmosphere.

From the land biota only rice paddies have been evaluated in more detail and found to produce methyl iodide. *Muramatsu and Yoshida* (1995) planted rice seedlings in soil mixed with radioactive iodide ions ( $^{125}\text{I}$ ), covered the plants with bags to collect the emitted substances in the air and measured the radioactive methyl iodide. From these experiments they estimated a global flux to the atmosphere of  $0.18 \text{ Gmol a}^{-1}$ . *Redeker et al.* (2000) covered small parts of a rice field with pots and measured the released methyl iodide from the air in these pots. From their results they estimated a global flux of  $0.50 \text{ Gmol a}^{-1}$ . In an additional study they gave a range for the flux from  $0.30 - 0.66 \text{ Gmol a}^{-1}$  (*Redeker et al.*, 2002). This source of methyl iodide contributes therefore about one tenth of the oceanic source. *Saini et al.* (1995) evaluated the methyl iodide production from leaf disks and leaf extracts from higher plants and found methyl iodide production via a methyltransferase reaction. No estimate about the global source strength was made, due to the differences between laboratory and environmental conditions.

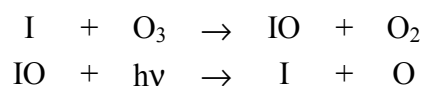
*Andreae et al.* (1996) measured enhanced concentrations of methyl iodide in the smoke plumes of savannah fires in Africa. They found a correlation between methyl iodide and carbon monoxide and carbon dioxide, which they used to calculate the global input of methyl iodide from this source, since the pyrogenic emissions of carbon monoxide and carbon dioxide are known. The estimate yielded a global input of  $0.024 - 0.060 \text{ Gmol a}^{-1}$  of methyl iodide into the atmosphere from this source. A similar approach by *Blake et al.* (1996) gave an input of  $0.014 - 0.028 \text{ Gmol a}^{-1}$ . Thus biomass burning is only a minor source of atmospheric methyl iodide. Other evaluated sources are emissions from volcanoes with  $0.14 - 17.6 \cdot 10^{-3} \text{ Gmol a}^{-1}$  (*Jordan et al.*, 2000) and peatland ecosystems with  $9.3 \cdot 10^{-3} \text{ Gmol a}^{-1}$  (*Dimmer et al.*, 2001), both insignificant compared with the oceanic source.

There are other possible sources of methyl iodide to the atmosphere, which have so far not been assessed in detail. *Harper* (1985) reported the ability of wood-rotting fungi to produce methyl iodide from iodide ions. However, *Watling and Harper* (1998) estimated that wood-rotting fungi are unlikely to produce globally significant amounts of methyl iodide, since the reaction is controlled by the concentration of iodide and this concentration is low in terrestrial plant matter. *Amachi et al.* (2001) reported methyl iodide production by terrestrial bacteria during incubation experiments with single strains growing on culture medium containing  $0.1 \text{ mmol L}^{-1}$  sodium iodide. No production was observed in controls containing the same media and strains but no sodium iodide. The authors gave no estimate about the source strength, because the laboratory conditions are quite different from the natural environments. There seems to be no study of methyl iodide production from bacteria and fungi under environmental conditions. *Keppler et al.* (2003) reported methyl iodide production in soils via oxidation of organic matter by iron(III). They suggested it to contribute significantly to the input of methyl iodide to the atmosphere, because the concentration of iodine in soil is higher, compared to seawater, and iron(III) is common in

the terrestrial environment. However, they did not estimate a global flux, since the soil parameters controlling this production are not fully known and the soil composition is quite variable at different locations.

### 1.2.2 Sinks in the atmosphere

Photolysis is believed to be the main sink of methyl iodide in the atmosphere. The carbon-iodine bond in methyl iodide is easily broken by solar UV radiation, with a maximum absorption at 260 nm (Roehl *et al.*, 1997). This reaction yields initially methyl radicals and reactive iodine atoms, which in turn take part in many reactions in the atmosphere (e.g. Jenkin, 1991, Solomon *et al.*, 1994, ). The iodine atoms react fast with ozone to form oxygen molecules and iodine monoxide, which in turn photodissociates again and regenerates iodine atoms (Carpenter *et al.*, 1999):



These two reactions cycle rapidly, leading to the destruction of ozone. I and IO can be depleted by reactions with nitrogen oxides, NO<sub>x</sub>, and reaction with HO<sub>2</sub>, the latter yielding HI and HOI. Further iodine monoxide can react with itself, giving the dimer I<sub>2</sub>O<sub>2</sub> and other products. These species are either oxidized or photolyzed, regenerating iodine atoms, or lost by dry deposition, wet deposition and/or to aerosols (McFiggans *et al.*, 2000).

The tropospheric lifetime due to photolysis was estimated by Zafiriou (1974) with 4 – 8 days. A similar lifetime of 4 days was reported more recently by Yvon-Lewis and Butler (2002). The lifetime increases at higher latitudes up to 2 weeks due to the lower incident radiation (Blake *et al.*, 1999). Due to the combination of a short lifetime with sources at ground level and the increasing solar radiation at higher altitudes, atmospheric methyl iodide concentrations decrease with increasing altitude (e.g. Davis *et al.*, 1996, Blake *et al.*, 1999). Its atmospheric influence seems thus to be limited to the troposphere, except at occasions with very strong vertical mixing like inside convective clouds (Solomon *et al.*, 1994), which are common in the tropics. In such cases, called deep convective events, short lived gases as methyl iodide may reach the lower stratosphere.

The global loss by photolysis was calculated by Chameides and Davis (1980) with 10.6 Gmol methyl iodide per year. They used the atmospheric dry gas mole fractions of 10 pmol mol<sup>-1</sup> for the tropics between 30°N and 30°S and of 5 pmol mol<sup>-1</sup> at higher latitudes from Lovelock *et al.* (1973) and a mean atmospheric lifetime of eight days. More recent studies reported lower dry gas mole fraction in the atmosphere of 1 – 2 pmol mol<sup>-1</sup> (see chapter 1.2 for details). With these values, which are about one fifth of the concentrations

used by *Chameides and Davis* (1980), their sink due to photolysis is accordingly reduced to about  $2.11 \text{ Gmol a}^{-1}$ . *Bell et al.* (2002) reported a similar sink of  $2.14 \text{ Gmol a}^{-1}$  from model calculations. A more comprehensive re-evaluation of the atmospheric methyl iodide sink by photolysis seems necessary considering its importance for the atmospheric budget.

*Yvon-Lewis and Butler* (2002) evaluated the oceanic uptake of atmospheric methyl iodide and found it to be only a minor sink. The dry deposition of methyl iodide was evaluated by *Baker et al.* (2001). They reported only low deposition fluxes compared to deposition of inorganic iodine species by rain and aerosol, which are coming from reactions of iodine after photolysis of methyl iodide. Another potential sink is the reaction of methyl iodide with hydroxyl-radicals, but this reaction yields only about 2 % of the loss due to photolysis (*Brown et al.*, 1990). *Cotter et al.* (2003) investigated the reaction of methyl iodide with hydroxyl radicals and chloride atoms, too. They measured the reaction rates for these reactions in laboratory experiments under different conditions. They compared the first order loss rates of methyl iodide by photolysis with those from the reaction with hydroxyl radicals and chloride atoms. The loss rate by photolysis is one order of magnitude higher than by reaction with hydroxyl radicals and two orders of magnitude higher than the loss rate due to the reaction with chloride atoms.

### **1.3 Methyl iodide in the ocean**

The first measurement of methyl iodide in seawater was reported from *Lovelock et al.* (1973). This was followed by many different studies of methyl iodide in the ocean. Typical methyl iodide concentrations in the surface water are between  $2.0 \text{ pmol L}^{-1}$  and  $10 \text{ pmol L}^{-1}$  (e.g. *Tanzer and Heumann*, 1992, *Happell and Wallace*, 1996, *Moore and Groszko*, 1999, *King et al.*, 2000). Occasionally higher concentrations were measured, e.g. *Singh et al.* (1983) found methyl iodide concentrations up to  $47.9 \text{ pmol L}^{-1}$  in the eastern Pacific and *Reifenhäuser and Heumann* (1992) measured concentrations up to  $52.8 \text{ pmol L}^{-1}$  around the Antarctic Peninsula. Depth profiles show that the methyl iodide concentrations decreases with depth and concentrations below 200 m depth are generally less than  $1 \text{ pmol L}^{-1}$  (*Moore and Tokarczyk*, 1993, *Groszko*, 1999). Based on this data the source of methyl iodide seems to be close to the surface of the ocean, between the air sea interface and a depth of about 50 m.

### 1.3.1 Sources for the ocean

The sources of methyl iodide in the ocean are quite uncertain. The finding of elevated methyl iodide concentrations in coastal areas and inside algae belts indicated a biological source by algae. *Manley and Dastoor*. (1988) found methyl iodide production in laboratory incubation experiments with tissue disks from several different species of macroalgae. From the measured production rates they concluded that macroalgae are only a minor source of methyl iodide to the ocean and calculated a global production from macroalgae of  $4 \cdot 10^{-3} \text{ Gmol a}^{-1}$ . *Nightingale et al.* (1995) did incubation experiments with whole algae, instead of tissue disks, and estimated an even lower global production of  $0.3 \cdot 10^{-3} \text{ Gmol a}^{-1}$  by macroalgae. Based on the maximum release rate from their incubation experiments with algae from various climate zones, *Giесе et al.* (1999) estimated a maximum input of methyl iodide in the ocean with  $0.078 \cdot 10^{-3} \text{ Gmol a}^{-1}$ . Despite the low global input of methyl iodide by macroalgae, it may locally be the dominant source, e.g. in coastal areas with large algae beds (*Manley et al.*, 1992, *Carpenter et al.*, 2000).

Since methyl iodide occurs in the open ocean far away from the occurrence of algae, with the highest concentrations close to the surface in depth profiles, *Moore and Tokarczyk* (1993) proposed it may be produced by phytoplankton. Subsequent laboratory incubation experiments showed that a variety of phytoplankton species can produce methyl iodide (*Itoh et al.*, 1997, *Scarratt and Moore*, 1999, *Murphy et al.*, 2000). The global input of methyl iodide from phytoplankton, however, was estimated to be only  $8.45 \cdot 10^{-3} \text{ Gmol a}^{-1}$  (*Manley and de la Cuesta*, 1997), which is insignificantly low compared to the total flux to the atmosphere.

During their incubation experiments with macroalgae, *Manley and Dastoor* (1988) evaluated the methyl iodide production by rotting kelp tissue during laboratory incubations and found that these cultures produced methyl iodide, too. They postulated that this production was by activity of bacteria, but had no information about the species involved. They estimated a maximum potential global release of methyl iodide by bacteria of  $2.11 \text{ Gmol a}^{-1}$ , if 80 % of the annual kelp production is degraded microbially and all iodine contained in the tissue is converted to methyl iodide. *Manley* (1994) evaluated the reaction between methylcobalamin with iodide ions. From the measured reaction rates and the methylcobalamin content in the bacteria cells, freed upon lysis of the cells, he estimated a potential production of methyl iodide between  $0.0042 - 13.33 \text{ Gmol a}^{-1}$ . These two studies only gave potential global input of methyl iodide into the ocean. *Amachi et al.* (2001) estimated a significantly lower input between  $0.007 \cdot 10^{-3} \text{ Gmol a}^{-1} - 0.07 \cdot 10^{-3} \text{ Gmol a}^{-1}$  from their incubation experiments with different bacteria species. Thus, despite their large potential for methyl iodide production, bacteria do not seem to contribute significantly to the overall source to the ocean.

*Moore and Zafiriou* (1994) reported methyl iodide production from filtered seawater samples under irradiation and proposed a photochemical production. Addition of iodide enhanced the

production, whereas oxygen inhibited the production. They discussed a reaction mechanism via radical recombination of methyl radicals and iodine atoms. They estimated the production rate and found that it can possibly account for the flux to the atmosphere. *Happell and Wallace* (1996) proposed a photochemical production of methyl iodide from their analysis of factors influencing its saturation anomaly at high and low latitudes. They found very low, and sometimes negative, saturation anomalies at high latitudes and attributed this to the lower light intensity. From the different factors tested by analysis of variance, methyl iodide concentration was most strongly correlated with light intensity. Additional support for a photochemical production came from *Li et al.* (2001). They found slightly higher atmospheric methyl iodide concentrations in the tropics and during the southern hemispheric (SH) summer, compared to the northern hemispheric (NH) winter. They stated, since the solar radiation is 5 – 6 times higher in SH summer than in NH winter, the decomposition of methyl iodide by photolysis will be enhanced in these regions, too. They speculated that this enhanced loss is compensated by a similar enhanced photochemical production. Despite these results, a photochemical production of methyl iodide is not proven yet, and the mechanism of such a reaction pathway and its contribution to the overall sources of methyl iodide to the ocean remains unknown.

### 1.3.2 Oceanic sinks

The oceanic sinks for methyl iodide are better known than the sources. One important sink of methyl iodide in the ocean is its flux to the atmosphere, which was already described in chapter 1.2.1. Another sink is the nucleophilic substitution reaction of methyl iodide with chloride and bromide, leading to the formation of methyl chloride and methyl bromide, respectively. The rate of these reactions were measured by *Zafiriou* (1975) and *Elliott and Rowland* (1993). The calculated amount of methyl iodide loss from these reactions is dependent on the seawater temperature and the methyl iodide content used in the calculation. *Bell et al.* (2002) calculated a global loss of  $1.85 \text{ Gmol a}^{-1}$  due to the reaction with chloride, which is in the same order of magnitude as the estimated flux to the atmosphere. In comparison, the loss due to the reaction with bromide is insignificant, since the concentration of bromide in sea water is three orders of magnitude lower than the chloride concentration, and the reactivity of bromide is lower than that of chloride. Another possible loss of methyl iodide is by hydrolysis, but *Elliott and Rowland* (1993) stated that the reaction rate for this reaction was too slow to be measured in their experiments. Photolytic decomposition, which is the main reaction of methyl iodide in the atmosphere, is assumed to be unimportant in the ocean on the global scale, since the necessary UV radiation with wavelengths less than 340 nm is absorbed by water and thus extinguished by a depth of 25 m. It can, however, have a significant influence in the upper mixed layer of the ocean, which is the region where the proposed photochemical production takes place.

There is apparently a large imbalance between the described sources and sinks of oceanic methyl iodide, because the combined sources are much lower than the combined sinks. Since the sinks are known fairly confident, there must be either another, hitherto unknown, source, or one or more of the known sources must produce more methyl iodide than estimated.

#### ***1.4 Goal of the present study***

The review of the literature shows that the oceanic budget of methyl iodide is still subject to substantial uncertainty. The estimates of the flux to the atmosphere vary considerably between different research groups. And the main source (or sources) of methyl iodide to the ocean are yet not known.

The goal of the present study was to evaluate factors influencing the net air-sea flux of methyl iodide, based on field measurements made with an equilibrator and a two-dimensional GC-ECD system in the Atlantic at different times of the year. To address the missing source of methyl iodide to the ocean, incubation experiments have been made at sea, under conditions as close to environmental conditions as possible. Particular attention has been paid to test the hypothesis that the missing methyl iodide source in the ocean may be the photochemical production.



## 2. Data collecting methods

### 2.1 Cruise tracks

The data for this thesis have been collected on four research cruises, one in the North Atlantic and three in the tropical Atlantic. The tracks are shown in Figure 1 and Figure 2, the dates and ports are given in Table 1. The three cruises in the tropical Atlantic had, in part, overlapping cruise tracks, which allowed data to be obtained from the same area at different times of the year.

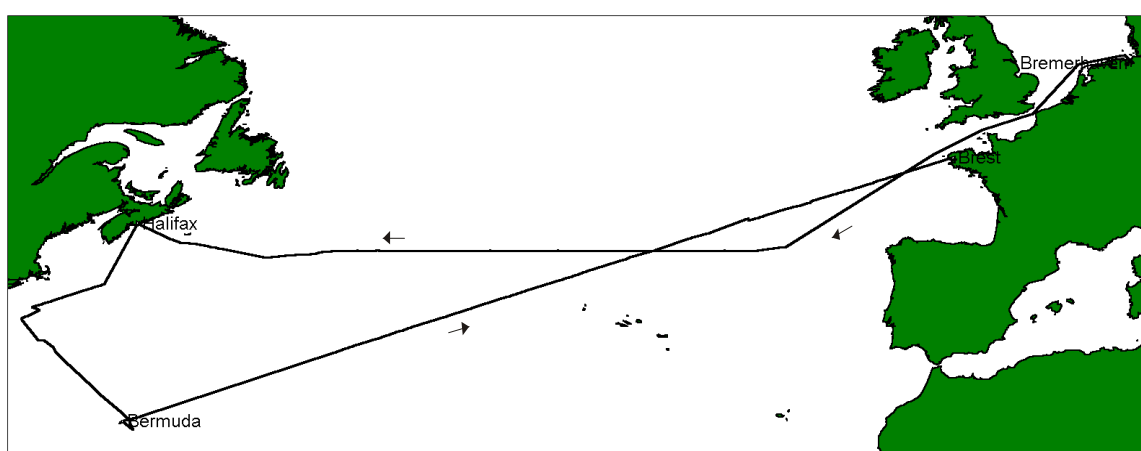


Figure 1: Cruise track of Pos255.

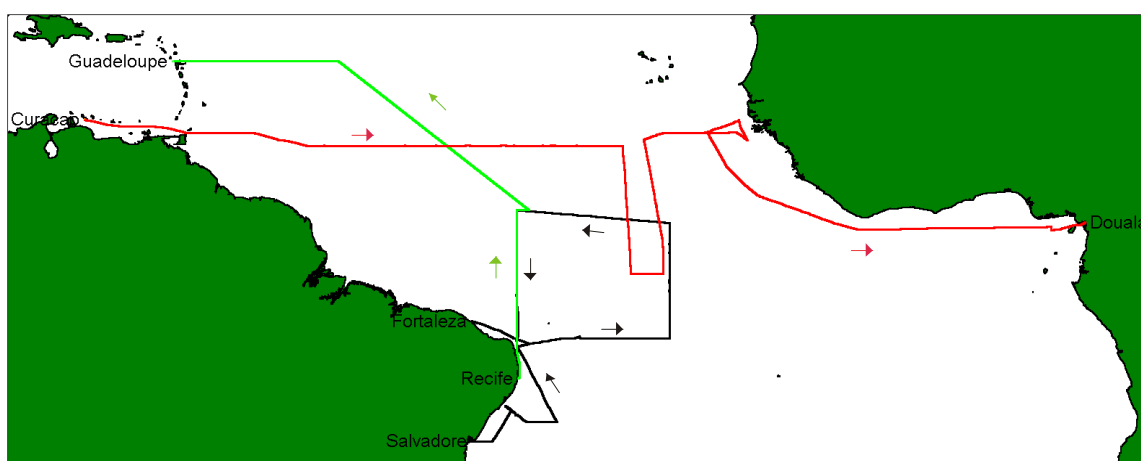


Figure 2: Cruise tracks of M47 (black), M55 (red) and So152 (green).

**Table 1: Overview of the cruise data.**

cruise name	vessel	from	to	time	area
Pos255	FS Poseidon	Bremerhaven, Germany	Brest, France	August to October 1999	North Atlantic
M47	FS Meteor	Salvadore, Brasil	Fortaleza, Brasil	March and April 2000	western tropical Atlantic
So152	FS Sonne	Recife, Brasil	Guadeloupe, France	November and December 2000	western tropical Atlantic
M55	FS Meteor	Curaçao	Douala, Cameroon	October and November 2002	tropical Atlantic

## **2.2 Methods for halocarbon measurements**

The analytical procedure for measuring halocarbons consists of four steps: separation from the matrix, concentration, separation of the different compounds from each other and detection. Three methods are used for the first two steps. There are the liquid-liquid extraction technique, the static headspace method and the dynamic headspace method, including purge and trap. The separation and detection of the organohalogenes is done by gas chromatography with an appropriate detector.

In the liquid-liquid extraction the seawater is well mixed with a suitable immiscible solvent, e.g. pentane (*Abrahamsson and Klick, 1990*, and literature cited therein). The efficiency of the extraction depends on the partition coefficient of the analyte between water and solvent, the phase ratio (volume of extracting solvent / sample volume) and the number of extraction steps (*Poole and Schuette, 1983*). This extraction is simple and does not need complex equipment, but the method has some practical problems. The separation of the two phases can be prevented by the formation of emulsions, especially in organic rich waters. Further, for a better extraction efficiency a higher phase ratio and therefore the use of more solvent is necessary, thus limiting the possibility to preconcentrate the halocarbons in the solvent by using a low solvent volume for extraction. Multiple extractions would increase the efficiency too, but require more solvent, thus again decreasing the concentration of the analytes in the solvent. Nevertheless this method has been used successfully for the determination of different halocarbons in seawater with extraction efficiency of 36 to 88 % and precision from 3 to 12 % depending on the compound (*Abrahamsson and Klick, 1990*). The same method can be used with sediment as well (*Abrahamsson and Ekdahl, 1993*,

*Peijnenburg et al.*, 1998). But overall the liquid-liquid-extraction is not often used for the determination of volatile halocarbons in seawater.

Static headspace analysis is an easy way to separate the sample from the matrix for volatile compounds since it requires only simple equipment. The water sample is put in a vessel, a headspace with inert gas is added and is shaken for an appropriate time until equilibrium is reached. Then a subsample of the equilibrated gas is measured (*Poole and Schuette*, 1983). The gas phase concentration is linked to the liquid phase concentration by the Henry's law constant, which is dependent on temperature and salinity. Depending on the Henry constant, the gas phase concentration can be quite low and therefore the sensitivity can be limited. The sensitivity can be increased, if a larger volume of the headspace is concentrated prior to the measurement (*Manley and Dastoor*, 1988, *King et al.*, 2000a). Static headspace analysis has been used for incubation experiments to measure the production of halocarbons including methyl iodide (*Manley and de la Cuesta*, 1997, *Itoh et al.*, 1997, *Urhahn and Ballschmiter*, 1998, *Amachi et al.*, 2001).

Closely related to the static headspace method are the "underway equilibrators". In these systems the sample water flows continuously through the equilibrator, where it is brought into close contact with a gas to reach equilibrium. The time for equilibration is thus reduced and the gas content comes to equilibrium with the real water content. In the static headspace described above the amount of a compound which enters the gas phase to reach equilibrium reduces the amount in the water. The advantage of equilibrators is that the measured concentration of a compound in the equilibrated gas gives a direct saturation anomaly after subtraction of its atmospheric concentration (*Groszko*, 1999, *King et al.*, 2000b), and this is especially useful for flux calculations. For that reason an equilibrator has been used in this thesis for the surface seawater and atmospheric measurements of methyl iodide.

Dynamic headspace analysis or purge and trap is a widely used method for sample work-up when measuring halocarbons. In this method the compounds are stripped with a stream of gas from a water sample and trapped in a sorbent filled or cold trap. This method works best with volatile compounds with a low water solubility (*Poole and Schuette*, 1983). This is true for most of the halocarbons with one or two C-atoms and this method has been used successfully for a wide range of halogenated compounds including methyl iodide (*Newman and Gschwend*, 1987, *Schall and Heumann*, 1993, *Krysell and Nightingale*, 1994, *Ekdahl et al.*, 1998, *Scarratt and Moore*, 1999, *Giese et al.*, 1999, *Baker et al.*, 2000a, *Tessier et al.*, 2002). Sometimes the purge vessel is heated to increase the gas phase / liquid phase partitioning coefficient (*Groszko*, 1999), because the purging efficiency is controlled mainly by the temperature, the bubble size, purging time and the amount of gas used for purging (*Abeel et al.*, 1994). For methyl iodide the efficiency is up to 100 %, when a choice of an effective trap allows the use of sufficient amounts of purge gas (*Ekdahl*, 1997). The different kinds of traps are discussed in chapter 2.4. In this thesis a purge and trap method has been used for incubation experiments, which is described in chapter 4.

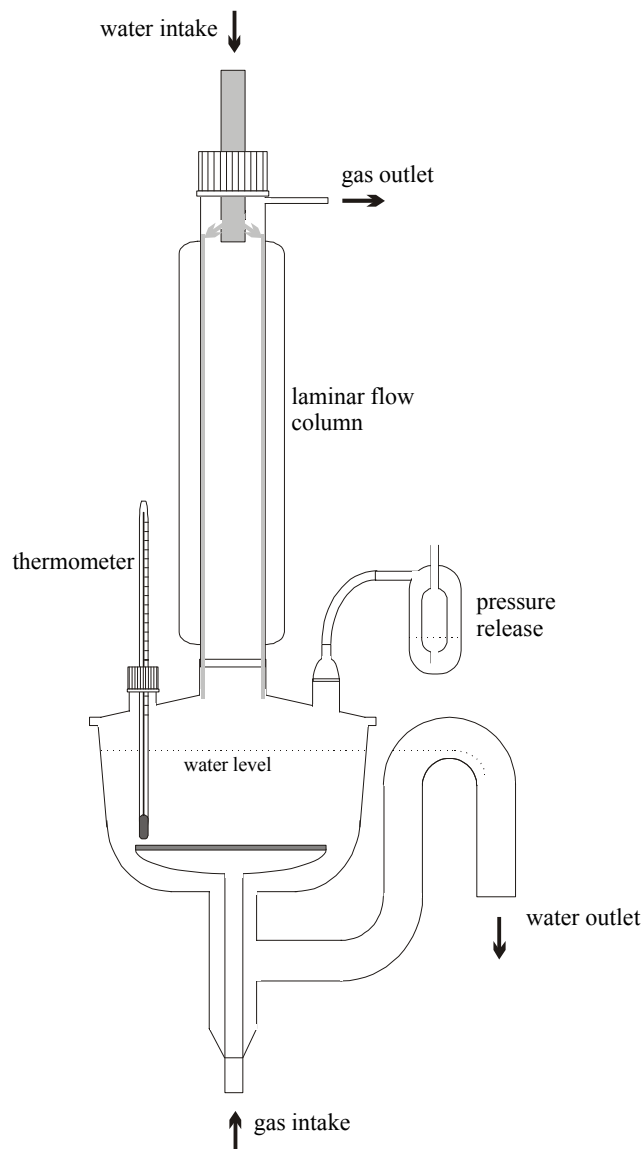
The separation of the different halocarbons is achieved by gas chromatography. The detectors used are flame ionisation detectors (FID), electron capture detectors (ECD) and mass spectroscopy (MS). The FID detector is suitable for all organic compounds, thus leading to problems with interfering peaks from other substances than halocarbons. It has been used for measuring halocarbons and hydrocarbons together (e.g. *Sanchez and Sacks*, 2003), but it is not widely used. The ECD detector is more specific since it is more sensitive for electron rich atoms like halogen atoms. Thus it is a semi-specific detector which does not detect most hydrocarbons at the concentrations encountered in seawater and air. This, and its high sensitivity for halocarbons has made it a widely used detector for organohalogenes (e.g. *Lovelock et al.*, 1973, *Manley and Dastoor*, 1987, *Schall and Heumann*, 1993, *Schauffler et al.*, 1993, *Laternus et al.*, 1996, *Scarratt and Moore*, 1996, *Ekdahl et al.*, 1998, *Amachi et al.*, 2001, *Berman et al.*, 2002). In recent time the MS detector is used more and more, because its sensitivity has reached that of the ECD detectors and the instruments are stable enough to be put on board of research ships. But the main advantage of the MS detector is that is compound specific if used in the single ion mode. Then it is sensitive for only a single mass-charge ratio, thus eliminating interference from other compounds, which have different mass-charge ratios, with the analytes. MS detection is now frequently used for the analysis of halocarbons (e.g. *Bianchi et al.*, 1989, *Moore et al.*, 1996b, *Yokouchi et al.*, 1997, *Li et al.*, 1999, *Jordan et al.*, 2000, *Amachi et al.*, 2001, *Christof et al.*, 2002).

In this thesis a two dimensional GC-ECD system has been used for all halocarbon measurements. It is described in detail in chapter 2.5.

## **2.3 Equilibrator**

In the context of this thesis an “equilibrator” refers to an apparatus used to bring a gas phase in equilibrium with a seawater sample. To achieve this a well mixed water phase is exposed to a well mixed gas phase, and a large surface area is established to decrease the time required for equilibrium to be reached. Four different types of equilibrators are used: the shower type, the bubble type, the thin film type and the membrane type. In the shower type the seawater drops through the gas phase (e.g. *Inoue et al.*, 1987, *Robertson et al.*, 1993, *Goyet and Peltzer*, 1994). In the bubble type the gas bubbles through the seawater (e.g. *Takahashi*, 1961). In the thin film type a laminar flow of seawater is in contact with a gas moving in the opposite direction (*Poisson et al.*, 1993). In the membrane type the gas phase moves through a long, thin tube made of a semi-permeable membrane (which is permeable for the substances to be measured, but not for water) and is immersed in the seawater sample, or the sample water flows through the tube with the gas phase at the outside (e.g. *Groszko and Moore*, 1998, *Groszko*, 1999).

The equilibrator used for this thesis combines the character of the thin film and bubble types and is build similar to the ones used for CO<sub>2</sub> measurements (*Körtzinger, 1999*). A schematic diagram of the equilibrator is shown in Figure 3. Seawater flows continuously with 1 L min<sup>-1</sup> through a laminar flow column and a bubble chamber. The gas is pumped with a clean metal bellows pump through a glass-frit in the bubble chamber and through the column back to the pump with a flow rate of about 2 L min<sup>-1</sup>. The bubble chamber is vented to the atmosphere through a glass bubbler with a small amount of water, so that the equilibrator is very close to atmospheric pressure and without direct contact to the outside air to avoid contamination. The column has an evacuated jacket to minimise temperature changes in the seawater. Samples are collected with a sample loop in the gas stream (called "gas mouse" with a volume of 30 or 126, see Figure 4) and concentrated on a cold trap (see next chapter).



**Figure 3: Scheme of the equilibrator**

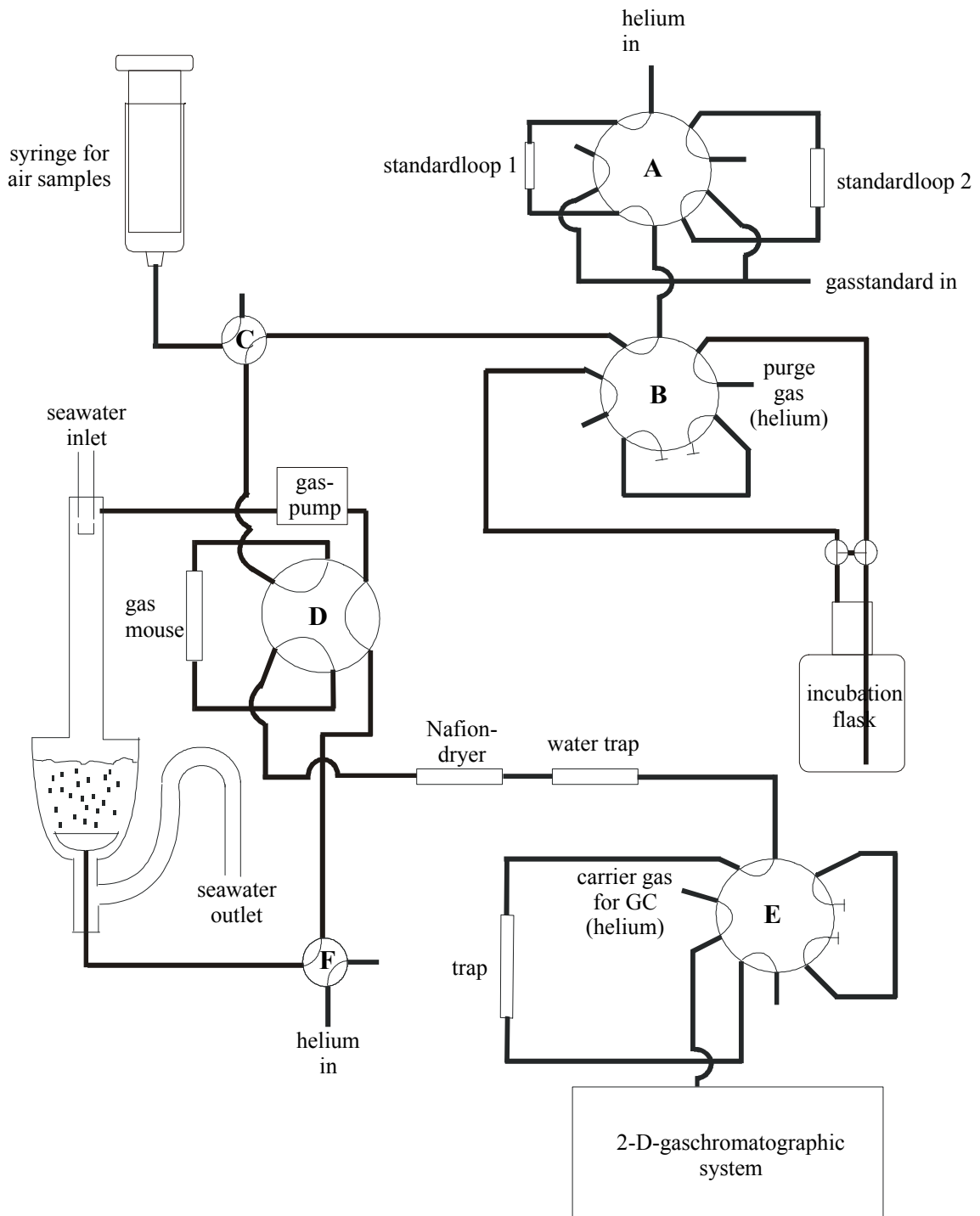


Figure 4: Schematic diagram of the analytic system

## 2.4 Traps

### 2.4.1 Traps for removing water

The gas phase of static headspace or equilibrator samples and from purge and trap techniques contains water vapour, which can plug cold traps or interfere with the separation and detection of the analytes. Several methods are used for drying the gas samples, including cold traps (or condensers) (*Ekdahl, 1997, Tessier et al., 2002*), adsorbent traps with sodium carbonate (*Laternus, 1995*), potassium carbonate (*Schall and Heumann, 1993, Giese et al., 1999*) or magnesium perchlorate (*Murphy et al., 2000, Tokarczyk and Saltzman, 2001*) and Nafion dryers (*Tanzer and Heumann, 1992, De Bruyn and Saltzman, 1997a*). *Moore et al. (1996a)* flushed their trap with helium for two minutes prior to desorption to remove enough water for their measuring system or combined this with a cold trap (*Moore and Tokarczyk, 1993*). Sometimes combinations of different drying methods are used. *Ekdahl (1997)* and *Groszko (1999)* used a cold trap followed by a magnesium perchlorate filled tube. *Christof et al. (2002)* combined a condenser with a Nafion dryer followed by a magnesium perchlorate tube. None of these drying methods is reported to interfere with the measurement of halocarbons.

During the first two cruises (Pos255 and M47) a cold trap held at about 2°C was used to remove excess water vapour. On the So152 cruise in the tropical Atlantic this method was not sufficient enough due to the warm water temperatures and a magnesium perchlorate trap was added after the cold trap. For the last cruise (M55) the cold trap was replaced with a 60 cm Nafion dryer with a counter-flow of dry air and Sicapent<sup>®</sup> (phosphorous pentoxide on an inert support, Merck) was used in the trap after the Nafion dryer instead of magnesium perchlorate, which had to be changed quite often. This worked efficiently. No interference with the measurements was detected with all drying procedures.

### 2.4.2 Traps for concentration of analytes

Two different types of traps are used for the concentration of the analytes in purge and trap or headspace analysis, cold traps and sorbent traps. A cold trap is either an open tube with a small diameter (*Krysell and Nightingale, 1994, Carpenter et al., 2000*) or a tube filled with glass wool or glass beads to increase contact surface area (*Camel and Caude, 1995, Laternus et al., 2000, Tessier et al., 2002*). Such traps are mostly cooled with liquid nitrogen (e.g. *Giese et al., 1999, Tessier et al., 2002*) and desorption is easily achieved by removing the coolant and/or heating the trap (e.g. *Groszko, 1999*). Cold traps are sensitive to water

vapour which clogs the trap (*Camel and Caude, 1995*) Very volatile gases may break through the trap, especially with open tubular traps (*Graydon and Grob, 1983*).

Sorbent traps are tubes filled with one or more sorbents to retain the analytes, sometimes at or close to room temperature. They therefore avoid the use of liquid nitrogen, and with the right sorbent there is no breakthrough of analytes. Two different kinds of sorbents are used, either based on carbon like Carboxen (*O'Doherty et al., 1993*), microcharcoal filters (*Atlas et al., 1993*), Carbotrap (*Urhahn and Ballschmiter, 2000*), Carbopack or Carbosieve (*Mosesman et al., 1987*) or polymers like Porapak (*Wallace et al., 1994, Ekdahl et al., 1998*), Tenax GR (*Quack and Suess, 1999*) or Tenax TA (e.g. *Gschwend et al., 1985, Baya and Siskos, 1996, Moore et al., 1996a, Li et al., 1999*). For special cases multisorbent traps with a combination of different sorbents are used (*Dewulf and van Langenhove, 1997, Pankow et al., 1998, Sanchez and Sacks, 2003*). The analytes are usually desorbed by quickly heating the trap.

For this thesis two different traps have been used for analyte concentration. For the first cruises (Pos255, M47 and So152) a sorbent trap was used to avoid the use of liquid nitrogen. The trap consisted of a glass tube with an inner diameter of 1.5 mm, filled with 30 mg Tenax TA between glass wool, and wrapped with a resistant heating wire. The sorbent was precleaned by flushing it with 4 mL distilled water, 4 mL methanol and two times with 4 mL n-hexane, followed by heating for 12 hours under nitrogen flux to 200°C, followed by 1 hour at 300°C. The trap was cooled in an ethanol bath to -30°C during trapping and quickly heated to 250°C with carrier gas counter-flow for desorption. The trapping efficiency was 100 % for CFC 11 and methyl iodide, no peaks could be obtained with a second trap after the first one. The recovery of analytes was also measured by comparing the peak areas of the same standard amount from direct injection in the GC and injection in the gas mouse and found to be 93 %. Since samples and standards are measured in the same way via the gas mouse, this recovery applies for both and no corrections need to be done in the calculations. The disadvantage of these traps was that they had to be replaced frequently, because the small glass tubes break very easily.

For the M55 cruise liquid nitrogen was available on board and an open tubular capillary cold trap was used to avoid the described problem. It consisted of a 20 cm long metal tubing with a diameter of 0.5 mm (tubing ultimetmetal uncoated, Chrompack), which is cooled with liquid nitrogen during trapping. For desorption the coolant is removed while carrier gas in counter-flow flushed the contents of the trap onto the column of the GC. The recovery of analytes was measured by comparing the peak areas of the same standard amount from direct injection in the GC and injection in the gas mouse and found to be 98 %. No breakthrough of CFC 11 or methyl iodide could be detected with a flow up to 75 mL min<sup>-1</sup> for 20 minutes by the use of a second trap of the same kind behind the one normally used.

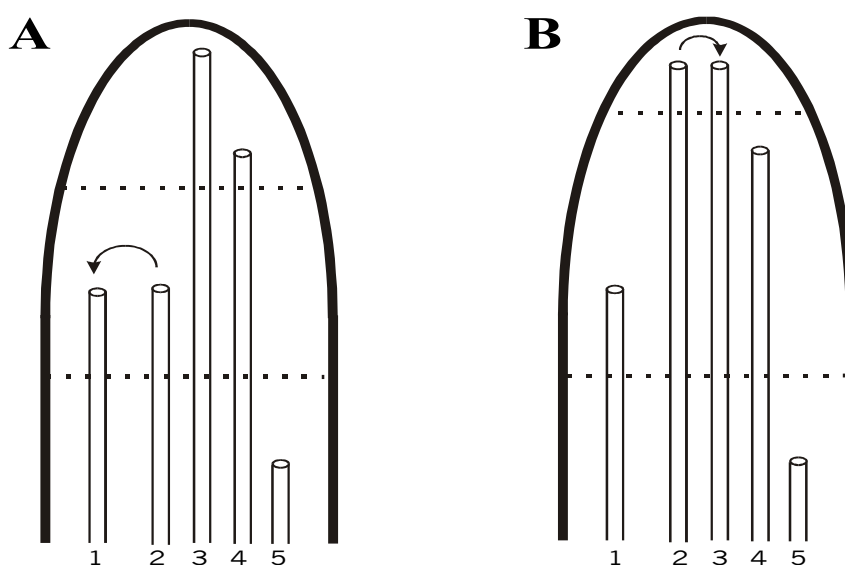


## 2.5 Gas chromatographic system

For the separation of the analytes a two dimensional gas chromatographic system was used. It consists of two gas chromatographs in series (GC 8160 and 8180, both from Fisons Instruments), both equipped with an electron capture detector (ECD 800) and a so called "dome" for the connection of the two gas chromatographs. The dome is located in the oven of the first GC at the end of the column (column 1) and permits the effluent of the column 1 to be directed either to the ECD of the first GC (the "monitor" detector) or onto the second column (column 2) in the second GC. The dome consists of a conical, vertical glass tube which is closed at the upper end (see Figure 5). The head of the column 2, the line leading to the monitor detector and two additional helium supply lines have fixed positions inside the dome, while the end of column 1 can be moved vertically.

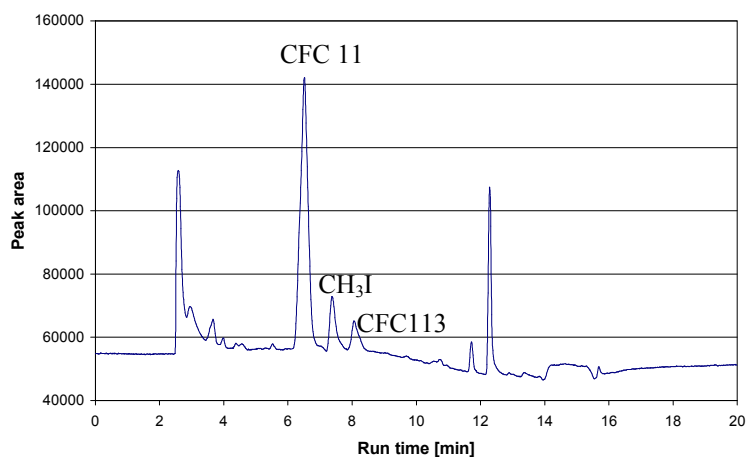
Figure 5 A shows the dome when the effluent from column 1 is directed to the monitor ECD. The end of column 1 is close to the opening of the line leading to the monitor ECD. The additional helium supply lines cause two pressure barriers (dashed lines in Figure 5). The upper pressure barrier, between the end of column 1 and the head of column 2, prevents that the effluent from column 1 can reach the opening from column 2. The lower pressure barrier prevents that effluent from column 1 can leave the dome. Thus the two pressure barriers and the co-location direct the effluent from column 1 to the monitor ECD.

If the end of column 1 is pushed upwards through the upper pressure barrier close to the head of column 2, the pressure barrier prevents that the effluent can reach the line to the monitor ECD and or leave the dome (Figure 5 B). In this case the effluent is directed by the pressure barrier and the co-location from the end of column 1 into column 2.

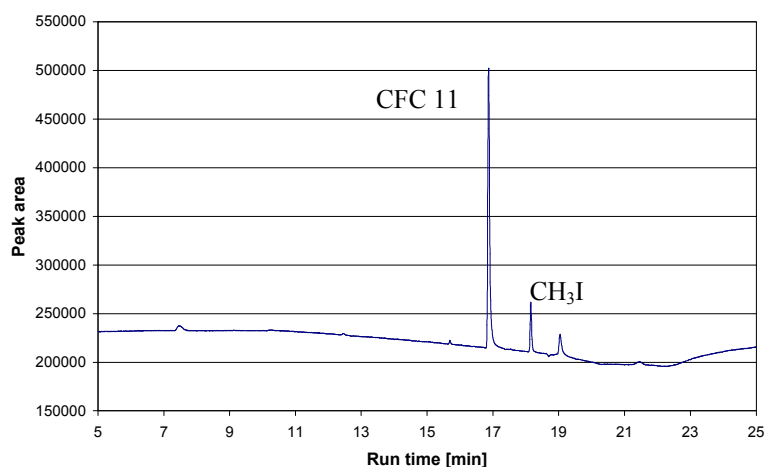


**Figure 5:** Scheme of the "dome" with the five lines. 1 is the line to the monitor ECD, 2 is the end of the column 1, 3 is the head of the column 2, 4 and 5 are additional helium supplies (see text for explanation)

The monitor detector allows the measurement of the retention times of analytes on column 1. Only the compounds of interest are switched onto column 2, thus avoiding contamination of column 2 and obtaining a far better separation. The disadvantage is that the different pressures of the two additional helium supplies and the head of column 1 have to be carefully regulated and have to have a fixed relation to each other to achieve good switching and prevent analytes moving in the wrong direction (e.g. reaching the monitor detector when directed to column 2). This limits the possibility to shorten retention times and leads to a relatively long time of 25 - 30 minutes for a full analytical cycle. Because the end of the first column moves frequently up and down, the ferrule sealing this connection is never completely gas tight. The lower helium supply line has the second task to flush this "leak" with helium to prevent loss of analytes or disturbance by air reaching the inside of the dome. These disadvantages are overcompensated by better separation, for the analysis of methyl iodide especially the separation of methyl iodide from CFC 11 and CFC 113 (see Figure 6 and Figure 7).



**Figure 6:** Sample chromatogram from the So152 cruise (measured with one column only, seawater sample).



**Figure 7:** Sample chromatogram from the M55 cruise (measured with 2-dimensional GC, seawater sample, CFC 113 was not measured).

During the Pos255, M47 and So152 cruises the system was used as a normal GC (1-dimensional mode) with one oven and column because of problems with the second GC. The column used in the first GC was a 60 m, 0.25 mm RTX 624 from Restek Corp. and the temperature program was: 5 minutes at 40°C, a first step with + 8°C min<sup>-1</sup> up to 120°C, a second step with + 20°C min<sup>-1</sup> up to 200°C, followed by 5 minutes at 200°C and cooling down.

For the M55 cruise the second GC was ready to use with a 30 m, 0.32 mm GS Gaspro column from J&W Scientific Inc.. The temperature programs were:

Column 1: holding 5 minutes at 40°C, with + 10°C min<sup>-1</sup> up to 100°C, with 25°C min<sup>-1</sup> up to 200°C, holding for 3 minutes and cooling down.

Column 2: holding 9 minutes at 50°C, with + 15°C min<sup>-1</sup> up to 200°C, holding for 2 minutes and cooling down.

This temperature program leads to a re-concentration of analytes at the beginning of column 2, because the oven temperature of the second GC is 40°C lower than that of the first one at the same time, thus increasing the separation and obtaining smaller peaks widths.

Helium was used as carrier gas with a constant pressure of 250 kPa, leading to a flux of about 3 mL min<sup>-1</sup> at an oven temperature of 40°C and 2 mL min<sup>-1</sup> at an oven temperature of 200°C. The ECD-detectors required nitrogen as make up gas with a flow rate of 50 ml min<sup>-1</sup>.

## **2.6 Water samples**

Seawater for sampling was pumped continuously through the equilibrator with a submersible pump, located in the ship's moon pool. The flow rate through the equilibrator was 1 L min<sup>-1</sup>. The gas phase of the equilibrator was circulated with a metal bellows pump at a rate of 2 L min<sup>-1</sup>. The gas mouse is included within the flushed lines of the equilibrator at least 15 minutes prior to measurement, to ensure equilibrium has been reached.

During the first two cruises (Pos255 and M47) the gas mouse had a volume of 30 mL, for the So152 cruise a gas mouse with a volume of 125 mL was used. For a measurement its content was flushed with a flow of 20 mL helium per minute (40 mL helium per minute during So152) for 15 minutes onto the sorbent trap held at -30°C. For desorption the carrier gas flow of the gas chromatograph was directed through the trap and the trap was heated for 20 sec with a current of 3 A followed by 50 s with 2 A, which gave a temperature of 250°C.

On the last cruise (M55) the gas mouse had a volume of 126 mL and its content was flushed with a helium flow of 50 mL min<sup>-1</sup> for 15 minutes onto an open tubular trap cooled with liquid nitrogen. Then the carrier gas flow was directed through the trap and the cooling was removed to desorb the analytes rapidly onto column 1.

## 2.7 Air samples

Air samples were collected with a gas tight 100 mL glass syringe, fitted with a shut-off valve. Samples were collected either from the uppermost deck or from the bow of the ship, always at the upwind side to avoid contamination by exhaust gases from the ship. During the Pos255, M47 and So152 cruises the samples were injected with a needle through a septum into the gas mouse of the equilibrator, while the helium flow through the gas mouse was directed onto the trap. After injection of the air sample the procedure was the same as described for water samples in chapter 2.6.

With this arrangement, occasional problems were encountered due to septum leakage after repeated penetration of the septa with the relatively large needle (0.9 mm) used for sampling. Therefore, for the last cruise (M55) an additional valve for air samples was build into the system. Now the syringe with its close off valve could be connected to the system with a Luer-lock adapter. After connecting the syringe to the valve the line was flushed with about 20 mL of the sample before turning the valve and injecting a sample volume of 77 mL into the gas mouse of the equilibrator. A stopper for the piston of the syringe was used while flushing the line to make sure that the same sample volume was always left in the syringe for trapping. A gas flow of 50 mL helium per minute for 15 minutes was used to flush the air sample completely onto the trap in the same way as for water samples (see chapter 2.6).

## 2.8 Standards

Quantification of the peak areas have been done by comparison with peak areas from injections of standards with a known methyl iodide content. The standards used were the S29, S30 and P5 standards from *Happell and Wallace (1997)*. They were gravimetrically prepared gas standards of halocarbons in nitrogen. Their methyl iodide and CFC 11 content is shown in Table 2.

**Table 2: Standard concentrations.**

	CFC 11 [nmol mol <sup>-1</sup> ]	CH <sub>3</sub> I [nmol mol <sup>-1</sup> ]
P 5	62.42 ± 0.35	171.2 ± 0.3
S 29	0.3180 ± 0.0019	0.8720 ± 0.0022
S 30	0.3141 ± 0.0019	0.8612 ± 0.0022

The injection of the S 29 and S 30 standards was done using standard sample loops with a volume of 0.5 and 1 mL (see Figure 4). They were connected to the equilibrator with a 10-port Valco valve, which allows multiple injections to inject larger standard volumes. This system was used during the Pos255, M47 and So152 cruises. The standard deviation of these standard injections was 9 %.

Injections of the P 5 standard during the M55 cruise were done with a gas-tight 100  $\mu$ L glass syringe (Hamilton) through a septum port directly into the gas mouse. The standard deviation of standard injection was 8.3 % (n = 36), after correction for differences in temperature, pressure and injected volume.

During underway sampling it was not possible to take two identical samples with the equilibrator due to the time lag between two samples and the movement of the ship. But for the incubation experiments sample water was collected in 1 litre glass bottles from which the different incubation flasks were filled. And every incubation bottle was measured prior to incubation. Therefore the methyl iodide contents for the untreated incubation flasks can be compared as a measure of system precision. The results are shown in Table 3.

**Table 3: Initial methyl iodide measurements from the incubation experiments [pmol].**

	Number of bottles	Mean CH <sub>3</sub> I content [pmol]	Standard deviation	
			[pmol]	[%]
Incubation 3	4	0.063	0.014	22.3
Incubation 4	4	0.077	0.031	40.2
Incubation 5	4	0.053	0.007	13.8
Incubation 6	4	0.286	0.026	9.0
Incubation 7	12	0.605	0.021	3.4
Incubation 8	11	0.481	0.015	3.1

The standard deviation in percent is in the same range for the gas standard injections (8.3 %) and from the last three incubations (3.1 to 9.0 %). The higher standard deviation (in percent) from incubations 3 to 5 is due to the lower methyl iodide content in these samples, which were taken from Niskin-bottles collected at 200 m depth, whereas incubations 6 to 8 were surface seawater taken from the same pump than the water samples. From these standard deviations of the incubation experiments and the standard injections an analytical precision of 9 % is estimated.

This relative precision is not reached for the incubations 3 to 5 with low methyl iodide contents. But as shown in Table 3 the standard deviation expressed as absolute methyl iodide content is in the same range for all 6 incubation experiments, with a mean of  $0.019 \pm 0.009$  pmol methyl iodide. Thus this value can be taken as an absolute precision for samples with a low methyl iodide content, as for example air samples.

From these considerations the precision of the analytical system is estimated to be 9 % of the measured concentration or 0.019 pmol methyl iodide absolute, whichever is higher.

## 2.9 Water vapour correction

The gas mole fraction of methyl iodide measured with the equilibrator is dependent on all gases in the sample loop. This includes the partial pressure of the water vapour which varies with temperature, and in the air samples with the relative humidity of the air. For comparing measured values, all gas mole fractions have been corrected for the water vapour partial pressure and calculated as dry gas mole fractions.

The partial pressure of the water at equilibrium with seawater was calculated with the equation from *Weiss and Price* (1980)

$$\ln p_{H_2O} = 24.4543 - 67.4509 \cdot \left( \frac{100}{T_K} \right) - 4.8489 \cdot \ln \left( \frac{T_K}{100} \right) - 0.000544 \cdot S \quad (1)$$

where  $p_{H_2O}$  is the saturated partial pressure of water in atm,  $T_K$  is the water temperature in K and  $S$  is the salinity of the seawater. Seawater samples measured with the equilibrator are assumed to be saturated with water vapour at the temperature of the water in the equilibrator. The “dry” pressure was calculated by subtracting this partial pressure of the water, converted to mbar, from the barometric pressure in mbar. The dry gas mole fraction of methyl iodide was then calculated by multiplying the gas mole fraction of the sample by the ratio of the barometric pressure to the dry pressure (equation 2).

$$c_w = c_{ww} \cdot \frac{p}{(p - p_{H_2O})} \quad (2)$$

where  $c_{ww}$  is the gas mole fraction of methyl iodide measured with the equilibrator and  $c_w$  is the dry gas mole fraction of methyl iodide,  $p_{H_2O}$  is the saturated partial pressure of water from equation 1 and  $p$  is the barometric pressure.

## 2.10 Chlorophyll measurements

During the first cruise water samples for the measurement of the chlorophyll concentration were taken. The analytical procedure was the same as described in the protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements, released from the UNESCO in 1994.

The water samples were taken from the same submersible pump as the sample water for the equilibrator measurements. Two litre of sample water were filled in polyethylene bottles. The samples were filtered through 25 mm GF/F filters (Whatman) immediately after sampling, using polycarbonate in-line filters and a vacuum less than 13.3 kPa. The filters were kept in the dark and frozen ( $-20^{\circ}\text{C}$ ) until analysis in the laboratory. For analysis the filters were placed in 15 mL polyethylene centrifuge tubes, than the filters were covered with glass beads (2 mm and 4 mm diameter) and 5 mL 90 % acetone was added. The tubes were placed in a grinder (Bühler Zelmühle) and their contents ground for 5 minutes. After adding another 5 mL 90 % acetone the tubes were placed in the dark in a freezer for about 10 minutes, to cool their contents down again after the grinding warmed it up. Thereafter the tubes were centrifuged under cooling ( $-10^{\circ}\text{C}$ , 4000 rpm) and 5 mL of the supernatant was placed in a cuvette. After measuring the fluorescence with a Turner design fluorometer (model 10), 100  $\mu\text{L}$  hydrochloric acid (1 mol  $\text{L}^{-1}$ ) were added to the cuvette, the content mixed and after 2 – 3 minutes the fluorescence was measured again.

The chlorophyll concentration is calculated with the following formula

$$[Chl] = 2.2 \cdot (F_o - F_a) \cdot K_X \cdot \left( \frac{V_{ex}}{V_S} \right) \quad (3)$$

where  $[Chl]$  is the chlorophyll *a* concentration in  $\mu\text{g L}^{-1}$ ,  $F_o$  and  $F_a$  are the instrument readings before and after acidification, respectively,  $K_X$  is calibration factor,  $V_{ex}$  is the extraction volume and  $V_S$  the volume of the sample. The calibration of the instrument was done on a regular basis by a technician, following the procedures described in the protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements, released from the UNESCO in 1994, and from *Holm-Hansen and Riemann (1978)*.

### 3. Underway data

In this chapter the measured surface water and air concentrations will be shown together with the equations and the Henry's law constant used for calculation. Then the flux is estimated and in the last subchapter the results will be discussed.

#### 3.1 Air samples

The dry air mixing ratios of methyl iodide measured during the three cruises in the tropical Atlantic are shown in Figure 8. The dry air mixing ratios in the atmosphere varied between 0.1 and 32.6  $\text{pmol mol}^{-1}$ , with a mean of 5.2  $\text{pmol mol}^{-1}$ . Two very high values of 64 and 72  $\text{pmol mol}^{-1}$  measured during M55 are most likely caused by contamination and have been discarded.

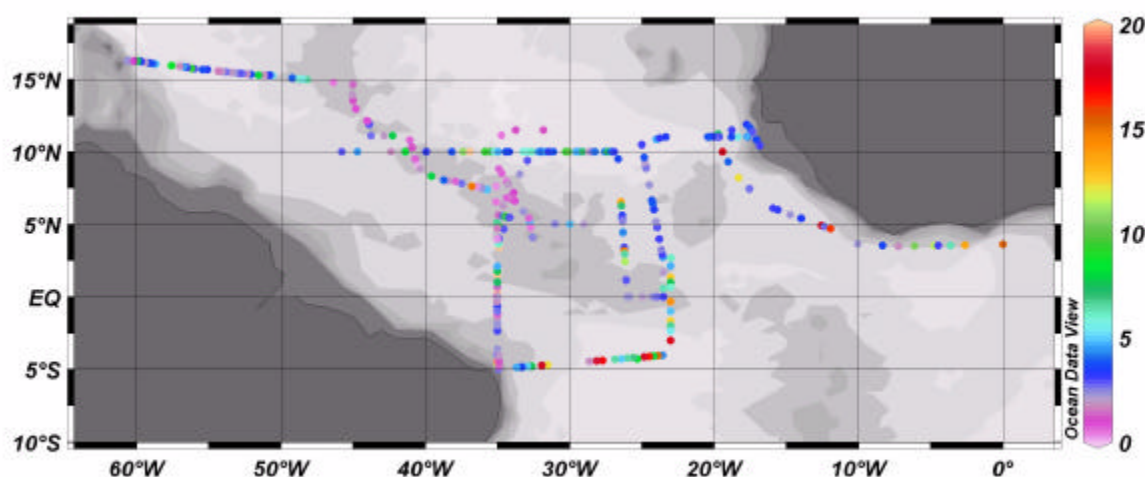
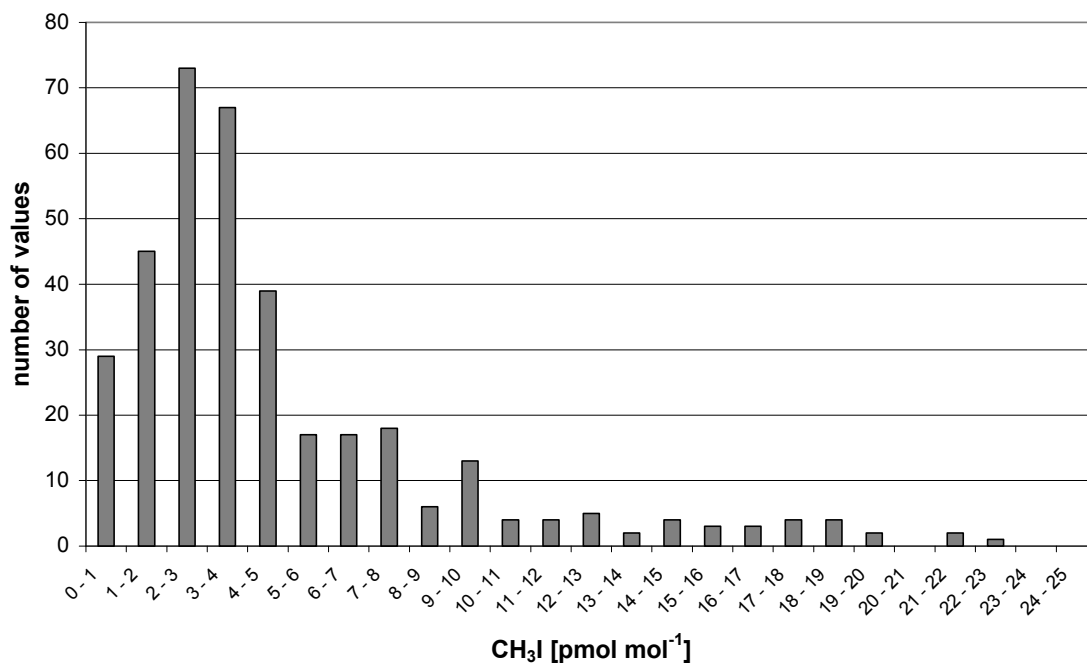


Figure 8: Atmospheric methyl iodide dry air mixing ratios [ $\text{pmol mol}^{-1}$ ] over the tropical Atlantic.

The measured dry gas mole fractions of methyl iodide are very scattered. In addition, a normal distribution is skewed significantly to higher concentrations (see Figure 9). The reason seems to be the absolute precision of the analytical system, which was calculated to be 0.019  $\text{pmol}$  (see chapter 2.8). This is in the same range (or higher) than the methyl iodide content of an average air sample (e.g. 0.008  $\text{pmol}$  for a 100 mL air sample with a dry gas mole fraction of 2  $\text{pmol mol}^{-1}$  and 0.020  $\text{pmol}$  for a 100 mL air sample with a dry gas mole fraction of 5  $\text{pmol mol}^{-1}$ ). Thus the higher results for the atmospheric dry gas mole fractions





**Figure 9:** Histogram of the measured atmospheric dry gas mole fractions of methyl iodide [pmol mol<sup>-1</sup>].

(above 10 pmol mol<sup>-1</sup>) must be doubted. For the intended flux calculations, however, the atmospheric dry gas mole fractions of methyl iodide are needed. The mean value (5.2 pmol mol<sup>-1</sup>) can not be used, since it is only valid for data sets which follow the normal distribution. Thus the median of the measured atmospheric dry gas mole fractions of 3.5 pmol mol<sup>-1</sup> is used for the calculation of the concentration anomaly ( $\Delta C$ ), since it is more representative for a data set that is not following the normal distribution. The median of this data set may still be higher than the real atmospheric dry gas mole fraction, because it is influenced by the doubtful high measured dry gas mole fractions. The dry gas mole fractions found in the literature for the tropical Atlantic are in the range of 0.5 - 2 pmol mol<sup>-1</sup> (e.g. Groszko, 1999, King *et al.*, 2000b). Since the literature values had to be estimated from figures, no exact numbers could be obtained. Therefore the median from the own atmospheric measurements was used to calculate the fluxes. To estimate the maximum resulting error in the flux calculations, the flux was calculated again with an atmospheric dry gas mole fraction of zero. The difference between both fluxes was less than 10 %. Since the real atmospheric dry gas mole fraction is not zero, but about 1 – 2 pmol mol<sup>-1</sup> (e.g. Bell *et al.*, 2002), the error is only about 5 – 7 %.

Only a few air samples have been measured during the Pos255 cruise in the North Atlantic and these values have been discarded due to analytical problems. The syringe used had only a volume of 30 mL and the resulting methyl iodide signals were too low for quantification. Thus the air concentration for the calculation of  $\Delta C$  had to be taken from the literature. Bassford *et al.* (1999) found a mean air concentration of 3.4 pmol mol<sup>-1</sup> at Mace Head, Ireland, but stated that this value is influenced by coastal algae beds. This is supported by

*Carpenter et al.* (2003) who gave a mean value of 3.8 pmol mol<sup>-1</sup> for the same location. *Groszko* (1999) measured concentrations from 0.8 to 4 pmol mol<sup>-1</sup> over the Atlantic between 30°N and 50°N with a mean of 1.7 pmol mol<sup>-1</sup> for his North Atlantic/Labrador Sea data. *Happell and Wallace* (1996) gave a mean value of 2.4 pmol mol<sup>-1</sup> for the Greenland and Norwegian Seas. *Lovelock et al.* (1973) gave a mean concentration of 1.2 pmol mol<sup>-1</sup> over the open Atlantic. Using these quite scattered literature values, a mean methyl iodide concentration in the air of 2 pmol mol<sup>-1</sup> was estimated, which was used to calculate the concentration anomaly during the Pos255 cruise.

## 3.2 Surface water samples

### 3.2.1 Henry's law constant

The use of an equilibrator for measuring water concentrations gives, as a direct result, the air concentration which is in equilibrium with the seawater at the seawater temperature. This equilibrium air concentration has to be converted to the corresponding seawater concentration. For a substance which is in equilibrium between gas phase and liquid phase Henry's law applies with

$$H = \frac{c_a}{c_w} \quad \text{or} \quad c_w = \frac{c_a}{H} \quad (4)$$

where  $c_a$  is the air concentration at equilibrium,  $c_w$  the water concentration at equilibrium and  $H$  is the Henry's law constant (dimensionless). Since the value of  $H$  is based on the solubility of a gas in the liquid and the solubility in seawater is a function of temperature and salinity, the value of  $H$  is a function of temperature and salinity as well. Different relationships for calculating  $H$  have been proposed in the literature (e.g. *Hunter-Smith et al.*, 1983, *Elliott and Rowland*, 1993, *Moore et al.*, 1995). In this work the relationship from *Moore et al.* (1995) is used, which was measured for seawater with an equilibrator (salinity 30.4), contrary to the relationship from *Hunter-Smith et al.* (1983), which was measured in distilled water. Following *Moore et al.* (1995) the value of  $H$  for methyl iodide was calculated in this thesis with

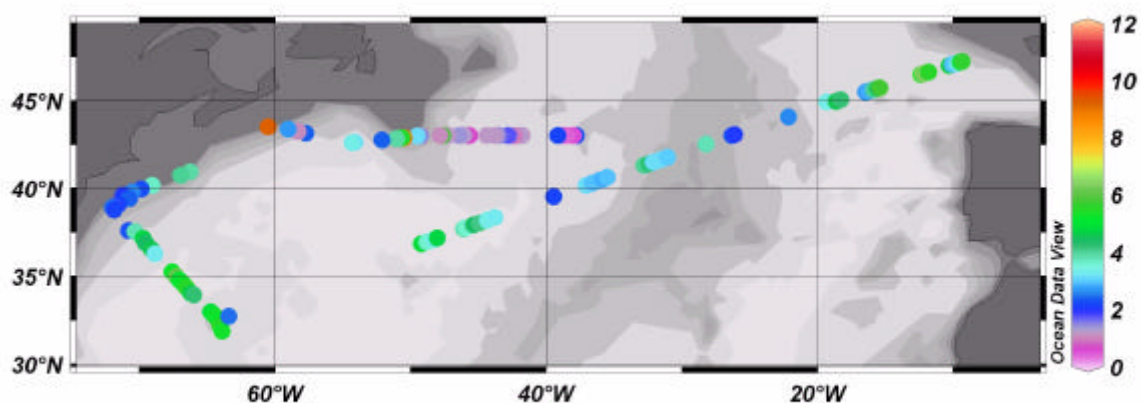
$$H = e^{\frac{13.32 - 4338}{T_K}} \quad (5)$$

where  $T_K$  is the absolute seawater temperature [K]. The effect of salinity was addressed by *Moore et al.* (1995) by measuring the Henry's law constant in seawater with two different salinities, 25.4 and 30.4. Their results showed no significant difference between the Henry's law constants measured at these two salinity's. The authors stated that therefore their relationship can be used for waters having salinity's in the range of 25 to 35 without further correction.

### 3.2.2 Surface water concentrations

The measured concentrations of methyl iodide in surface waters are shown in Figure 10 for the Pos255 cruise and in Figure 11 for the other cruises (M47, M55, So152). The concentrations are generally higher in the tropics ( $0.8 - 16.4 \text{ pmol L}^{-1}$ , mean  $5.8 \text{ pmol L}^{-1}$ ) than in the North Atlantic ( $0.4$  to  $9.2 \text{ pmol L}^{-1}$ , mean  $3.4 \text{ pmol L}^{-1}$ ).

In the North Atlantic the lowest values were found east of the Grand Banks of Newfoundland with  $< 2 \text{ pmol L}^{-1}$ . Higher methyl iodide concentrations of  $3 - 6 \text{ pmol L}^{-1}$  were found between the American coast and Bermuda. The highest value ( $9.2 \text{ pmol L}^{-1}$ ) was found just before entering the harbour of Halifax and may indicate coastal influence. On the other hand relatively low concentrations of  $2 - 4 \text{ pmol L}^{-1}$  were found during the northeast – southwest transect along the U.S. east coast. The data collected along the southwest – northeast transect from Bermuda to Brest is quite scattered from  $2.0$  to  $6.6 \text{ pmol L}^{-1}$  with no clear pattern.



**Figure 10:** Surface water methyl iodide concentrations [ $\text{pmol L}^{-1}$ ] from Pos255.

The data from the tropical Atlantic show some variability between different cruises and regions. The methyl iodide concentrations measured during M47 fall in the range between  $0.8$  and  $7.9 \text{ pmol L}^{-1}$  (mean  $4.6 \text{ pmol L}^{-1}$ ). The distribution was quite uniform along the cruise track. The So152 data were in the range from  $2.1$  to  $7.6 \text{ pmol L}^{-1}$  (mean  $5.0 \text{ pmol L}^{-1}$ ). The distribution is again relatively uniform with some concentrations from the higher end of the range at the western part of the cruise around  $60^\circ\text{W}$ , approaching the Caribbean islands. The data from the M47 and the So152 cruises are in the same concentration range. The data from the M55 cruise show two regions with different methyl iodide concentrations. The western part of the cruise between  $45^\circ\text{W}$  and about  $25^\circ\text{W}$  show slightly higher methyl iodide concentration than the M47 and So152 cruises, with values between  $2.0$  and  $9.6 \text{ pmol L}^{-1}$  (mean  $6.3 \text{ pmol L}^{-1}$ ). During the eastern part of the M55 cruise between about  $24^\circ\text{W}$  and  $0^\circ\text{W}$  very high methyl iodide concentrations between  $7.1$  and  $16.4 \text{ pmol L}^{-1}$  (mean

10.9 pmol L<sup>-1</sup>) were measured. This area included both coastal and oceanic regions, thus the high concentrations are not exclusively from coastal influence (algae beds etc.). A possible explanation for these higher methyl iodide concentrations is given in the discussion in chapter 3.4.

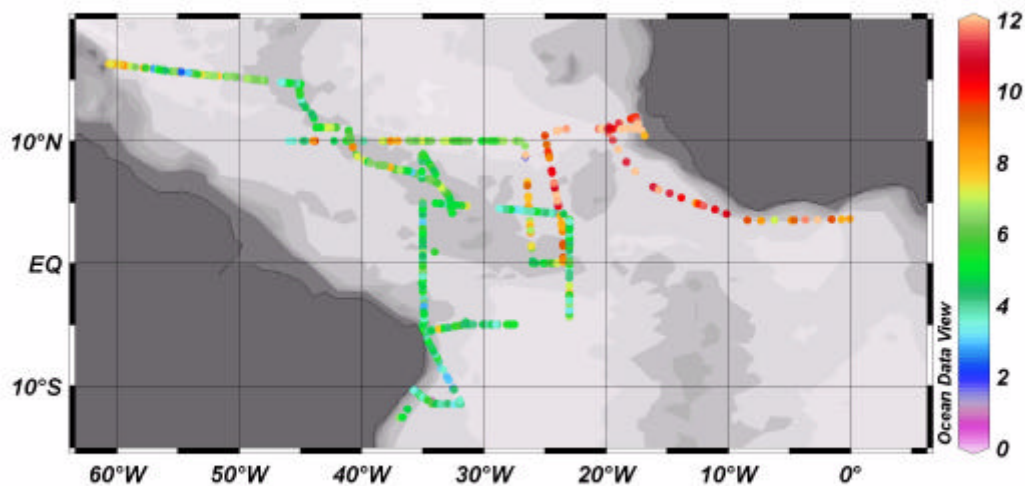


Figure 11: Surface water methyl iodide concentrations [pmol L<sup>-1</sup>] in the tropical Atlantic (from M47, M55, So152).

### 3.3 Flux calculations

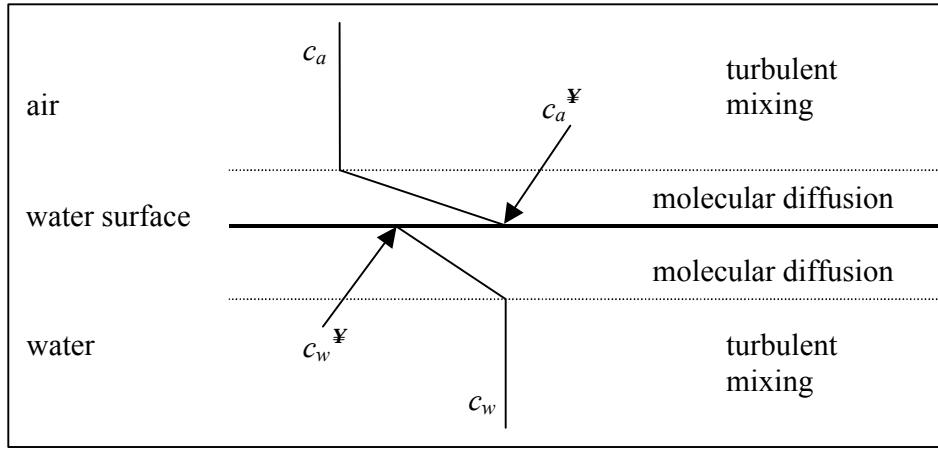
The air-sea flux of gases has received considerable interest in recent years due to its importance for biogeochemical cycling. Any net flux is driven by a concentration gradient  $\Delta C$  between air and sea water and is controlled by the so called “transfer” or “piston” velocity  $k$  (Liss, 1983, Wanninkhof, 1992, McGillis *et al.*, 2001). This transfer velocity is influenced by various factors, such as wind speed, friction velocity, wave type, bubble formation, temperature and surface films (e.g. Liss, 1983, Nightingale *et al.*, 2000a, Frew *et al.*, 2002, Tsai and Liu, 2003). The flux  $F$  [nmol m<sup>-2</sup> d<sup>-1</sup>] is then calculated with

$$F = k \cdot \Delta C \quad (6)$$

where  $k$  is the transfer velocity [m d<sup>-1</sup>] and  $\Delta C$  is the concentration anomaly [pmol L<sup>-1</sup>]. Different models have been introduced to describe the air-water gas transfer. These include the film model (Whitmann, 1923, Liss and Slater, 1974), the surface renewal model (Higbie, 1935, Danckwerts, 1951) and the boundary-layer model (Deacon, 1977).

The stagnant film model proposes two laminar layers adjacent to both sides of the interface with no mixing, where the transport is solely by molecular diffusion, and the two bulk phases

above and below the boundary layer, which are well mixed. Figure 12 shows the air-water interface with the two laminar layers.



**Figure 12:** The air-water interface in the film model (from *Liss and Slater, 1974*).

In the figure  $c_a$  is the bulk air concentration,  $c_a^{\infty}$  is the air concentration directly at the interface,  $c_w$  the bulk water concentration and  $c_w^{\infty}$  the water concentration directly at the interface. The values of  $c_a^{\infty}$  and  $c_w^{\infty}$  are assumed to be always at equilibrium and connected via the dimensionless Henry's law constant  $H$

$$H = \frac{c_a^{\infty}}{c_w^{\infty}} \quad \text{so that} \quad c_a^{\infty} = H \cdot c_w^{\infty} \quad (7)$$

The transfer velocity  $k$  can be viewed as a resistance towards flux with  $R = k^{-1}$ . From Figure 12 it is clear that the resistance  $R$  can be separated into two terms, one for the resistance in the airside laminar boundary layer  $R_a$  and one for the laminar boundary layer in the water  $R_w$  (*Liss and Merlivat, 1986*). Methyl iodide is a nonreactive gas with a low solubility and in this case the resistance by the water phase  $R_w$  dominates over  $R_a$ . Thus no significant error results when the gas phase resistance is ignored, so that  $R = R_w$ . The corresponding waterside transfer velocity  $k_w$  is taken as the total transfer velocity  $k$ .

When the gas phase resistance is close to zero ( $R_a \approx 0$ ), the concentration at the surface is the same than the bulk air concentration ( $c_a^{\infty} = c_a$ ). Using equation (7) it is possible to calculate the water concentration directly at the interface from the air concentration for the case that the water is at equilibrium with the air. With these values equation (6) converts to (*Whitman, 1923*)

$$F = k_w \cdot \Delta C \quad (8)$$

The fluxes calculated by (4) are net fluxes across the air-sea interface. The values for  $k_w$  [ $\text{m d}^{-1}$ ] and  $\Delta C$  [ $\text{pmol L}^{-1}$ ] used in this thesis will be explained in the subchapters 3.3.1 - 3.3.4.

### 3.3.1 Transfer velocity

The importance of the transfer velocity for flux calculation has led to several attempts to measure or estimate it. From all variables influencing the transfer velocity only the dependence on the wind speed is commonly used, because it is a major factor, it is easy to measure and most of the other factors (e.g. wave type, friction velocity or bubble formation) are also wind speed dependent. Several different wind speed dependencies of  $k_w$  have been proposed.

*Liss and Merlivat* (1986) used a linear relationship between wind speed and transfer velocity, with different factors for different wind speed ranges. Their parameterization was based mainly on results from wind tunnel experiments and on a data set from a deliberate tracer experiment in a lake (*Wanninkhof et al.*, 1985). A different linear relationship, with no flux at low wind speeds, was proposed by *Smethie et al.* (1985), based on radon deficit measurements in the Atlantic. *Tsai and Liu* (2003) used a linear relationship between wind speed and transfer velocity for surfactant covered surfaces.

The nonlinearity of the wind speed dependence at higher wind speeds led *Wanninkhof* (1992) to apply a quadratic relationship, which was normalized to global measurements of  $^{14}\text{CO}_2$  uptake and partially reconciled with global  $^{222}\text{Rn}$  data (*Yvon and Butler*, 1996). This relationship has been widely used for flux calculations (e.g. *Kuß*, 1994, *Quack*, 1994, *Pilson*, 1998, *Moore and Groszko*, 1999) and is hereafter referred to as W92. Other slightly different quadratic relationships have been proposed (*Nightingale et al.*, 2000b, *Frost and Upstill-Goddard*, 2002).

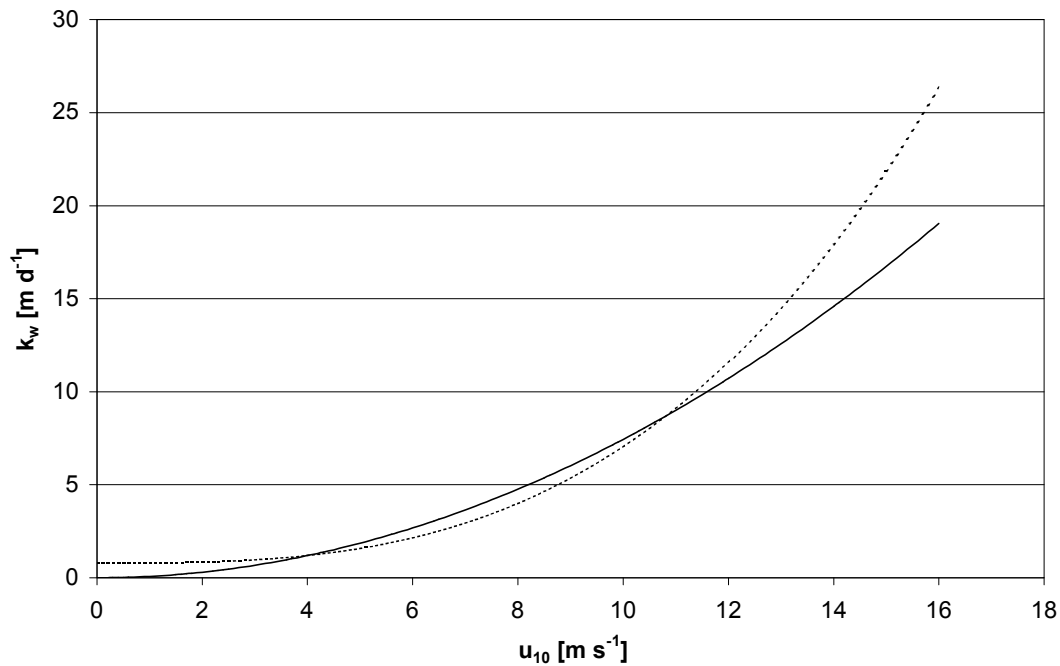
Recently, direct covariance  $\text{CO}_2$  flux measurements suggested a cubic relationship between transfer velocity and wind speed (*Wanninkhof and McGillis*, 1999, *McGillis et al.*, 2001). The relationship of *McGillis et al.* (2001) has an additional term which causes a flux even at zero wind speed (hereafter referred to as McG01).

To estimate the difference between the W92 and the McG01 relationship, the resulting transfer velocities are plotted against wind speed (Figure 13). For wind speeds below  $4 \text{ m s}^{-1}$  the McG01 relationship gives higher transfer velocities than the W92 relationship. At wind speeds between 4 and  $11 \text{ m s}^{-1}$  the calculated transfer velocity is higher with the W92 relationship, whereas the McG01 relationship gives higher transfer velocities at wind speeds above  $11 \text{ m s}^{-1}$ .

In this thesis both the W92 and the McG01 relationships have been used. The W92 formula for the wind speed dependence of  $k_w$  with wind speeds from single anemometer measurements is

$$k_{w,660}^{W92} = 0.31 \cdot u_{10}^2 \quad (9)$$

with the wind speed  $u_{10}$  given in  $\text{m s}^{-1}$  and corrected to a height of 10 m above sea level. It yields  $k_w$  in  $\text{cm h}^{-1}$  and for a Schmidt number of 660, which corresponds for  $\text{CO}_2$  at  $20^\circ\text{C}$  in



**Figure 13: The wind speed dependence of the transfer velocity from the W92 relationship (solid line) and the McG01 relationship (dotted line).**

seawater (*Wanninkhof, 1992*). This value has to be converted to the units used in the flux calculations in this thesis ( $\text{m d}^{-1}$ ). The conversion to the appropriate Schmidt number for methyl iodide, and the measured seawater temperature, will be explained in the next section.

The formula for the McG01 relationship for a gas with a Schmidt number of 660 is

$$k_{w,660}^{McG01} = 3.3 + 0.026 \cdot u_{10}^3 \quad (10)$$

The transfer velocity from (10) is again given in  $\text{cm h}^{-1}$  and has to be converted to  $\text{m d}^{-1}$  and for methyl iodide. The dependency of the transfer velocity on wind speed is illustrated in Figure 13. As mentioned before the picture shows clearly the similarity between the two relationships for wind speeds between 2 and 11  $\text{m s}^{-1}$ .

The measured transfer velocities will be shown in chapter 3.3.5.

### 3.3.2 Schmidt number

The Schmidt number is the ratio of the kinematic viscosity of seawater to the molecular diffusivity of the gas in seawater ( $Sc = \nu D^{-1}$ ). The kinematic viscosity is the dynamic viscosity divided by the density. The  $k_{w, 660}$  values calculated with the above relationships are valid for a Schmidt number of 660 (which is the Schmidt number of CO<sub>2</sub> in seawater at 20°C). For other gases and other temperatures, the appropriate Schmidt number must be calculated and the value of  $k_w$  corrected with

$$k_w = k_{w,660} \cdot \left( \frac{Sc}{660} \right)^{-\frac{1}{2}} \quad (11)$$

where  $k_w$  is the transfer velocity and  $Sc$  is the Schmidt number for the specific gas in question at the temperature of measurement (*Wanninkhof, 1992, McGillis et al., 2001*). The exponent of 0.5 in the Schmidt number conversion seems to be valid for most common conditions (e.g. *Pilson, 1998*), but other values up to 0.67 have been proposed for very low wind speeds (e.g. *Holmén and Liss, 1984, Clark et al., 1995, Crusius and Wanninkhof, 2003*). In this thesis the value of 0.5 is used which gives for equation (9) and (10):

$$k_w^{W92} = 0.31 \cdot u_{10}^2 \cdot \left( \frac{Sc}{660} \right)^{-\frac{1}{2}} \quad (12)$$

$$k_w^{McG01} = (3.3 + 0.026 \cdot u_{10}^3) \cdot \left( \frac{Sc}{660} \right)^{-\frac{1}{2}} \quad (13)$$

For the calculation of the Schmidt number for methyl iodide the diffusivity of methyl iodide is needed, since the Schmidt number is the ratio of the kinematic viscosity of seawater to the molecular diffusivity of the specific gas in question in seawater. It seems that the diffusivity of methyl iodide in seawater has not yet been measured. The only methyl halide diffusivity measured is that for methyl bromide (*De Bruyn and Saltzman, 1997b*). They gave a Schmidt number dependency from temperature of

$$Sc = 2004 - 93.5 \cdot T + 1.39 \cdot T^2 \quad (14)$$

where  $T$  is the temperature in °C in the range from 5 – 30°C. From this number the Schmidt number for methyl iodide will be estimated following the relationship of *Wilke and Chang (1955)*, as cited by *Groszko (1999)*. In the *Wilke and Chang (1955)* relationship the diffusion coefficient is dependent on the inverse molar volume at the normal boiling point raised to the power of 0.6 as follows

$$D_c = \frac{7.4 \cdot 10^{-8} \cdot (q \cdot M_w)^{0.5} \cdot T_K}{h_w \cdot V_b^{0.6}} \quad (15)$$

where  $D_c$  is the diffusion coefficient [ $\text{cm}^2 \text{s}^{-1}$ ],  $q$  is the association factor of water,  $M_w$  is the molecular weight of water [g],  $T_K$  is the absolute temperature [K],  $h_w$  is the dynamic



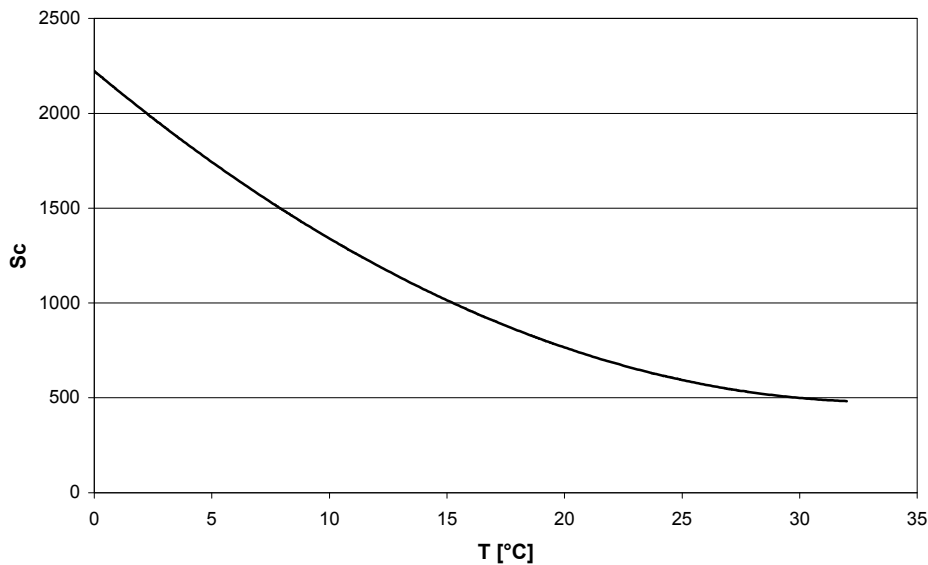
viscosity of pure water and  $V_b$  is the molar volume of the substance at its normal boiling temperature. The ratio of diffusion coefficients from methyl bromide and methyl iodide can thus be calculated from the inverse ratio of their molar volumes at the normal boiling point  $V_b$  to the power of 0.6.

$$\frac{D_c(CH_3I)}{D_c(CH_3Br)} = \left( \frac{V_b(CH_3Br)}{V_b(CH_3I)} \right)^{0.6} \quad (16)$$

Because the Schmidt number is inversely proportional to the diffusion coefficient, the Schmidt number of methyl iodide can be calculated from that of methyl bromide. The molar volumes have been estimated with the additive method of *Le Bas* as cited in *Reid et al.* (1987) to be  $52.9 \text{ cm}^3 \text{ mol}^{-1}$  for methyl bromide and  $62.9 \text{ cm}^3 \text{ mol}^{-1}$  for methyl iodide. This gives following equation for the Schmidt number of methyl iodide

$$Sc_{CH_3I} = \left( \frac{62.9}{52.9} \right)^{0.6} \cdot (2004 - 93.5 \cdot T + 1.39 \cdot T^2) \quad (17)$$

where  $T$  is the water temperature in  $^{\circ}\text{C}$ . Figure 14 shows the temperature dependence of the Schmidt number for methyl iodide in seawater.



**Figure 14: Schmidt number  $Sc$  for methyl iodide in seawater as a function of temperature.**

### 3.3.3 Wind speed corrections

The wind speed close to a surface is influenced by the surface and hence the measured wind speed is dependent on the height of measurement above the surface. The wind speeds used for this thesis are instantaneous wind speeds from the ships anemometers. Since the anemometers on different research vessels are at different heights above the sea surface, the measured wind speed has to be corrected to a common reference height of 10 metres. For the calculation a logarithmic wind profile is used (e.g. *Donelan*, 1990, *Roedel*, 1992, *Oost*, 1998).

$$u_z = \frac{u_*}{k} \cdot \ln\left(\frac{z}{z_0}\right) \quad (18)$$

where  $u_z$  is the wind speed at the height  $z$ ,  $u_*$  is the friction velocity,  $k$  is the Kármán constant ( $= 0.41$ ) and  $z_0$  is the roughness length. The friction velocity  $u_*$  cannot be measured directly and is calculated using the drag coefficient  $C_D$  with

$$C_D = \left(\frac{u_*}{u_{10}}\right)^2 \quad (19)$$

where  $u_{10}$  is the wind speed at 10 metres height. The drag coefficient has to be measured for a variety of meteorological conditions and different calculations for  $C_D$  have been proposed (e.g. *Garratt*, 1977, *Large and Pond*, 1981, *Large and Pond*, 1982, *Erickson*, 1993). The different calculations gave similar 10 metre wind speeds with a difference of only  $0.1 \text{ m s}^{-1}$  for the wind speeds encountered during my cruises. In this thesis the unitless neutral drag coefficient of *Garratt* (1977) is used with

$$C_D = 0.75 \cdot 10^{-3} + 0.067 \cdot 10^{-3} \cdot u_{10} \quad (20)$$

where  $u_{10}$  is the wind speed in 10 m height. Combining equation (18), (19) and (20) yields the following formula for the calculation of the wind speed at a height of 10 metres from a measured wind speed  $u_x$  at the height  $z_x$

$$u_{10} = \frac{u_x \cdot \frac{k}{\sqrt{C_D}}}{\frac{k}{\sqrt{C_D}} + \ln \frac{z_x}{10}} \quad (21)$$

The drag coefficient  $C_D$  in equation (21) is calculated with equation (20). Since the wind speed  $u_{10}$  appears in both equations this requires an iterative procedure.

### 3.3.4 Concentration anomaly

The concentration anomaly  $\Delta C$  for this thesis was calculated according to *Groszko* (1999) who made similar equilibrator measurements. The formula is

$$\Delta C = H' \cdot (c_w - c_a) \cdot (p - p_{H_2O}) \quad (22)$$

where  $c_w$  is the dry gas mole fraction of an equilibrator sample and  $c_a$  is the dry gas mole fraction of the corresponding air sample (both in  $\text{pmol mol}^{-1}$ ),  $p$  is the atmospheric pressure [atm],  $p_{H_2O}$  is the water vapour pressure [atm] at the sea surface temperature and salinity and  $H'$  is the solubility of methyl iodide in seawater [ $\text{pmol L}^{-1} \text{atm}^{-1}$ ]. In this calculation it is assumed that the ideal gas law holds and that air directly above the sea surface has a relative humidity of 100%. The use of the ideal gas law for nonreactive gases at concentration levels found for methyl iodide in the  $\text{pmol mol}^{-1}$  range causes insignificant error.

The solubility  $H'$  is calculated from the dimensionless Henry's law constant  $H$  at the absolute temperature of the water during measurement (equation (5) in chapter 3.2) by applying the ideal gas law which gives

$$H' = \frac{12.188}{T_K \cdot H} = \frac{12.188}{T_K \cdot e^{\frac{13.32 - 4338}{T_K}}} \quad (23)$$

where  $T_K$  is again the absolute water temperature [K]. By inserting this calculation of  $H'$  in equation (22) the concentration anomaly is calculated by the following formula:

$$\Delta C = \frac{12.188}{T_K \cdot e^{\frac{13.32 - 4338}{T_K}}} \cdot (c_w - c_a) \cdot (p - p_{H_2O}) \quad (24)$$

where  $T_K$  is the absolute water temperature [K],  $c_w$  and  $c_a$  are the dry gas mole fractions [ $\text{pmol mol}^{-1}$ ] of an equilibrator sample and the corresponding air sample, respectively,  $p$  is the atmospheric pressure [atm] and  $p_{H_2O}$  is the water vapour pressure [atm] at  $T_K$ .

The measured concentration anomalies  $\Delta C$  are shown in the next section.

### 3.3.5 Methyl iodide flux calculations

The flux of a compound across the air-sea interface is given by equation (6) with

$$F = k \cdot \Delta C \quad (6)$$

In the following the data used for the flux calculations are first presented and finally the calculated fluxes.

The estimated transfer velocities  $k$  for methyl iodide (calculated with W92) are shown in Figure 15 and Figure 16. Moderate to strong winds and hence high transfer velocities up to  $20 \text{ m d}^{-1}$  were encountered during the Pos255 cruise in the North Atlantic. The data are scattered without a clear trend. During the cruises in the tropical Atlantic low to moderate wind speeds led to transfer velocities between  $0.03 \text{ m d}^{-1}$  and up to  $55 \text{ m d}^{-1}$ , with most values falling in the range between  $2 - 12 \text{ m d}^{-1}$ . In the eastern part of the tropical Atlantic the wind speed was very low with extended regions with values of less than  $1 \text{ m s}^{-1}$ , thus leading to transfer velocities below  $3 \text{ m d}^{-1}$ .

The piston velocities calculated with the W92 formula (9), using the measured wind speeds, are in general higher than those calculated with the McG01 formula (10).

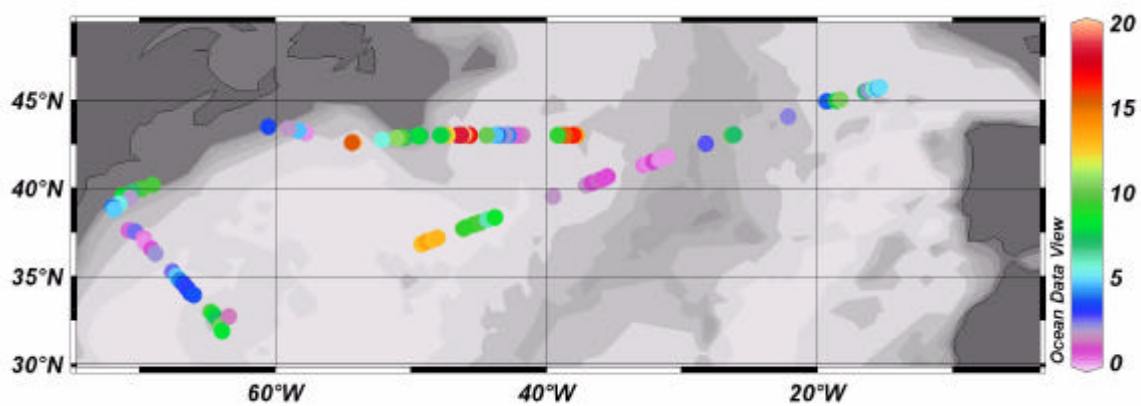


Figure 15: Transfer velocities [ $\text{m d}^{-1}$ ] for methyl iodide in the North Atlantic during Pos255.

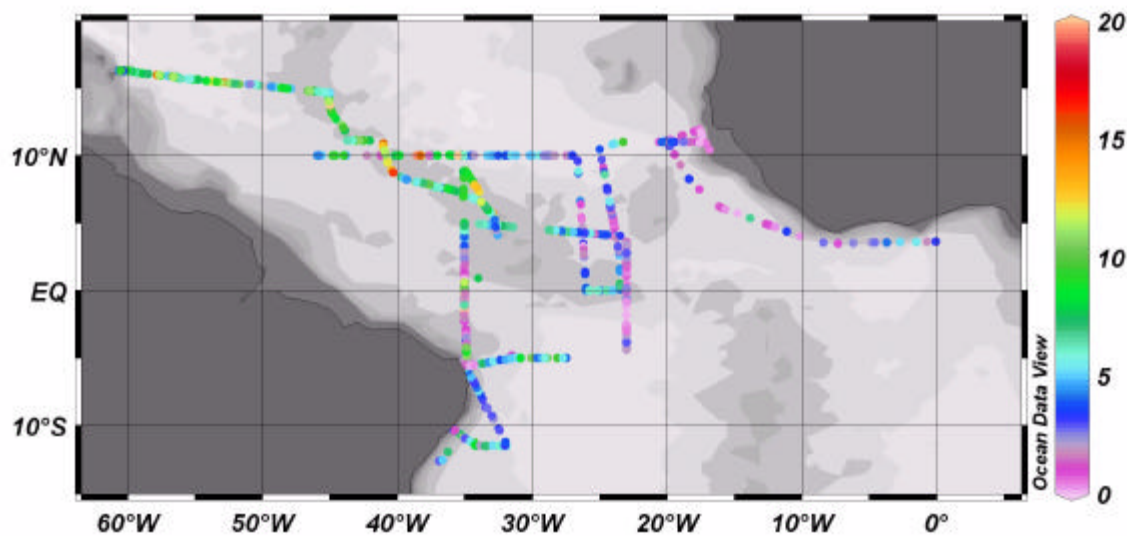


Figure 16: Transfer velocities [ $\text{m d}^{-1}$ ] for methyl iodide in the tropical Atlantic.

The concentration anomalies from the different cruises are shown in Figure 17 and Figure 18. The North Atlantic data show values from 0 - 5 pmol L<sup>-1</sup>, with one higher concentration anomaly of 7.7 pmol L<sup>-1</sup>. In the tropical Atlantic values in the range of 2 - 7 pmol L<sup>-1</sup> have been measured, but during M55 high concentrations anomalies of 6 - 14 pmol L<sup>-1</sup> were found east of about 20°W in a region with very low wind speeds and transfer velocities (Figure 16). The concentration anomaly was slightly lower during M47 in March and April with 2 - 5 pmol L<sup>-1</sup> than during the So152 cruise in December in the same region with 4 - 7 pmol L<sup>-1</sup>.

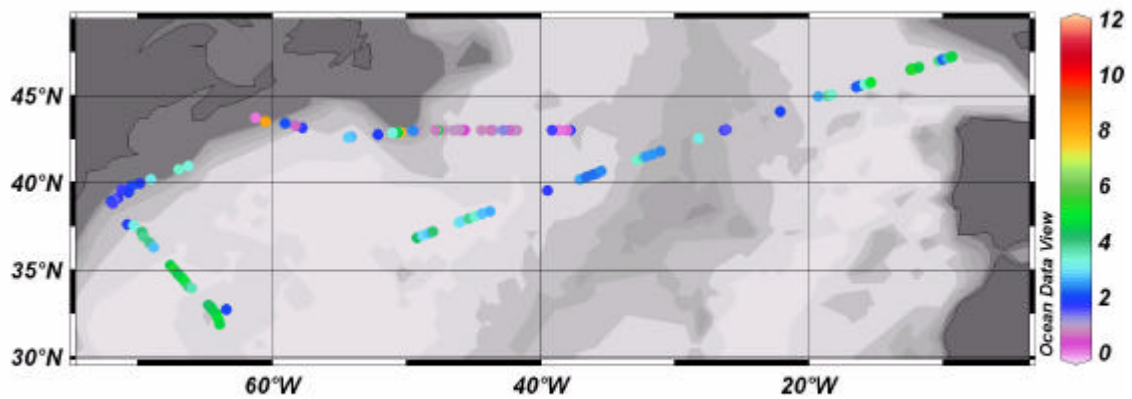


Figure 17: Concentration anomalies DC [pmol L<sup>-1</sup>] in the North Atlantic.

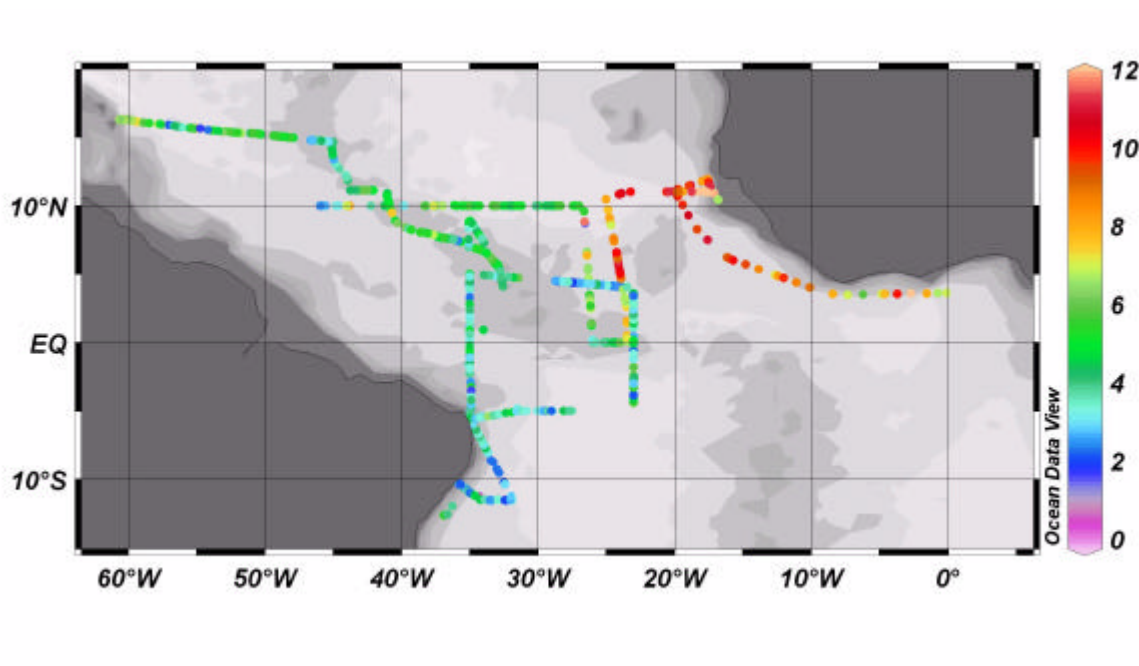


Figure 18: Concentration anomalies DC [pmol L<sup>-1</sup>] in the tropical Atlantic.

The variability in the concentration anomaly is caused by the variability of methyl iodide concentration of the surface seawater, because the average (Pos255) or the median (M47, So152, M55) of the atmospheric dry gas mole fractions were used in the calculation of concentration anomalies (equation 24).

The flux is calculated with equation (6) for every single methyl iodide measurement, with the mean air concentration from the cruise and the measured wind speed corrected to 10 m height. The results are shown in Figure 19 for the Pos255 cruise data and in Figure 20 for the tropical Atlantic data (the scale in the figures was limited to an upper value of  $80 \text{ nmol m}^{-2} \text{ d}^{-1}$ , despite three higher values, to achieve a more detailed colour coding for the range of most calculated fluxes of  $0 - 50 \text{ nmol m}^{-2} \text{ d}^{-1}$ ). The flux is calculated using the W92 relationship for the calculation of the transfer coefficient  $k$  (equation (9)). A second calculation of the fluxes was done, using the McG01 relationship for calculating  $k$  (equation (10), results not shown). These second calculation gave results with a similar pattern, but overall with slightly lower fluxes, compared with the fluxes calculated using the W92 relationship. The calculated fluxes are similar in the tropical and the North Atlantic during Pos255, M47 and M55, but about  $10 - 20 \text{ nmol m}^{-2} \text{ d}^{-1}$  higher during So152. The lowest, highest and mean flux for each cruise is shown in Table 4. The fluxes calculated with the McG01 relationship show lower mean fluxes for every cruise compared with the fluxes calculated with the W92 relationship, but the lower limits are generally higher and the upper limits are higher in two cases (Pos255 and So 152). This reflects the wind speed dependence of the transfer velocity as shown in Figure 13 and discussed in section 3.3.1.

**Table 4: Overview of the flux calculation results.**

<b>Cruise</b>	<b>calculated with</b>	<b>lowest value</b> [nmol m <sup>-2</sup> d <sup>-1</sup> ]	<b>highest value</b> [nmol m <sup>-2</sup> d <sup>-1</sup> ]	<b>mean (s<sub>d</sub>)</b> [nmol m <sup>-2</sup> d <sup>-1</sup> ]
<b>Pos255</b>	W92 (9)	0.1	59.1	16.4 (15.6)
	McG01 (10)	0.5	62.5	12.7 (12.6)
<b>M47</b>	W92 (9)	0.0	52.0	13.3 (10.8)
	McG01 (10)	2.8	40.3	9.5 (7.2)
<b>So152</b>	W92 (9)	5.2	109.9	33.2 (15.0)
	McG01 (10)	5.0	119.6	24.4 (14.0)
<b>M55</b>	W92 (9)	0.3	93.5	22.7 (17.7)
	McG01 (10)	3.4	81.0	16.7 (11.5)

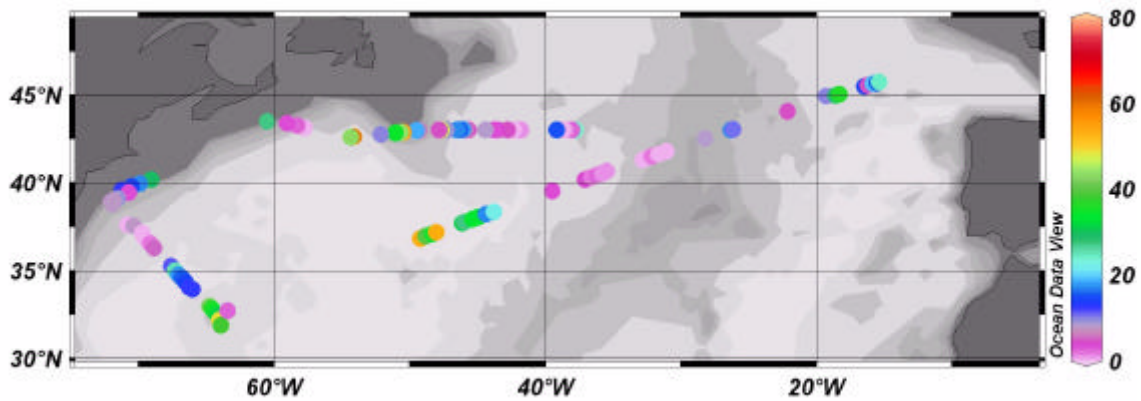


Figure 19: Calculated fluxes in the North Atlantic [ $\text{nmol m}^{-2} \text{d}^{-1}$ ].

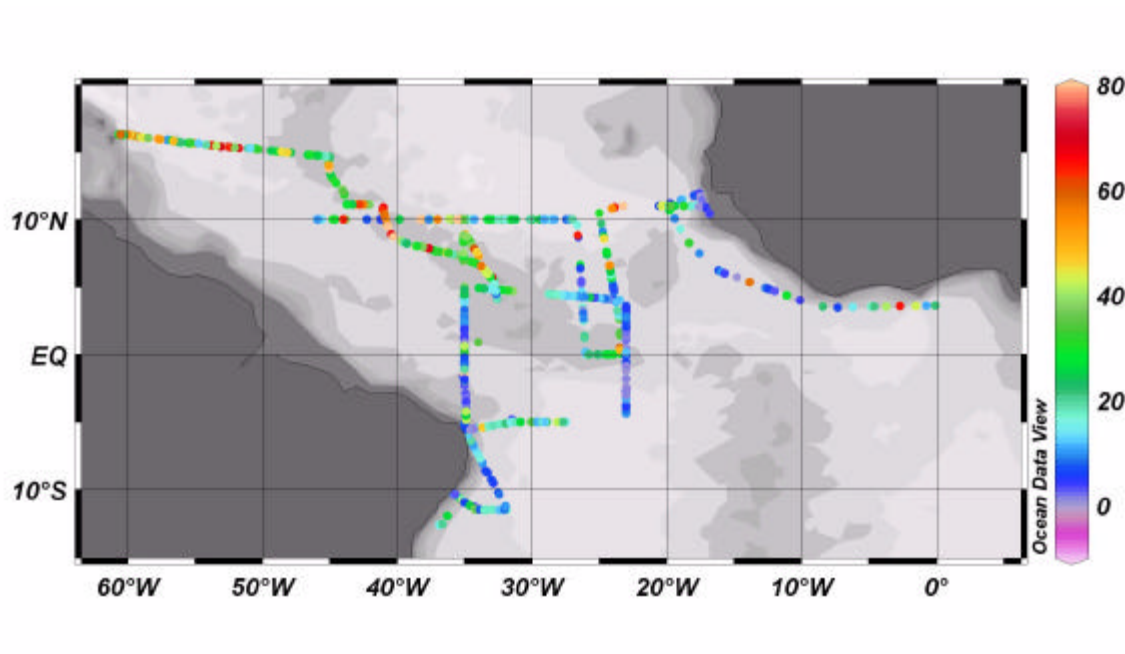


Figure 20: Calculated fluxes in the tropical Atlantic [ $\text{nmol m}^{-2} \text{d}^{-1}$ ].

The values of the calculated fluxes are quite scattered without a clear trend. The variability was not caused by the variance of the concentration anomalies, which is very obvious for the flux data from the eastern part of the M55 cruise. Very high concentration anomalies were measured in the eastern part of M55 (see Figure 18), but the calculated flux was not elevated with respect to the other cruises (see Figure 20 and Table 4), because in this region also low wind speeds were encountered. The highest overall fluxes were calculated from the So152 data. During this cruise a concentration anomaly that was close to the average from all cruises was encountered, together with higher transfer velocities than measured during the other cruises, resulting in higher fluxes. These points will be discussed further in the next section.

### 3.4 Discussion of the underway data

The measured mean surface water methyl iodide concentrations of  $6.7 \pm 2.7 \text{ pmol L}^{-1}$  (range 0.8 - 14.7  $\text{pmol L}^{-1}$ ) from all tropical Atlantic data and of  $3.4 \pm 1.7 \text{ pmol L}^{-1}$  (range 0.4 - 9.2  $\text{pmol L}^{-1}$ ) for the North Atlantic are within the range of concentrations reported in the literature of 1.8 - 11.3  $\text{pmol L}^{-1}$  for open ocean measurements and 1 - 24  $\text{pmol L}^{-1}$  for coastal sites and estuaries (see Table 5).

**Table 5: Methyl iodide concentrations in surface seawater from the literature (in  $\text{pmol L}^{-1}$ ).**

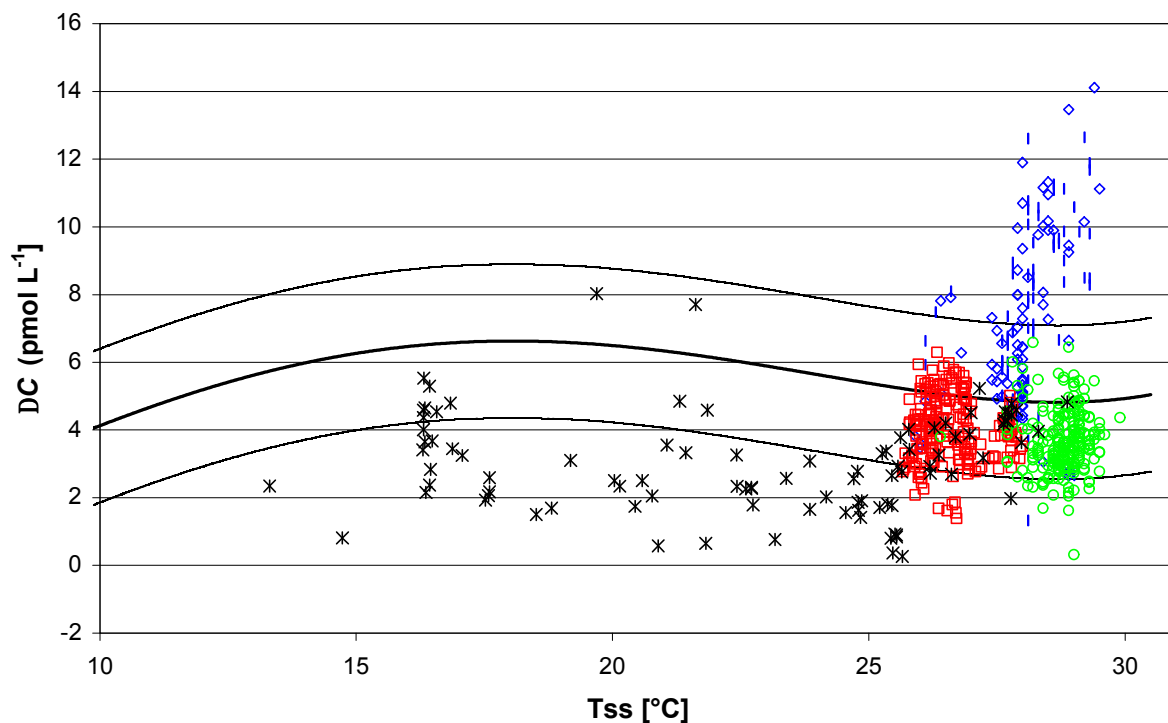
Mean ( $s_d$ )	Range	Area	Source
5.6	50 - 141	Atlantic Ocean coast in Ireland and Dorset	<i>Lovelock, (1975)</i>
11.3 (9.9)	0.4 - 6.8	eastern Pacific	<i>Singh et al. (1983)</i>
	0.37 - 1.4	Californian coast	<i>Manley et al. (1992)</i>
18.3 (14.8)	1.4 - 52.8	Antarctic Peninsula	<i>Reifenhäuser and Heumann (1992)</i>
4.2 (2.1)	1.5 - 8.2	Atlantic	<i>Tanzer and Heumann (1992)</i>
3.5 (2.8)	<0.07 - 34.0	Spitzbergen	<i>Schall and Heumann (1993)</i>
8.2 (0.6)	6.1 - 12.3	southern tropical Atlantic	<i>Happell and Wallace (1996)</i>
1.8 (0.1)	1.0 - 2.9	western tropical Atlantic	
2.8	<0.07 - 9.7	Atlantic	<i>Schall et al. (1997)</i>
	2 - 6	Pacific	<i>Moore and Groszko (1999)</i>
	0.8 - 7	northwest Atlantic	
15.07 (4.15) 9.72 (1.90)		“coastal” sites at Mace Head “offshore” sites at Mace Head	<i>Carpenter et al. (2000)</i>
1.3 – 24.0*	1 - 100	European estuaries	<i>Tessier et al. (2002)</i>
3.4 (1.7)	0.4 - 9.2	North Atlantic (Pos255)	this work
4.6 (1.0)	0.8 - 7.9	western tropical Atlantic (M47)	
5.0 (1.1)	2.1 - 7.6	western tropical Atlantic (So152)	
8.7 (2.9)	3.4 - 14.7	tropical Atlantic (M55)	

\* mean values from different estuaries.



Mean surface water concentrations of  $4.6 (\pm 1.0) \text{ pmol L}^{-1}$ ,  $6.2 (\pm 1.4) \text{ pmol L}^{-1}$  and  $5.5 (\pm 1.6) \text{ pmol L}^{-1}$  were measured during M47, So152 and the western part of M55, respectively, which are all in the same region but at different times of the year. These concentration are not different from each other within the given uncertainties. Thus no seasonal pattern can be deduced from the data. But the cruises fell all in spring (March and April) and autumn (October, November and December) which makes it impossible to see a seasonal cycle with high and low values during summer and winter. More extended data sets are needed to estimate if there is a seasonal cycle in the methyl iodide concentration in the tropical open ocean. A diurnal cycle, which might be present, has changes in concentrations that are too low to be seen in the scatter of the data. It seems that other influences dominate the variability of the methyl iodide distribution.

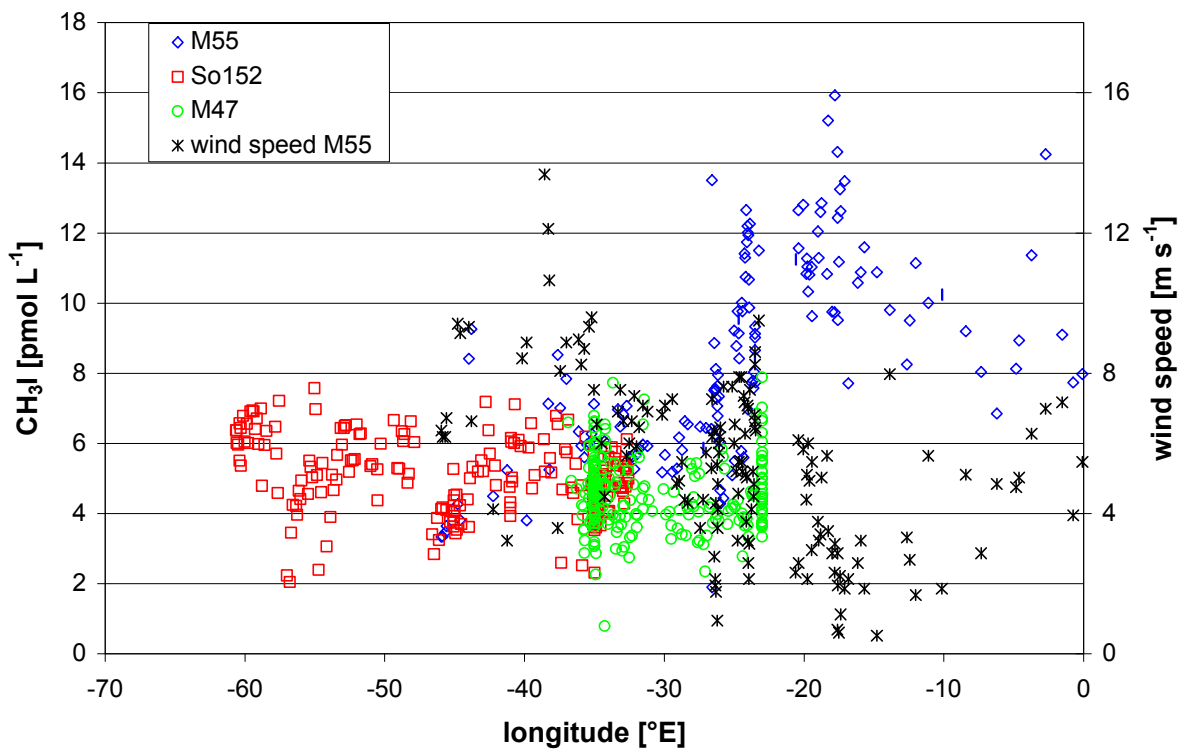
*Happell and Wallace (1996)* reported saturation anomalies of  $7.7 \text{ pmol L}^{-1}$  in the southern tropical Atlantic and  $1.5 \text{ pmol L}^{-1}$  in the northwest tropical Atlantic. *Groszko (1999)* found concentration anomalies between about  $0 - 11 \text{ pmol L}^{-1}$  in the Pacific, the North Atlantic and the Labrador Sea. The mean concentration anomalies from this work of  $2.8 \pm 1.6 \text{ pmol L}^{-1}$  (Pos255),  $3.1 \pm 0.9 \text{ pmol L}^{-1}$  (M47),  $5.4 \pm 1.3 \text{ pmol L}^{-1}$  (So152) and  $7.3 \pm 2.6 \text{ pmol L}^{-1}$  (M55) are consistent with these literature data. *Groszko (1999)* gave an empirical best fit function for the relationship between the concentration anomaly and sea surface temperature. Figure 21 shows the concentration anomalies from this thesis together



**Figure 21:** Concentration anomalies DC as a function of sea surface temperature Tss. Pos255 (black crosses), M47 (green open circles), So152 (red open squares) and M55 (blue open diamonds) together with the empirical curve from Groszko (1999) with upper and lower limits (black lines).

with the best fit curve from *Groszko* (1999). Most concentration anomalies from M47, So152 and partly from M55 fall within the indicated error lines of the best fit curve. The concentration anomalies from Pos255 are below and some of the M55 concentration anomalies are above the curve. The higher concentration anomalies from the M55 cruise are all from the eastern part of the cruise and will be discussed later.

The higher mean surface water concentration of methyl iodide of  $8.7 \text{ pmol L}^{-1}$  from the M55 cruise is caused by the high methyl iodide concentrations measured in the eastern part of the Atlantic. This is illustrated in Figure 22 where the methyl iodide concentration in the tropical Atlantic and the wind speed measured during M55 are plotted against longitude. During the M55 cruise the methyl iodide concentrations east of  $23^\circ\text{W}$  are seen to be elevated with respect to the other tropical Atlantic data. The separation of the data set from M55 in a western and eastern part yields mean methyl iodide concentrations of  $5.5 (\pm 1.6) \text{ pmol L}^{-1}$  and  $10.8 (\pm 2.0) \text{ pmol L}^{-1}$ , respectively. The latter is higher than previously reported concentrations for the open ocean. A coastal influence can be excluded because the region where these high values have been encountered extends from the African coast to the Mid-Atlantic ridge. The most likely explanation for the elevated concentrations is the lower wind speed (mean  $4.5 \pm 2.1 \text{ m s}^{-1}$ ) encountered in this region during the M55 cruise. On a long term basis the sources and sinks for methyl iodide must be at steady state and the flux is one of the most important sinks for oceanic methyl iodide. A lower wind speeds leads



**Figure 22: Methyl iodide concentrations from in the tropical Atlantic as function of longitude, together with the wind speed from M55.**

initially to a lower flux. Since the other sinks and the sources are not dependent on the wind speed, the concentration anomaly will increase until the flux and the other sinks are again in steady state with the sources. Thus a decrease in wind speed leads to an increase in the surface water concentration of methyl iodide. To illustrate the correlation between wind speed and methyl iodide surface water concentration during M55, the wind speed measured during M55 is added in Figure 22.

To test the possible influence of wind speed on the concentration anomaly of methyl iodide, a simple model was developed (Model A). For the model a steady state between net production  $P_a$  (given per unit area) and flux to the atmosphere  $F$  is assumed (Net production means production in the surface water minus all sinks of methyl iodide in the surface water, except the flux to the atmosphere). With these assumptions, and using the flux definition from equation (6), the net production per area  $P_a$  and the concentration anomaly  $\Delta C$  are connected via

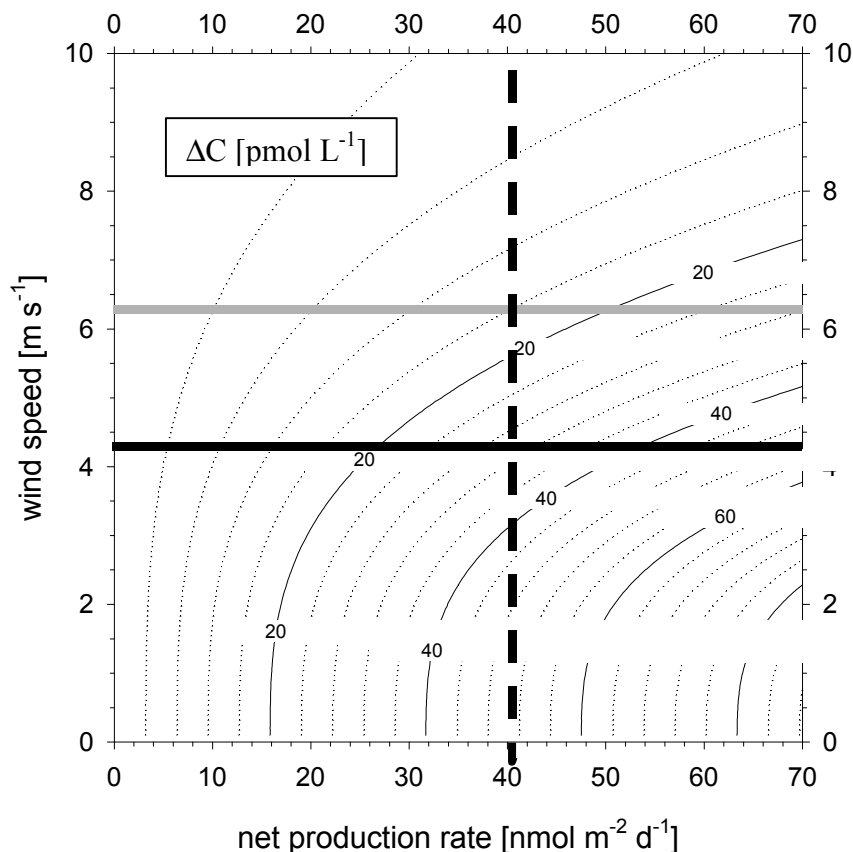
$$P_a = F = k \cdot \Delta C \quad (25)$$

The McG01 relationship for the calculation of the transfer velocity  $k$  is used, giving following equation for the dependency of  $\Delta C$  [pmol L<sup>-1</sup>] on the wind speed  $u_{10}$  in 10 m height

$$\Delta C = \frac{100 \cdot P_a}{24 \cdot (3.3 + 0.026 \cdot u_{10}^3) \cdot \left(\frac{530}{660}\right)^{\frac{1}{2}}} \quad (26)$$

where 530 is the mean Schmidt number from the M55 cruise and 660 is the Schmidt number for CO<sub>2</sub> at 20°C. The factors 24 and 100 are from the unit conversion of  $k$  (from [cm h<sup>-1</sup>] to [m d<sup>-1</sup>]). The concentration anomaly was calculated with equation (26) for different wind speeds  $u_{10}$  and different net production rates per area. The resulting concentration anomalies are shown as a contour plot in Figure 23. From incubation experiments, which will be described in chapter 4, a net production rate of 0.12 nmol m<sup>-3</sup> h<sup>-1</sup> was calculated and a rough estimate of the depth of 14 m, over which production occurs, was done. This gives a net production per area of 40.32 nmol m<sup>-2</sup> d<sup>-1</sup>. The mean wind speed measured during M55 was 6.6 (± 2.8) m s<sup>-1</sup> in the western part (indicated by a grey line in Figure 23) and 4.5 (± 2.1) m s<sup>-1</sup> in the eastern part of the cruise (indicated by a black line in Figure 23). Calculating the resulting concentration anomaly with the mean wind speeds and the net production of 40.32 nmol m<sup>-2</sup> d<sup>-1</sup> (indicated by a black broken line in Figure 23), gives a  $\Delta C$  of 14 pmol L<sup>-1</sup> for the western and a  $\Delta C$  of 28 pmol L<sup>-1</sup> for the eastern part of the M55 cruise. The McG01 relationship was used in the model instead of the W92 relationship, because the latter yields extremely high concentration anomalies exceeding 1000 pmol L<sup>-1</sup> at wind speeds below 1 m s<sup>-1</sup>. This is because in the W92 model the flux approaches zero when the wind speed approaches zero, as discussed before. Calculating the concentration anomalies again, but using the W92 relationship instead of the McG01 relationship, gives  $\Delta C$  values of

11 pmol L<sup>-1</sup> and 24 pmol L<sup>-1</sup> for the western and eastern part of M55, respectively (using the same mean wind speeds of 6.6 m s<sup>-1</sup> and 4.5 m s<sup>-1</sup>, together with the net production per area of 40.32 nmol m<sup>-2</sup> d<sup>-1</sup>). Thus both relationships give similar results for these wind speeds.



**Figure 23:** Contour plot of concentration anomaly  $\Delta C$  [pmol L<sup>-1</sup>] as function of production rate and wind speed [m s<sup>-1</sup>] (results from model A, assuming steady state and flux equals net production, as explained in the text), with mean wind speed from M55 (grey line: western part; black line: eastern part) and the mean net production from the incubation experiments (black broken line).

The mean concentration anomalies measured during M55 were 5.2 ( $\pm$  1.5) pmol L<sup>-1</sup> (western part) and 9.2 ( $\pm$  1.7) pmol L<sup>-1</sup> (eastern part). Comparing these measured concentration anomalies with the ones calculated with model A (14 pmol L<sup>-1</sup> and 28 pmol L<sup>-1</sup>, McG01, or 11 pmol L<sup>-1</sup> and 24 pmol L<sup>-1</sup>, W92) shows clearly, that the observed increase in the concentration anomalies can be caused by the decrease in the wind speed. Since the concentration anomaly was calculated with the median of the measured atmospheric dry gas mole fractions of methyl iodide, any change in  $\Delta C$  represents a change in the surface water concentration of methyl iodide. Thus the surface water concentration of methyl can be strongly influenced by the wind speed.

If the concentration anomaly is influenced by the wind speed, the concentration anomalies from the Pos255 cruise, which are lower than the  $\Delta C$  – sea surface temperature relationship proposed by *Groszko* (1999), might also be explained by this mechanism, or by a different production rate compared to the tropics. During the Pos255 cruise the mean wind speed was  $7.7 (\pm 3.6) \text{ m s}^{-1}$  and thus only slightly higher than the mean wind speed measured in the tropics (M47, So152 and western part of M55) with  $7.0 (\pm 2.7) \text{ m s}^{-1}$ . But the standard deviation shows that the wind was more uniform in the tropics than in the North Atlantic. During Pos255 the wind speed exceeded  $10 \text{ m s}^{-1}$  at several occasions, especially on the east-west transect from the English Channel to Halifax, where the lowest surface water concentrations of methyl iodide were found (see Figure 10 and Figure 15). To estimate the influence of changing wind speeds, another model was developed.

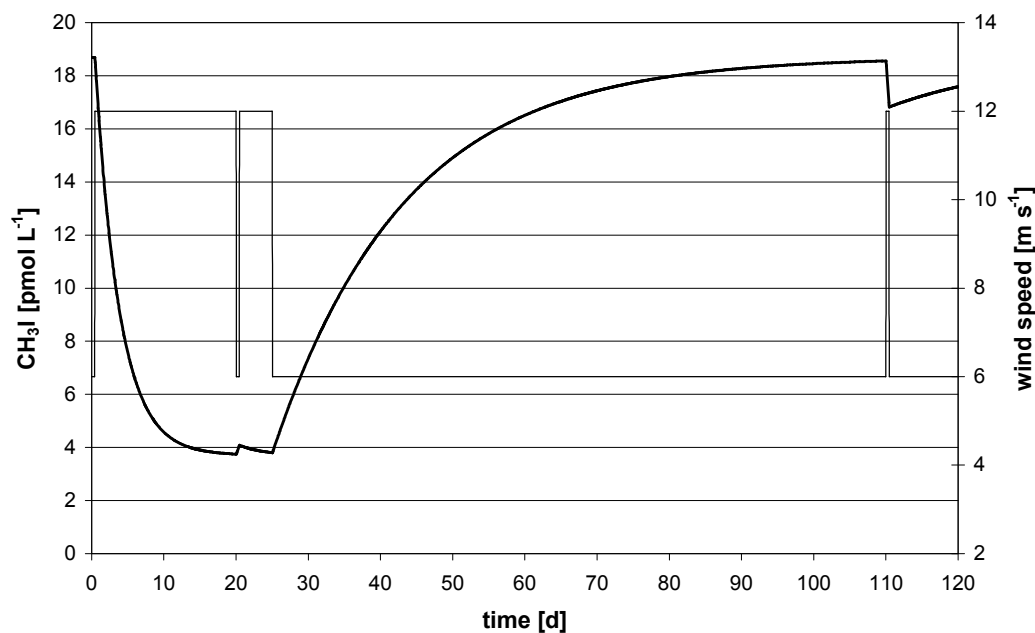
One assumption for model A was, that the wind speed is constant and thus a steady state between flux and net production per area is reached. In reality the wind speed varies. To evaluate the influence of varying wind speeds on the surface concentration of methyl iodide, and the time the systems needs to reach a new steady state, a second model (model B) was done. The same net production rate per area of  $40.32 \text{ nmol m}^{-3} \text{ d}^{-1}$  as for model A was used. A mixed layer depth  $d_{ML}$  of 40 m was assumed. Then the methyl iodide concentration was calculated for a wind speed of  $6 \text{ m s}^{-1}$  for the steady state between net production per area and flux to the atmosphere, in the same way as in model A. Using a mean atmospheric dry gas mixing ratio of  $2 \text{ pmol mol}^{-1}$  for the North Atlantic (taken from the literature, as described for the Pos255 cruise in chapter 3.1), the methyl iodide concentration in the mixed layer  $c_w$  was calculated for the steady state (in  $[\text{pmol L}^{-1}]$  or  $[\text{nmol m}^{-3}]$ , which is the same). With this concentration the methyl iodide content of the mixed layer per unit area  $U$   $[\text{nmol m}^{-2}]$  was calculated by

$$U = \frac{c_w}{d_{ML}} \quad (27)$$

This is the starting point, where the net production  $P_a$  and the flux  $F$  are equal and the content (and hence the methyl iodide concentration) does not change with time. Now the wind speed was doubled to  $12 \text{ m s}^{-1}$ , thus changing the flux. The change of the methyl iodide content of the mixed layer  $U$  was calculated with

$$\Delta U = \frac{P_a - F}{t} \quad (28)$$

with time intervals of  $t = 1$  hour. The new mixed layer content was calculated ( $U + \Delta U$ ) and from this the new methyl iodide concentration  $c_w$  of the mixed layer with equation (27). The new  $c_w$  value was used to calculate a new concentration anomaly  $\Delta C$  and with this the new flux  $F$ . The flux was used to calculate the next  $\Delta U$ , and so on. The resulting concentration anomalies from this model calculation are plotted against time (Figure 24).



**Figure 24:** Surface water methyl iodide concentration (thick line, [pmol L<sup>-1</sup>]) from model B, plotted against time [d], together with the wind speed used in the calculation (thin line [m s<sup>-1</sup>]). The concentration at time 0 is the equilibrium concentration for a wind speed of 6 m s<sup>-1</sup>.

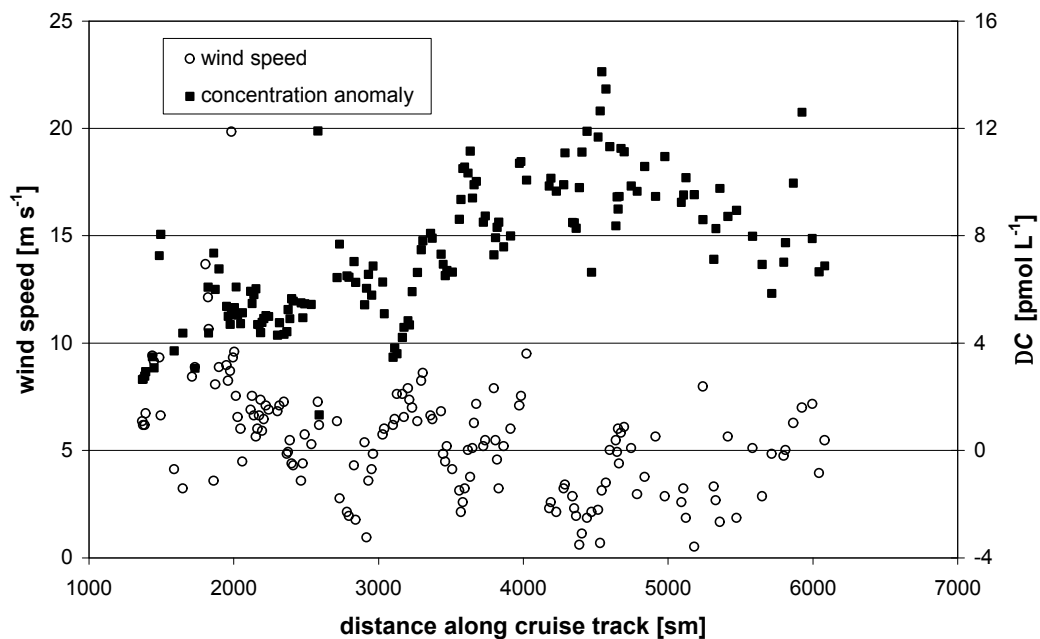
The results from the model calculation show clearly that the time, which it takes for the surface water concentration of methyl iodide to reach a steady state again, is dependent on the direction of the change in wind speed. After increasing the wind speed it took about 20 days to reach the steady state with a lower surface water concentration of methyl iodide. After decreasing the wind speed, however, it took more than threefold the time (about 75 days) to reach the steady state that had been before. To illustrate this point further, the wind speed was changed again for a period of 10 hours, when the steady state was reached (at day 20 and day 110, see Figure 24). The change in the methyl iodide concentration is four times higher (1.6 pmol L<sup>-1</sup>), when the wind speed is set to 12 m s<sup>-1</sup> for 10 hours during a period with a wind speed of 6 m s<sup>-1</sup>, than the change which results if the wind speed is set to 6 m s<sup>-1</sup> during a period with a wind speed of 12 m s<sup>-1</sup> (0.34 pmol L<sup>-1</sup>). The pattern of the results from the model is not influenced by the estimated mixed layer depth. A different mixed layer depth changes the overall time needed to reach the steady state, but the relation of the times needed for decrease and increase of the methyl iodide concentration stays the same.

Thus, the results from model B shows that a short period of high wind can decrease the seawater concentration much faster than it can be rebuild when the wind speed decreases again. Following these model result the lower methyl iodide concentrations measured during Pos255 may be explained with the periods of higher wind speeds encountered during the cruise, despite the only slightly elevated mean wind speed compared with the wind speeds in the tropics. A second conclusion from model B is that the methyl iodide concentration in the

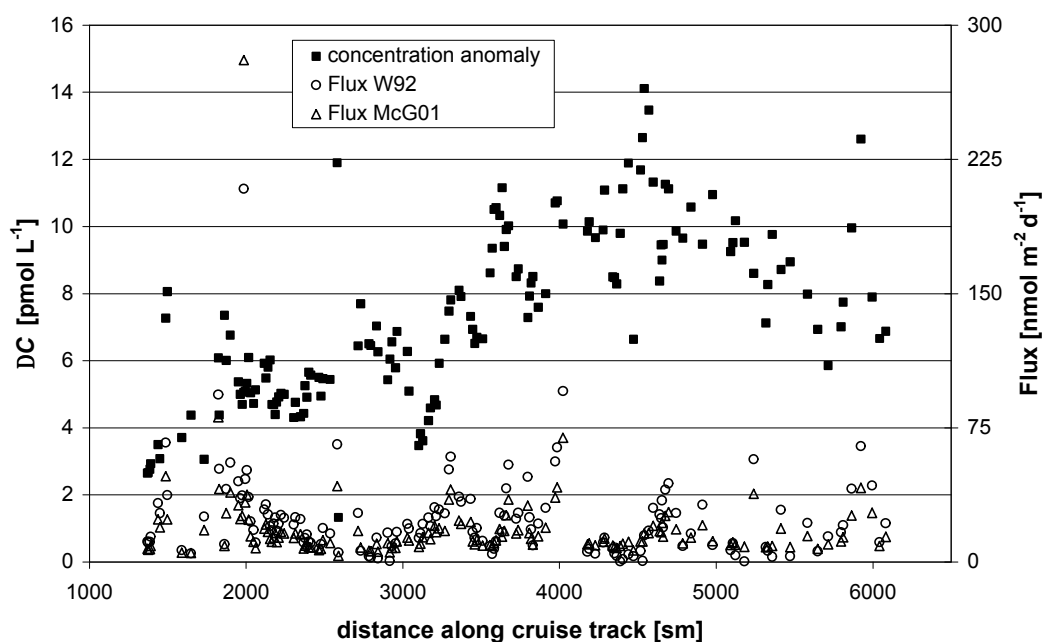
surface water reacts to wind speed changes in time scales of hours to days. Thus daily averaged wind speeds or wind speeds averaged over 12 hours should be used for the calculation of methyl iodide ocean-atmosphere fluxes, because neither long-term, climatological wind speeds nor “spot” wind speeds, from a single anemometer measurement, are representative for the relevant time scale of changes in the methyl iodide concentration.

The results from both models together indicates, that the concentration anomaly of methyl iodide and the transfer velocity should be negatively correlated. The data from M55 show this correlation, with high concentration anomalies correlated with low wind speeds. This is illustrated in Figure 25, where the concentration anomalies and the wind speeds from M55 are plotted together along the cruise track. Since the flux is calculated by multiplying the concentration anomaly and the transfer velocity (equation (6)), the resulting fluxes do not change significantly. This is illustrated in Figure 26, where the calculated fluxes from M55 are plotted along the cruise track, together with the concentration anomalies. The fluxes do not increase, despite a doubling in the measured concentration anomalies. The conclusion from this observation and the model results is, that the production of methyl iodide in the ocean seems to determine the ocean-atmosphere flux, not the concentration anomaly or the transfer velocity.

Since the concentration anomaly seems to be influenced so strongly by the wind speed, the usefulness of the sea surface temperature as a proxy for the methyl iodide concentration anomaly as suggested by *Groszko* (1999) is limited. Using it to replace missing data for the calculation of air-sea fluxes must be doubted.



**Figure 25:** Concentration anomalies and spot wind speeds from M55, plotted against distance along the cruise track.



**Figure 26: Concentration anomalies and calculated fluxes from M55, plotted against distance along the cruise track.**

The calculated fluxes (using the W92 relationship) from the different cruises are  $13.3 (\pm 10.8) \text{ nmol m}^{-2} \text{ d}^{-1}$  (M47),  $22.7 (\pm 17.7) \text{ nmol m}^{-2} \text{ d}^{-1}$  (M55),  $16.4 (\pm 15.6) \text{ nmol m}^{-2} \text{ d}^{-1}$  (Pos255) and  $33.2 (\pm 15.0) \text{ nmol m}^{-2} \text{ d}^{-1}$  (So152). The mean values for Pos255, M47 and M55 are in good agreement with the fluxes given by *Moore and Groszko* (1999) with  $16.0 \text{ nmol m}^{-2} \text{ d}^{-1}$  for the Pacific,  $11.9 \text{ nmol m}^{-2} \text{ d}^{-1}$  for the Labrador Sea and  $25 \text{ nmol m}^{-2} \text{ d}^{-1}$  for the eastern Atlantic. *Singh et al.* (1983) estimated a similar flux of  $27.0 \text{ nmol m}^{-2} \text{ d}^{-1}$  from their measurements in the eastern Pacific which they reduced to  $17.4 \text{ nmol m}^{-2} \text{ d}^{-1}$  by excluding some high values thought to be not representative for large areas of the ocean. The flux calculations from *Liss and Slater* (1974) of  $14.7 \text{ nmol m}^{-2} \text{ d}^{-1}$  fits well with this data, too. The flux calculated from the So152 data was somewhat higher with  $33.2 (15.0) \text{ nmol m}^{-2} \text{ d}^{-1}$  than the previously reported ones. From the data no explanation for these elevated flux could be found. But calculating the fluxes with the McG01 relationship decreases the results about 25 %, giving a mean flux of  $24.4 (\pm 14.0) \text{ nmol m}^{-2} \text{ d}^{-1}$  for the So152 cruise. This value is in the range of the previously reported fluxes (within the given uncertainties). Which of the both estimates is a better representation of the real flux can not be decided without a better understanding of the oceanic methyl iodide cycle.

Further results from the flux calculations will be discussed in more detail in chapter 5.



## 4. Incubation experiments

### 4.1 Introduction

In the previous chapters it has been shown that the surface ocean is supersaturated with methyl iodide with respect to the atmosphere. At this point the question arises what are the sources of methyl iodide to the surface ocean. *Moore and Groszko* (1999) and *Groszko* (1999) measured depth profiles of methyl iodide and found the highest concentration at or near the surface up to 50 m depth, depending on the location. The sites with a subsurface maximum had a deep chlorophyll maximum too. The concentration decreased with increasing depth below this maximum. The source of methyl iodide to the seawater is therefore located in the surface water. Two principle sources have been discussed, biological production by algae, plankton and/or bacteria and photochemical production.

Algae have been investigated and shown to produce a variety of halocarbons including methyl iodide. *Manley and Dastoor* (1987) showed in short term incubations of blade tissues that giant kelp produces methyl chloride, methyl bromide and methyl iodide. In a second step they found methyl iodide production in axenic blade cultures (*Manley and Dastoor*, 1988), confirming that the production is from the kelp itself and not from associated microbes. Other studies found that many algae species, living in different climate zones, are able to produce methyl iodide and a variety of other halocarbons (*Schall et al.*, 1994, *Collén et al.*, 1994, *Nightingale et al.*, 1995, *Laternus and Adams*, 1998, *Giese et al.*, 1999). *Manley et al.* (1992) measured elevated concentrations of methyl iodide in seawater from within algae beds compared to the outside. A kind of in-situ incubation was done at Mace Head, Ireland, by measuring the halocarbon concentrations in an intertidal rock pool during low tide when the pool was separated from the open sea (*Carpenter et al.*, 2000). They found increased halocarbon concentrations with methylene iodide  $\text{CH}_2\text{I}_2$  as the main iodine carrier to the atmosphere. Elevated concentrations were also measured by *Carpenter et al.* (2000) in seawater and atmosphere close to the shoreline which indicate production in the algae beds. Thus algae have an influence on the local halocarbon budget. But due to the limited spatial distribution of macroalgae they can contribute only about 0.1 % of the estimated global oceanic source (*Manley and Dastoor*, 1987, *Nightingale et al.*, 1995, *Giese et al.*, 1999).

Then the focus shifted to phytoplankton which is much more abundant than macroalgae because planktonic species are not restricted to the coast. *Klick and Abrahamsson* (1992) reported indication of another halocarbon source as macroalgae from halocarbon measurements in surface seawater in different regions of the ocean and proposed plankton as a possible source. This was followed by a variety of incubation experiments of different

plankton species in the laboratory. These experiments showed evidence for the production of methyl iodide and other halocarbons by some plankton species (*Moore et al.*, 1996a, *Itoh et al.*, 1997, *Manley and de la Cuesta*, 1997, *Scarratt and Moore*, 1998, *Scarratt and Moore*, 1999). With the use of GC-MS systems the production of different halocarbons including methyl iodide has been confirmed by an isotope labeling experiment (*Murphy, Moore and White*, 2000). Even the cell-free extracts from some plankton species showed methyl halide production from S-adenosyl-L-methionine (SAM) by the enzyme methyl halide transferase (*Itoh et al.*, 1997). This is supported by *Amachi et al.* (2001), who showed methyl iodide production by many different bacteria including marine species. Again cell-free extracts show methylation of iodine with SAM as methyl donor. However, the authors gave no estimate for the effect of this mechanism on the sea-air flux because of the difference in physiological conditions between laboratory and sea water, which strongly influences the production rates. *Manley and de la Cuesta* (1997) estimated the total source strength by plankton based on their experiments with 15 different plankton species and found it to be insignificant.

Only a few studies have addressed the photochemical production of methyl iodide. *Moore and Zafiriou* (1994) found methyl iodide production in filtered seawater (0.45  $\mu\text{m}$  silver filters) under irradiation in sunlight and artificial sunlight. The production was enhanced by addition of iodine or by deoxygenating the water. The authors proposed a mechanism with formation of iodine atoms and methyl radicals by light and recombination of these radicals. Coastal waters gave higher production rates compared to offshore waters which could be due to the higher level of organic material in these waters. The production rates calculated for this reaction under environmental conditions are in a range that this pathway may have a significant contribution to the total production of methyl iodide in the ocean. However it could not be ruled out that the samples had been contaminated with bacteria which may have produced the observed methyl iodide. The possibility of methyl iodide production by bacteria was evaluated by *Amachi et al.* (2001), who did incubation experiments with different marine and terrestrial bacteria species and found several of them are able to produce methyl iodide. In another study (*Happell and Wallace*, 1996) a photochemical production of methyl iodide was proposed because of a linear relationship between saturation anomaly and incident photosynthetically active radiation found in their data. Biological production was found to be unlikely because the highest saturation was in areas with low chlorophyll content and in a highly productive upwelling zone the methyl iodide content was significant lower than outside, in less productive areas. *Bell et al.* (2002) developed a model for the surface water concentration of methyl iodide which calculates the local seawater concentration of methyl iodide as

$$[CH_3I(aq)] = \frac{P + \left(\frac{k}{d_{ML}}\right) \cdot H \cdot [CH_3I(g)]}{\left(\frac{k}{d_{ML}}\right) + k_{Cl} \cdot [Cl^-]} \quad (29)$$

where  $k$  is the transfer velocity after *Nightingale et al. (2000)*,  $d_{ML}$  is the mixed layer depth,  $H$  is the Henry's law constant for methyl iodide,  $[CH_3I]$  are the concentration in the atmosphere (g) and surface seawater (aq),  $[Cl^-]$  is the chloride ion concentration,  $k_{Cl}$  is the rate constant for the reaction of  $CH_3I$  with  $Cl^-$  from *Elliott and Rowland (1993)* and  $P$  is the production rate per unit volume. For the latter they used a scaling against solar radiation flux at the surface (RAD) and the dissolved organic carbon concentration (DOC) as follows

$$P = \mathbf{b} \cdot [RAD \cdot DOC] \quad (30)$$

where  $\mathbf{b}$  is a scaling factor. The resulting model methyl iodide concentrations matched the measured ones better than a similar calculation where  $P$  was scaled to the net primary production. Thus the model gives more consistent results with a photochemical source in the oceans than with a biological source. Other authors discussed the possibility of photochemical production of methyl iodide because its uniform distribution in the oceanic atmosphere despite the short lifetime, which suggests a uniform oceanic source which does not respond to changes in biological productivity (*Li et al., 2001, Yokouchi et al., 2001*). But so far the contribution of photochemical production to the overall oceanic source is not understood.

After all the sources for methyl iodide in the ocean and their strength under environmental conditions are even now not well understood. The incubation experiments in this thesis are designed to give more information about which factors influence the methyl iodide production in the ocean. The main question will be to see if there is a photochemical production and how important it is compared to the biological production. The experiments were done outside the laboratory at sea to investigate the production under conditions as close to environmental conditions as possible, especially with natural seawater and seawater temperature under natural light conditions.

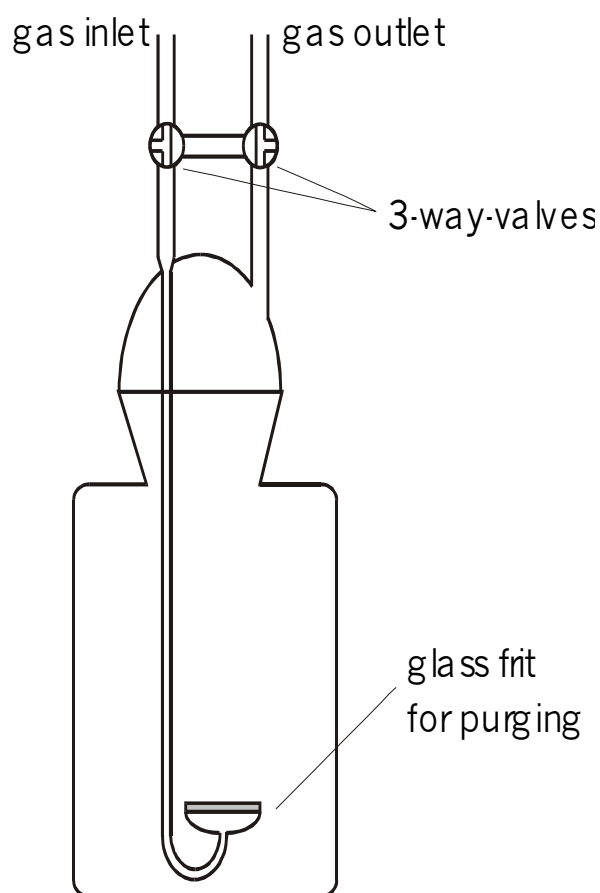
## 4.2 Methods

### 4.2.1 Incubation flasks

For the incubation experiments special flasks were developed, which were used both for the incubation and as purge vessels for the measurements. After incubation the flasks were connected to the measuring system, the lines were flushed with helium and the flasks were

opened to purge the volatile gases directly on to the trap. Thus contamination due to contact with the outside is avoided.

The incubation flasks consisted of a 100 mL quartz bottle with a specially designed stopper head. The use of quartz glass ensured that the flasks are transparent for UV-radiation. The head has two 6 mm glass tubes on the outside with a glass three-way-valve each. The upper ends of the valves are short 6 mm glass tubes for connection to the measuring system with the trap via 1/4" swagelock fittings with Teflon ferrules (The inlet and outlet of the incubation flask). The third lines from both valves are connected to each other, resembling the letter "H" (see Figure 27). The inlet-line is connected inside the flask to a 3 mm glass tube with a glass frit for purging. The outlet-line opens to the top of the flask to collect the purged gases. When the valves are turned, the flask is closed off and the inlet line is connected trough the direct line between the valves to the outlet. Thus the connecting lines can be flushed with gas to clean them after the flask is built into the measuring system. To purge the flask the gas is directed to the trap and the two three-way valves are turned. With this procedure the content of the incubation flask will not have contact with the outside after the measurement at the beginning of the incubation, and any chance of contamination is minimised.



The three-way-valves and the ground glass connection between the bottle and the head required the use of grease to give a gas tight seal. To see if the used grease (GLISSEAL<sup>®</sup>, high vacuum quality, from Borer Chemie) causes any interference with the measurements, empty incubation flasks with greased connections were purged until no peaks could be seen (30 min with 60–70 mL Helium per minute) and allowed to stand for 12 to 24 hours at room temperature and in the light (artificial plus sunlight through the windows). No CFC 11 and methyl iodide could be detected. This shows the incubation flasks are gas tight because otherwise CFC 11 from the air would have been found inside the flask. And the grease released no substances which interfered with the ECD detection under the chromatographic conditions used.

Figure 27: Sketch of an incubation flask

When the bottles were filled with deionized water or seawater from the Kiel Bight and allowed to stand over night, an unknown peak at the same retention time as methyl iodide occurred after purging, incubating and measuring the flasks as just described. The content of the flasks was measured with GC-MS in single ion mode and no methyl iodide found. In scan mode only some hydrocarbon compounds but no methyl iodide was found. The unknown peak could not be removed by using phosphorous acid instead of grease for sealing the bottles or boiling the water under reflux for 4 hours with 85%  $\text{H}_3\text{PO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$  to oxidise all organic material. The unknown peak had the same area as 0.014 – 0.049 pmol methyl iodide after 12 to 20 hours of incubation. The measured methyl iodide content after an incubation was an order of magnitude higher, therefore comparing incubations under different conditions was not affected by this unknown peak. No further actions has been taken to investigate and remove these blank peaks prior to the cruise. More tests have been done at sea and will be discussed together with incubation results (chapter 4.4).

## 4.2.2 Experimental protocol

Seawater for the incubation experiments was taken either from Niskin-bottles from the CTD-Rosette or from a submerged pump in the ship's moon pool, which was also used for all the underway water samples and was located about 5 m below sea level. The samples were transferred to the lab in two 1 L- glass bottles. Depending on the course of the incubation the water in one bottle was poisoned with 5 mL of a  $10 \mu\text{g L}^{-1}$  mercury (II) chloride solution or filtered through a  $0.1 \mu\text{m}$  membrane filter (Isopore<sup>TM</sup> from Millipore) with a reduced pressure of 200 kPa (see chapter 4.3). Each incubation flask was then filled with 80 mL ( $\pm 2$  mL) of sample water and closed with the glass stopper head. The bottles were connected to the measuring system and the connection lines were flushed with helium ( $25 \text{ mL min}^{-1}$ ) for 10 minutes. Then the gases were purged with helium ( $50 \text{ mL min}^{-1}$  for 15 minutes) onto the cold trap and measured (For details of the measurement see chapter 2.5 and chapter 2.6).

To replenish oxygen and carbon dioxide after purging 100 mL air were flushed through the bottle with a 100 mL gastight glass syringe. The air had a mean concentration of methyl iodide of  $3.5 \text{ pmol mol}^{-1}$  during the M55 cruise (see chapter 3.1), which is about  $0.14 \text{ pmol L}^{-1}$ . Therefore about 0.014 pmol methyl iodide has been introduced in each bottle. The results for methyl iodide from the incubations have been corrected by this amount. Tests in the laboratory with the same incubation flasks and water from the Kiel Bight were done to evaluate the oxygen content before and after the flushing with 100 mL air as described above. The mean oxygen content was  $7.0 \pm 0.7 \mu\text{mol L}^{-1}$  before and  $77.5 \pm 18.0 \mu\text{mol L}^{-1}$  after the air injection, respectively. Tests in the laboratory with standard seawater showed that the purge step and the bubbling with air change the pH by about 0.15 units.

The flasks were then incubated for about 24 hours including the full daylight time in water basins that were constantly flushed with surface seawater for temperature control (seawater temperature between 27 – 29 °C) and under different light conditions (see chapter 4.3 for the conditions for the individual incubation experiments). At the end of the incubation, every bottle was connected to the measuring system and the methyl iodide content was measured as described above.

Some bottles were measured twice consecutively without disconnecting them from the measuring system to get information about the purge efficiency. The results from the second measurement were 11.0, 8.9, 9.0, 10.1, 12.4 and 8.3 % (mean  $10.0 \pm 1.5$  %) of the results from the first measurement, yielding a purge efficiency of 90 %. An extended purge time would increase the efficiency, but with the risk of break-through of the more volatile compounds during trapping. Therefore no further attempts were made to increase the purge efficiency and the results from the incubation experiments have been corrected accordingly.

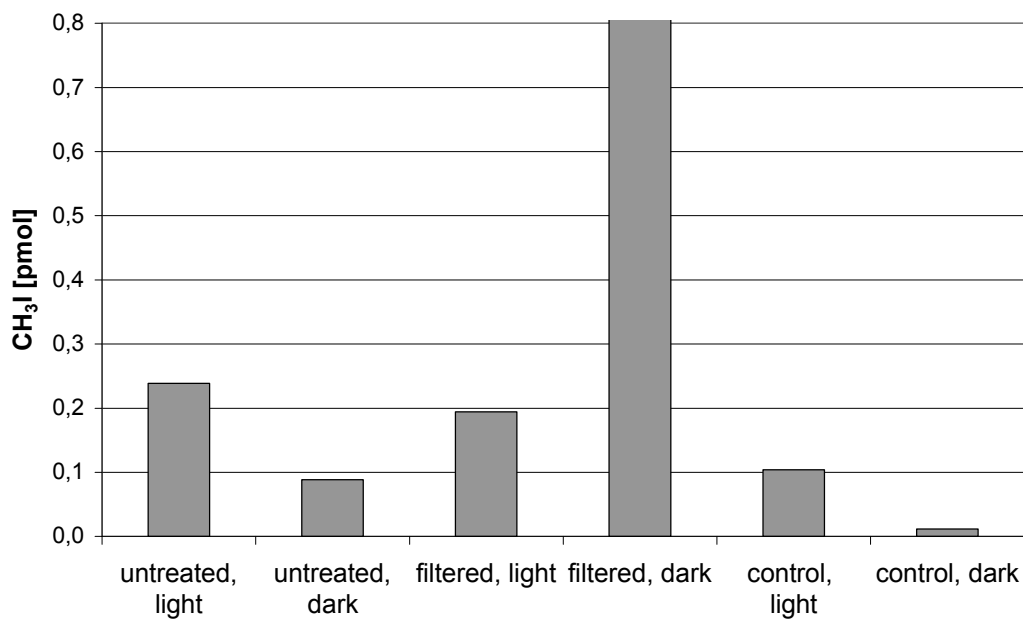
### 4.3 Results

Eight incubations were performed during the M55 cruise. The results from the single experiments will be shown separately followed by a discussion in the next chapter. An overview about the incubation treatments and results is shown in Table 6.

**Table 6: Overview of incubation treatments and results (numbers are methyl iodide content after incubation in pmol). For the incubations indicated by an <sup>A</sup> water from 200-240 m depth was used instead of surface water. The two results indicated with # are from incubations with reduced light instead of dark incubations.**

No.	sampling location	untreated water			filtered water (0.1 µm Isopore™ filters)			Poisoned water (5 mL of 10 µg L <sup>-1</sup> HgCl <sub>2</sub> )		
		light	light with reduced UV	dark	light	light with reduced UV	dark	light	light with reduced UV	dark
1	0°00.4'N 23°30.0'W	0.24		0.09	0.19					
2 <sup>A</sup>	0°00.0'N 23°30.0'W	0.77		0.02 0.05 <sup>#</sup>	0.31		0.00 0.03 <sup>#</sup>			
3 <sup>A</sup>	9°30.5'N 24°48.9'W	0.62		0.05	0.32		0.07			
		0.33		0.01	0.10		0.03			
4 <sup>A</sup>	11°00.0'N 29°20.0'W	0.20		0.07	0.28		0.02			
		0.18		0.03	0.21		0.03			
5 <sup>A</sup>	11°02.1'N 17°41.9'W	0.21	0.25	0.15	0.11	0.13	0.01			
		0.26			0.17					
6	10°43.5'N 19°49.9'W	0.34	0.20	0.09	0.28	0.25	0.09			
		0.35	0.52	0.09	0.19	0.29	0.10			
7	6°00.4'N 19°38.3'W	0.29		0.03				0.23		0.07
		0.45		0.07				0.54		0.04
		0.45		0.06				0.55		0.07
8	3°31.6'N 8°15.0'W	0.29	0.16	0.07				0.25	0.18	0.06
		0.23	0.15	0.04				0.23	0.15	0.03

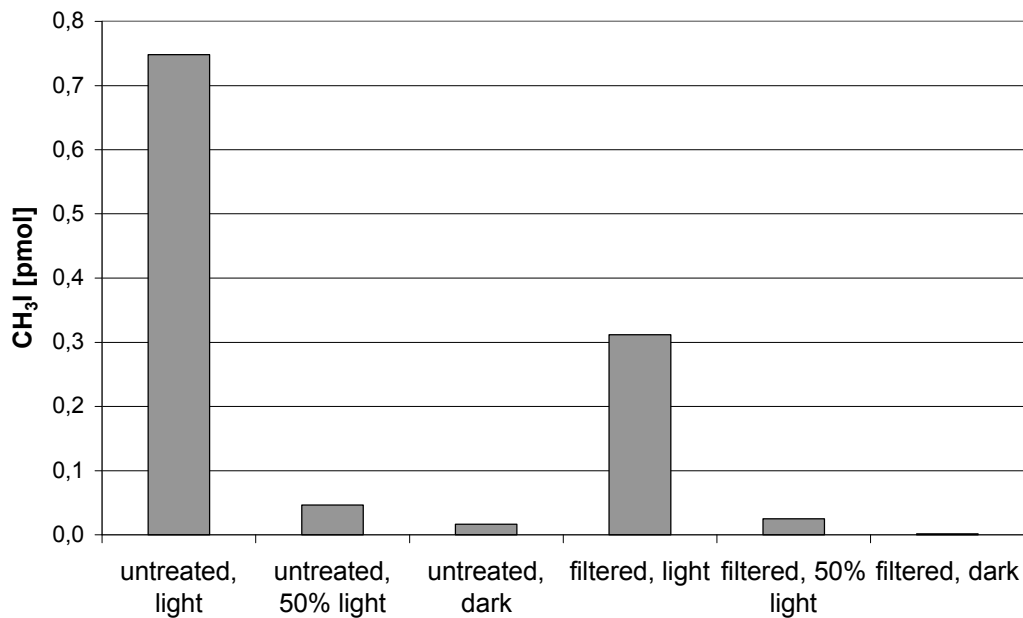
In the first incubation 6 bottles were filled with surface water from the submersible pump in the ship's moon pool. Two bottles contained filtered (0.1  $\mu\text{m}$ ) seawater, two were untreated seawater and two were freshwater controls with tap water from the ships system (i.e. seawater processed by reverse osmosis and filtration to make drinking water). One bottle each was kept in the full daylight and the other one in the dark. The methyl iodide content after incubation is shown in Figure 28. The very high methyl iodide content of 1.97 pmol for the filtered sample kept in the dark is most likely due to contamination because the methyl iodide content prior to the incubation was already very high (8.32 pmol) and due to the purging efficiency of 90 % a methyl iodide content of 0.83 pmol is expected as a blank alone from the inefficiency of the purging. No other experiment in any of the incubations gave a similar result. Both seawater samples (untreated and filtered) kept in the light had methyl iodide contents of 0.24 pmol and 0.19 pmol, respectively, about twice the content from the untreated one kept in the dark (0.089 pmol). The tap water samples show a similar behaviour on a lower level, the difference is with a methyl iodide content of 0.104 pmol for the sample kept in the light and 0.012 pmol for the dark sample nearly the same than before (about 0.1 pmol).



**Figure 28: Results from incubation 1.**



For the second incubation water from a Niskin-bottle from 240 m depth was used. Three bottles were filled with untreated and the other three with filtered water. One bottle each was incubated in full sunlight, one with reduced sunlight by covering the basin with a foil which blocks about 50% of the light (no information about the reduction at different wave lengths and of UV was available), and one in the dark. The samples kept in the dark and at ~50% light had similar low methyl iodide contents of 0.046 and 0.017 pmol for the untreated and 0.025 and 0.002 pmol for the filtered samples, respectively. The bottles kept in full sunlight gave a higher production with 0.31 pmol for the filtered one and 0.75 pmol for the untreated sample (see Figure 29). The covering with a foil blocking about 50 % of the sunlight seems to have the same effect as keeping the incubations in the dark.



**Figure 29: Results from incubation 2.**

Incubation 3 was done with seawater from a Niskin-bottle from 200 m depth and with 12 incubation flasks. Four flasks were filled with untreated and four with filtered water, the other four were again freshwater controls. Thus all incubations have been done in duplicate (full sunlight and dark). The results show a quite large scatter between the two flasks with the same treatment (see Figure 30). The reason for this remains reproducibility unclear. But again the seawater samples kept in full sunlight showed a higher methyl iodide content of 0.33 pmol and 0.62 pmol (untreated) and 0.10 pmol and 0.32 pmol (filtered) then the ones kept in the dark with values between 0.012 pmol and 0.074 pmol (mean 0.04 pmol). This time there is no clear pattern in the freshwater controls and their methyl iodide content between 0.025 pmol and 0.11 pmol (mean 0.06 pmol) is in the same range as for the seawater samples kept in the dark.

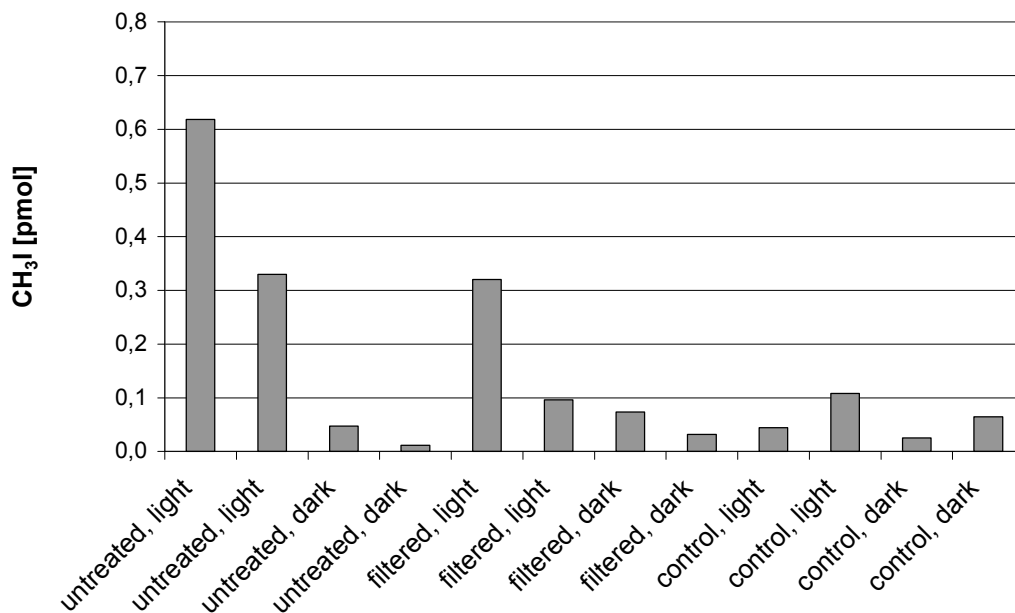
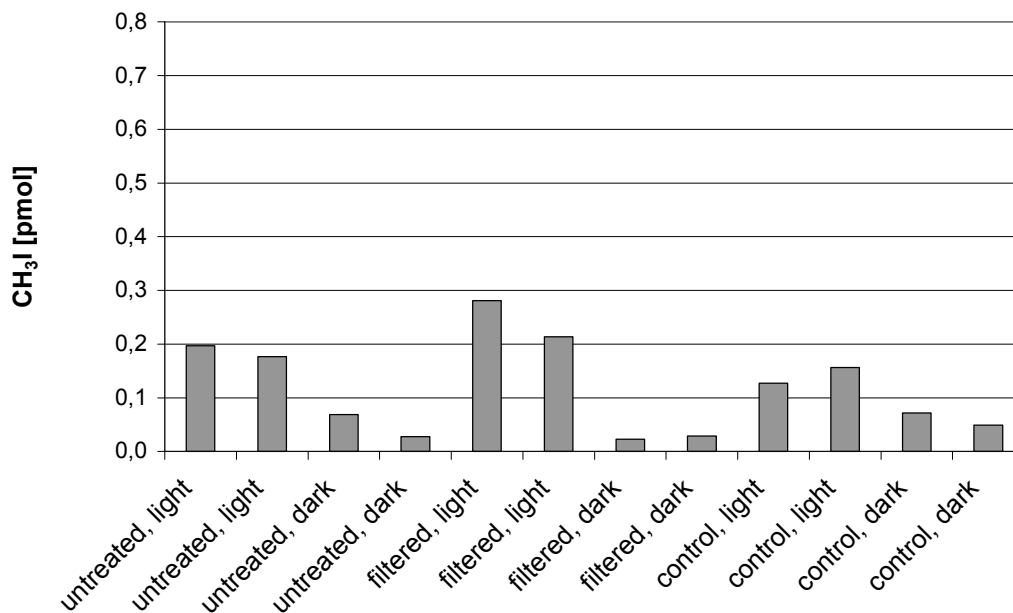


Figure 30: Results from incubation 3.

Incubation 4 was done in the same way as incubation 3 (12 bottles, four bottles with untreated, four with filtered and four with tap water, two of each kept in light and two in the dark), again with water from a Niskin-bottle from 200 m depth. The flasks with seawater samples kept in the dark gave result in the same range as in incubation 3, with values between 0.023 and 0.069 pmol (mean 0.04 pmol) methyl iodide (see Figure 31). The seawater samples kept in full sunlight gave with 0.18 pmol and 0.20 pmol (untreated) and 0.21 pmol and 0.28 pmol (filtered) higher results than the ones kept in the dark. The controls also show higher methyl iodide contents for the bottles kept in the light (0.13 pmol and 0.16 pmol) than for the ones kept in the dark (0.049 pmol and 0.072 pmol), but the difference between them is smaller than that from the seawater samples. In this experiments the results from duplicate measurements are closer to each other than during incubation 3.



**Figure 31: Results from incubation 4.**

With incubation 5 the influence of UV radiation in the sunlight was investigated. For that purpose two bottles were incubated in full sunlight, one in the dark and another one in sunlight, but inserted with the incubation fluid in a glass beaker (DURAN® glass) to block UV radiation. These four incubations have been done each with untreated seawater, filtered seawater and tap water as control. Seawater was taken from a Niskin-bottle from 200 m depth. The experiment gave similar results for the samples kept in the sunlight, with or without a beaker around the flask. The untreated water samples kept in the light show methyl iodide contents of 0.26 pmol, 0.21 pmol (full sunlight) and 0.25 pmol without UV radiation (see Figure 32). The dark sample has a only slightly lower value of 0.15 pmol. The same pattern is repeated in the filtered samples with lower values, although here the light-dark difference is clearer. The samples kept in the light (with or without UV radiation) have methyl iodide contents of 0.11 pmol, 0.17 pmol and 0.13 pmol, the dark one has 0.012 pmol. The results from the controls are similar to the filtered ones with 0.014 pmol (dark) and 0.17 pmol and 0.20 pmol (light), except the flask incubated in the light without UV which has a high value of 0.51 pmol. No explanation could be found for this value, but contamination of the sample during incubation is possible.

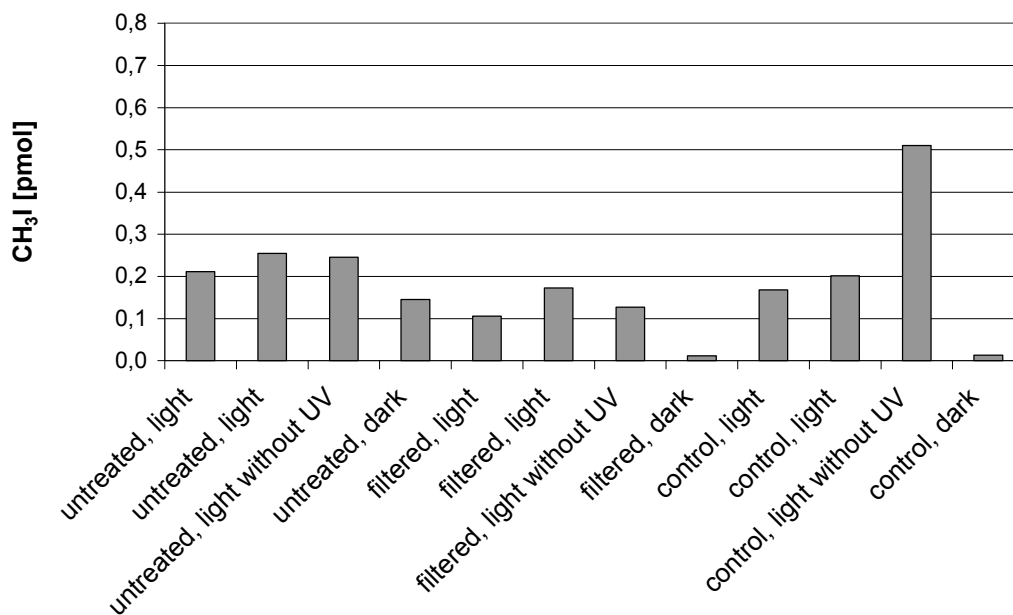


Figure 32: Results from incubation 5.

Incubation 6 repeated incubation 5 with surface seawater from the pumped supply, but without freshwater controls with tap water. There have been two bottles each kept in the dark, full sunlight and full sunlight without UV radiation. This set of incubations has been done both with untreated and filtered surface seawater. The UV radiation was again reduced by inserting the incubation flasks in glass beakers. The methyl iodide content after incubation shows a higher production for samples kept in the light than in the dark, but with no significant difference between the incubations with and without UV radiation (see Figure 33). The untreated samples had a methyl iodide content of 0.34 pmol, 0.35 pmol (with UV), 0.20 pmol and 0.52 pmol (without UV), with a mean of 0.35 pmol for all samples kept in the light. There is a big difference in the two samples without UV radiation, but we have no explanation for this result. The filtered samples follow a similar pattern with lower methyl iodide levels. The flasks kept in the light had methyl iodide contents of 0.19 pmol, 0.28 pmol (with UV), 0.25 pmol and 0.29 pmol (without UV) with a mean of 0.25 pmol. The samples kept in the dark show no significant difference with values of 0.086 pmol and 0.093 pmol for the untreated water and 0.089 pmol and 0.097 pmol for the filtered water. That gives a mean methyl iodide content of 0.09 pmol for all dark samples.

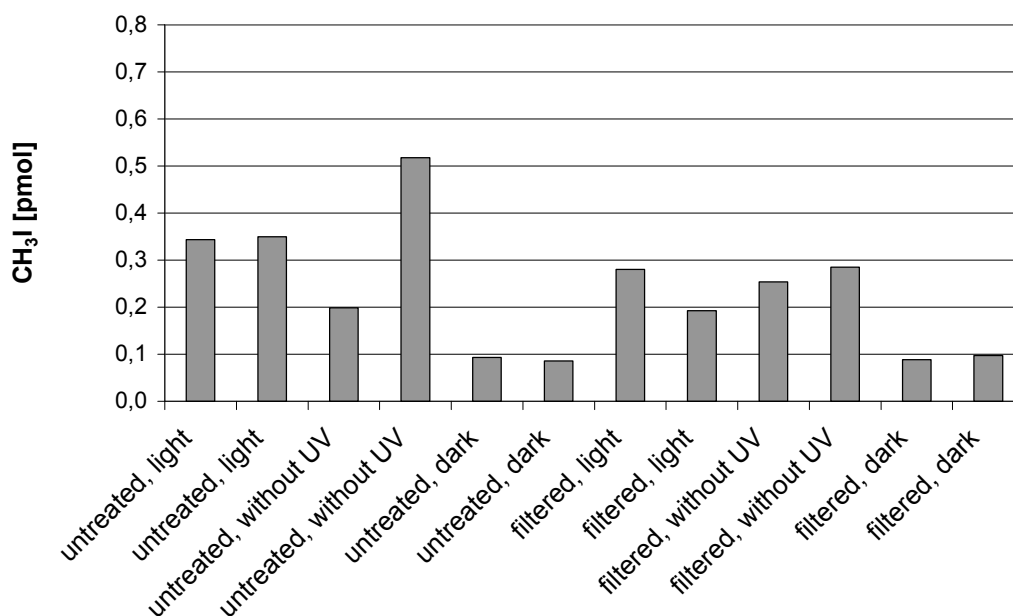


Figure 33: Results from incubation 6.

In incubation 7 an additional "biology free" treatment was introduced by poisoning with 5 mL of a  $10 \mu\text{g L}^{-1}$  mercury (II) chloride solution instead of filtration. The reason was that filtered samples are not axenic since some small living organisms may slide through the filters during filtration. And other organisms may stick to the walls of the incubation flasks, especially bacteria. Thus the filtered incubations may contain some living cells, instead of being "biology free", which means they contain no living cells. The water was surface seawater from the submerged pump in the ship's moon pool. Three samples each from poisoned and untreated seawater were incubated in full sunlight, and three in the dark.

The methyl iodide contents after incubation in the dark showed no significant difference between untreated and poisoned samples with 0.029 pmol, 0.058 pmol and 0.069 pmol (untreated) and 0.041 pmol, 0.069 pmol and 0.074 pmol (poisoned) with a mean of 0.06 pmol for all dark samples (see Figure 34). The samples kept in sunlight had higher values with 0.29 pmol, 0.45 pmol and 0.45 pmol (mean 0.39 pmol) for the untreated ones and 0.54 pmol and 0.55 pmol (mean 0.55 pmol) for the poisoned ones.

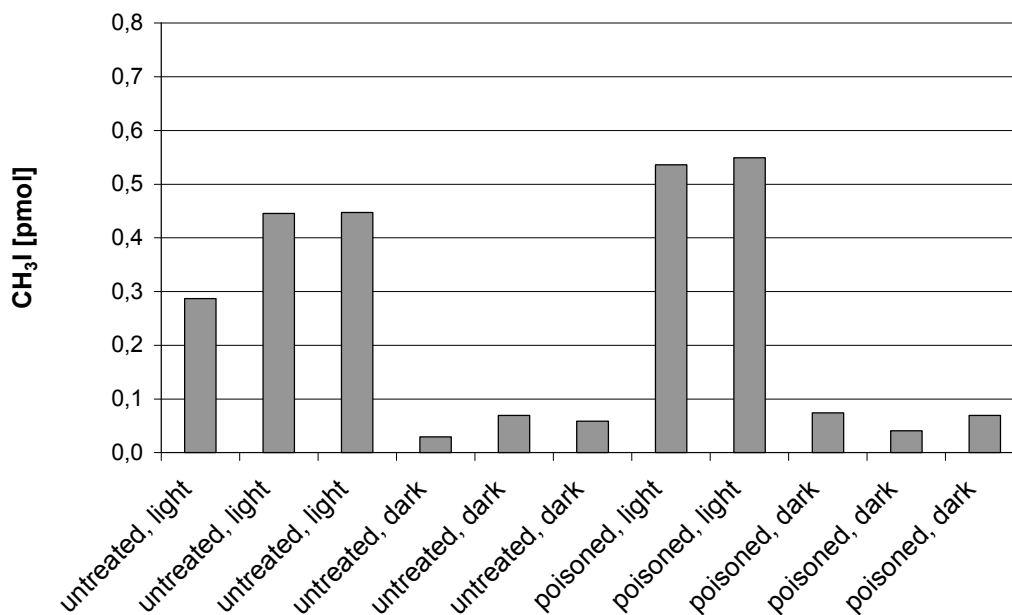


Figure 34: Results from incubation 7.

Incubation 8 was done with untreated and poisoned surface seawater from the submersible pump. Two flasks each were incubated in full sunlight, two in the dark and two in sunlight without UV radiation. To block the UV radiation this time a special foil was used which is described in chapter 4.4. The methyl iodide contents after incubation for the dark samples were 0.043 pmol, 0.073 pmol (untreated), 0.034 pmol and 0.059 pmol (poisoned) with a mean of 0.05 pmol (see Figure 35). The samples kept in full sunlight had methyl iodide contents of 0.23 pmol and 0.29 pmol for the untreated ones and 0.23 pmol and 0.25 pmol for the poisoned ones. The samples incubated without UV radiation had a slightly lower methyl iodide content 0.15 pmol and 0.16 pmol for the untreated ones and of 0.15 pmol and 0.18 pmol for the poisoned ones.

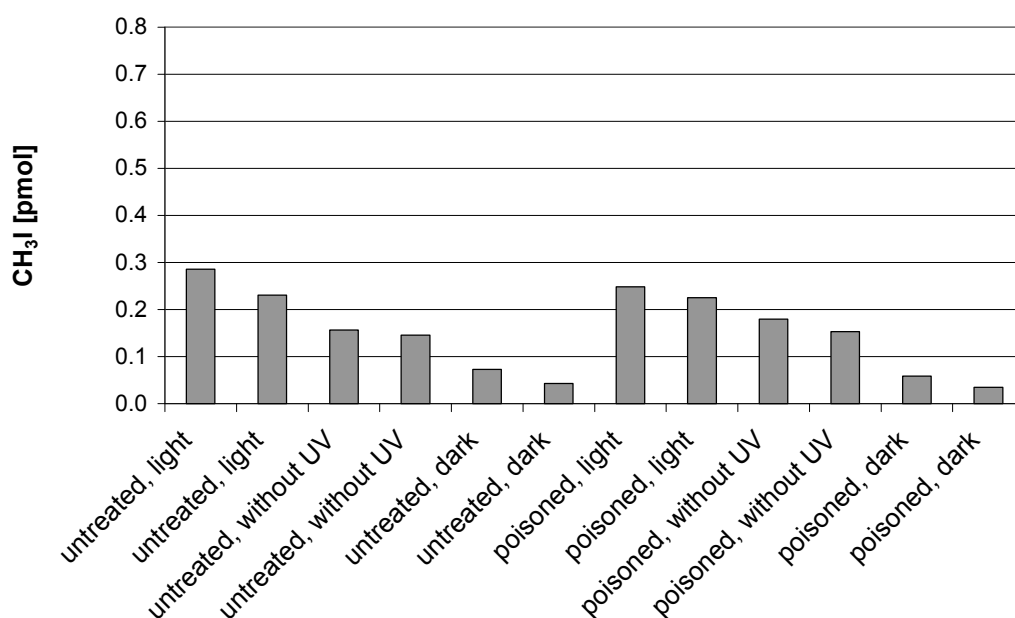


Figure 35: Results from incubation 8.

## 4.4 Discussion

The incubation experiments were done to test the hypothesis that the main methyl iodide production in the open ocean is by a photochemical pathway, and thus is dependent on the presence of light, and not by biological production from plankton or bacteria. The latter may be dependent on light, too, but will be influenced if the samples used for incubation are filtered or poisoned.

The different treatments (untreated, filtered and poisoned) have been chosen to test this hypothesis. Filtering and poisoning have been used as alternative treatments, because neither technique removes all “biology” and both can influence on the composition of the sample water. The filtered water contains no algae and plankton cells but may contain some bacteria which passed the filter or came from the walls of the incubation flask, which were not autoclaved before the experiments. The disruption of cells during filtration may increase the DOC content of the water. The poisoned water still contains all the cells, but without metabolism. The mercury(II) chloride used for poisoning should not influence photochemical reactions in the water because it is not photoreactive itself. In our study no significant difference is shown between these two treatments (see below).

The results from all incubations are shown in Figure 36 and Table 6. The results show quite large variations in the values from different (and sometimes even the same) incubations, but despite this one result is obvious: In every case the samples kept in the light gave higher production (mean:  $0.33 \pm 0.15$  pmol), compared to the samples kept in the dark (mean  $0.08 \pm 0.03$  pmol), with only insignificant differences between untreated (mean:  $0.37 \pm 0.16$  pmol), filtered (mean:  $0.24 \pm 0.08$  pmol) and poisoned (mean:  $0.42 \pm 0.18$  pmol) samples (see Figure 36 and Table 6). This is confirmed by t-tests (see Table 7), calculated with a confidence level of  $\alpha = 5\%$ . By comparing all the different treatments with each other no significant difference is observed between untreated, filtered or poisoned samples kept in the light or between incubations with surface water and water from 200-240 m depth. The only significant difference is between samples kept in the light and samples kept in the dark. For this comparison a modified t-test has to be done, because the standard deviation of the two data sets are significantly different from each other (confidence level  $\alpha = 5\%$ ). The usual t-test is based on two different data sets with not significantly different standard deviations so a modified one for data sets with significantly different standard deviations was used, following *Snedecor and Cochran* (1967).



**Table 7: t-test calculations for the different incubation treatments.  $n_1$  and  $n_2$  are the number of data points used for the calculation of the mean  $\bar{x}_1$  and  $\bar{x}_2$ , respectively, with the standard deviation of  $s_1$  and  $s_2$ .  $s_d$  is the standard deviation for both data sets merged together and  $t$  is the test value calculated for the comparison with tabulated  $t$  values. The last column  $\bar{x}_1 \neq \bar{x}_2$  indicates if the two different data sets compared are significantly different from each other.**

\* = values from *Funk et al., 1985*, <sup>+</sup> =  $t$  value from *Snedecor and Cochran, 1967*, for independent samples with  $s_{d1}$  <sup>1</sup>  $s_{d2}$ , <sup>#</sup> =  $t$ -value for  $\alpha = 0.1$  %

treatments to compare	$n_1$	$\bar{x}_1$	$s_{d1}$	$n_2$	$\bar{x}_2$	$s_{d2}$	$s_d$	$t_t$	$t_t$ from table*	$\bar{x}_1 \neq \bar{x}_2$
		[pmol]	[pmol]		[pmol]	[pmol]	[pmol]			
all light / all dark	29	0.33	0.15	27	0.08	0.03	0.12	7.69	2.05 <sup>+</sup> 3.68 <sup>#</sup>	yes
untreated / filtered (light)	15	0.37	0.16	10	0.24	0.08	0.20	1.63	2.07	no
untreated / poisoned (light)	15	0.37	0.16	4	0.42	0.18	0.23	0.39	2.11	no
poisoned / filtered (light)	4	0.42	0.18	10	0.24	0.08	0.23	1.34	2.18	no
surface water / water from 200 m (light)	8	0.35	0.08	7	0.39	0.23	0.27	0.29	2.16	no
surface water / water from 200 m (dark)	8	0.09	0.02	6	0.08	0.05	0.05	0.34	2.18	no
all light / all without UV	29	0.33	0.15	5	0.28	0.15	0.17	0.60	2.04	no
all treated / filtered (light)	14	0.29	0.13	10	0.24	0.08	0.18	0.659	2.074	no
all treated / poisoned (light)	14	0.29	0.13	4	0.42	0.18	0.22	1.060	2.120	no
untreated / all treated (light)	15	0.37	0.16	14	0.29	0.13	0.23	0.928	2.052	no

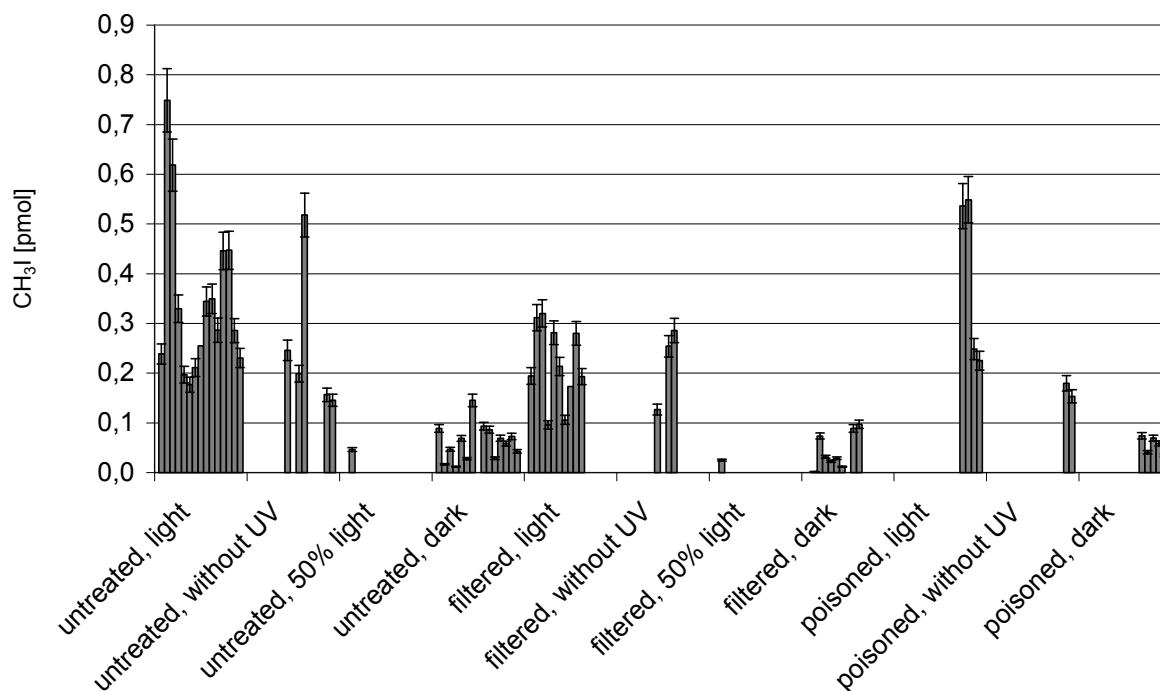
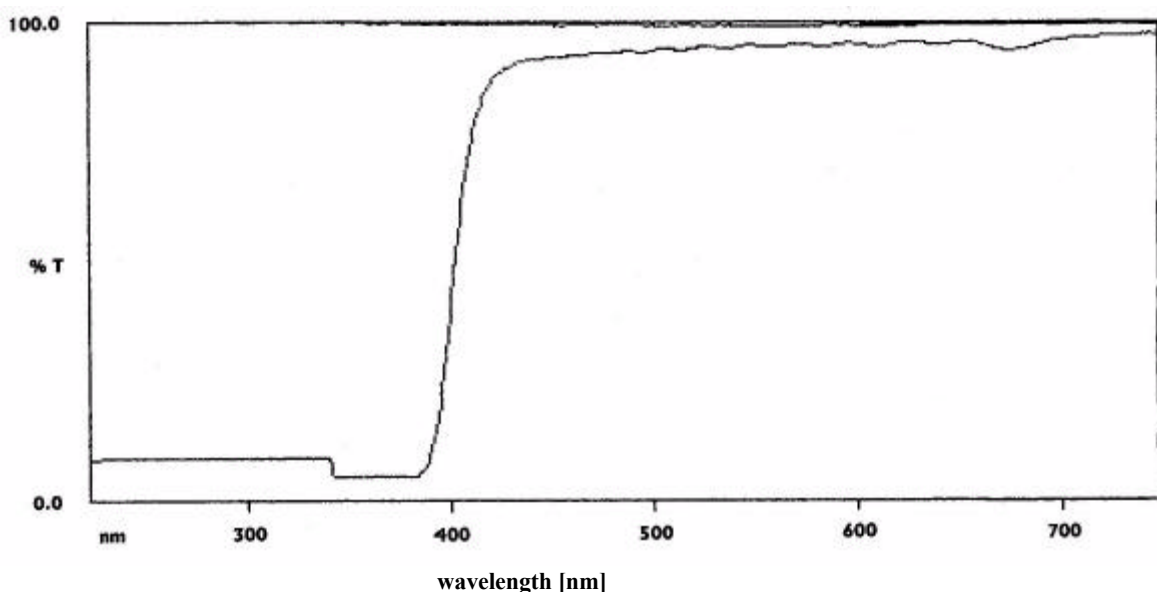


Figure 36: Overview of incubation results.

From these results the production of methyl iodide in the tropical Atlantic ocean appears to be dominated by a photochemical pathway. Despite the fact that many plankton species have been shown to produce methyl iodide in incubation experiments (e.g. Moore *et al.*, 1996a, Itoh *et al.*, 1997, Manley and de la Cuesta, 1997, Scarratt and Moore, 1998, Scarratt and Moore, 1999, Murphy, Moore and White, 2000), their contribution to the measured production of methyl iodide is too small to be seen in our data. The fact that neither filtering nor poisoning have any significant influence on the production strongly limits the influence by bacteria which may had been present in filtered water samples, but had been inactive in the poisoned ones.

The nature of the photochemical pathway for methyl iodide production remains unknown (Moore and Zafiriou, 1994, Happell and Wallace, 1996, Bell *et al.*, 2002). Moore and Zafiriou (1994) suggested a pathway with radical recombination of a methyl and a iodine radical, and calculated that the radical sources are sufficient to produce the measured amounts of methyl iodide. The iodine atoms are formed readily by many photochemical oxidants and the photolysis of organic iodides (Moore and Zafiriou, 1994, and literature cited therein). The direct photolysis of a carbon-iodine bond requires about  $209 \pm 21 \text{ kJ mol}^{-1}$  and that of a carbon-carbon bond about  $607 \pm 21 \text{ kJ mol}^{-1}$  (Kerr, 1990). These energies require wavelengths of  $572 \pm 60 \text{ nm}$  and  $197 \pm 7 \text{ nm}$ , respectively. During incubation 5 and 6 some flasks were incubated without UV by covering them with glass beakers. The values without UV show no significant difference to the ones kept in full sunlight (see Table 7).



**Figure 37: Transmission spectrum of the special UV blocking foil used in incubation 8 (from W. Gaul, personal communication).**

Simple tests on board with the glass beakers showed that the glass only partly reduced the UV radiation to about 60% of the value without the glass. For a third incubation (incubation 8) a special foil for blocking UV radiation was used. It blocks all wavelengths under 400 nm to less than 10% (see Figure 37). Again no significant difference between samples with full sunlight and without UV were found. But in this case the energy of the sunlight penetrating the foil has insufficient energy for direct photolysis of carbon-carbon bonds to produce methyl radicals. Thus the source for the methyl radicals in the radical recombination pathway proposed by *Moore and Zafiriou* (1994) remains unknown. *Pos et al.* (1998) postulated a possible photoproduction pathway for carbon monoxide (CO) from pyruvate-like substances via an acetyl-radical, which releases a methyl radicals as a side product. They stated that the production of CO by this pathway can be neglected in natural waters since the concentrations of the necessary ketoacids are very low and the microbial uptake of these acids is fast compared to photolysis rates. No numbers for the production rate or the necessary wave lengths are given by the authors. Another possible mechanism which produces methyl radicals is the reaction of hydroxyl radicals with dimethyl sulfoxide (DMSO) (e.g. *Mezyk and Madden*, 1996). Unfortunately no reaction rates are given for this reaction, but at DMSO concentrations of about  $6$  to  $8 \cdot 10^{-9}$  mol L<sup>-1</sup> (*Hatton*, 2002) this mechanism can yield a maximum of  $6$  to  $8 \cdot 10^{-9}$  mol L<sup>-1</sup> methyl radicals, if all DMSO reacts to give methyl radicals. This seems unlikely given a hydroxyl radical concentration of about  $4 \cdot 10^{-19}$  mol L<sup>-1</sup> (*Quian et al.*, 2001). Methyl radicals react very fast with oxygen and *Moore and Zafiriou* (1994) estimated a half live of 1 ms for methyl radicals in air-saturated solutions, requiring a steady state formation rate of  $1 \mu\text{mol L}^{-1} \text{s}^{-1}$  to sustain a steady state methyl

radical level in the  $\text{pmol L}^{-1}$  range. This concentration is needed for their observed methyl iodide production. Additional reactions, which compete with the methyl iodide formation for methyl radicals, like the recombination of methyl radicals (*Mezyk and Madden, 1996*), will increase the necessary formation rate even further. From these arguments the availability of methyl radicals from the discussed sources seems to be too low to sustain the measured methyl iodide production, unless other, not known, sources of methyl radicals exists.

Another production pathway of methyl iodide without involvement of methyl radicals has been proposed. A significant covariance between methyl iodide and dimethyl sulfide (DMS) concentrations lead *Bassford et al. (1999)* to speculate over related formation mechanisms for both species. A direct production of methyl iodide from DMS during the incubation experiments performed during M55 is unlikely, because the contents of the incubation flasks have been purged during the measurement prior to incubation. Hence the volatile DMS has been removed during the purging. The production of methyl iodide from dimethyl sulphonium propionate (DMSP), a precursor of DMS, is not influenced by the purge step prior to incubation. The reaction rate for the reaction of DMSP with iodide has been measured by *Hu and Moore (1996)*, who calculated a maximum production of methyl iodide from DMSP of  $3.36 \cdot 10^{-10} \text{ nmol L}^{-1} \text{ d}^{-1}$  with a iodide concentration of  $0.47 \mu\text{mol L}^{-1}$  and the highest reported seawater concentration for DMSP of  $200 \text{ nmol L}^{-1}$ . The methyl iodide source by this reaction can be neglected.

The formation pathway of methyl iodide in the incubation experiments seems to be photochemical since it is solemnly dependent on light, but no information about the mechanism was gained with the incubations. Further experiments are necessary to investigate the formation pathway of methyl iodide, for example incubation experiments with artificial light for a better control over wavelengths and light intensities.

#### 4.4.1 Freshwater controls

In the incubation experiments 1 and 3 to 5, freshwater controls had been done with tap water from the ships drinking water supply. The results showed a large scatter with higher values in the light (mean  $0.13 \pm 0.5 \text{ pmol}$ ) than in the dark (mean  $0.04 \pm 0.026 \text{ pmol}$ , see Table 8), but overall these results are lower than the results from untreated seawater samples ( $0.33$  and  $0.08 \text{ pmol}$  for samples kept in light and dark, respectively, see Table 7). The result of incubation 1 for the freshwater controls kept in the dark is with  $0.012 \text{ pmol}$  lower than the estimated blank value of  $0.028 (\pm 0.008) \text{ pmol}$ , the latter calculated from the purging efficiency of 90 % with the initial methyl iodide content of  $0.28 (\pm 0.08) \text{ pmol}$  prior to the incubation. During incubation 3 to 5 the blank was lower with  $0.007 (\pm 0.002) \text{ pmol}$ , because this incubations had been done with water from 200 m depth which has lower methyl iodide concentrations, thus the methyl iodide content after incubations 3 to 5 can not be explained

as a blank. We had expected the controls to show no production but it seems that the tap water (or drinking water) still contains some iodide and organic carbon. The drinking water on board is cleaned seawater. The cleaning process consists of filtration followed by reverse osmosis. The resulting water contains no salt or organic material but it is mixed with some filtered seawater to adjust a salt level required for drinking water. It seems that this dilution introduces enough iodine and organic carbon to the water to give some limited production of methyl iodide during the incubation experiments. For this reason no more controls were done during incubation experiments 6 to 8. For the future, controls should obviously be done with distilled water which does not contain iodine or organic carbon.

**Table 8: Results from freshwater control measurements during the incubation experiments.**

	kept in the light [pmol]	kept in the dark [pmol]
Incubation 1	0.104	0.012
Incubation 3	0.044 0.108	0.025 0.065
Incubation 4	0.127 0.156	0.072 0.049
Incubation 5	0.168 0.201	0.014

#### 4.4.2 Production rates

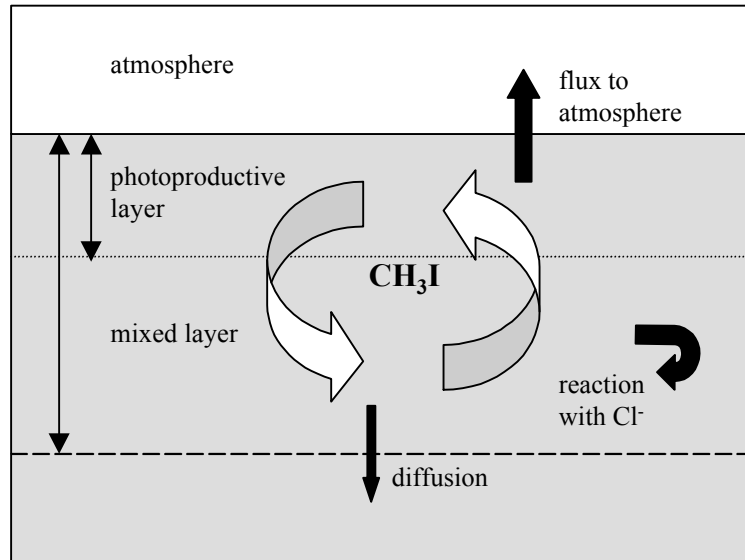
Production rates were estimated from the incubation experiments by dividing the produced amount of methyl iodide by the incubation time and the incubated seawater volume. A daily rate of photoproduction was estimated from these values by subtracting the dark from the light value. The results are shown in Table 9. The photoproduction rates from the different treatments show no significant difference (t-test,  $\alpha = 5\%$ ), which again indicates that the observed methyl iodide production is not by direct biological processes which would have been inhibited or influenced by filtering or poisoning. The calculated production rates are net rates, because they do not account for losses of methyl iodide due to photolysis and halogen exchange reaction with chloride during the incubation.

**Table 9: Net production rates from incubation experiments.**

treatment	production rate (light) [nmol m <sup>-3</sup> h <sup>-1</sup> ]	production rate (dark) [nmol m <sup>-3</sup> h <sup>-1</sup> ]	photoproduction rate [nmol m <sup>-3</sup> h <sup>-1</sup> ]
untreated	0.17 ± 0.06	0.03 ± 0.02	0.14 ± 0.07
filtered	0.10 ± 0.04	0.02 ± 0.02	0.08 ± 0.04
poisoned	0.21 ± 0.10	0.03 ± 0.01	0.18 ± 0.11
all	0.15 ± 0.07	0.03 ± 0.02	0.12 ± 0.07

The calculated daily photoproduction rates of 0.1 to 0.2 nmol m<sup>-3</sup> h<sup>-1</sup> are somewhat lower than the 0.2 – 0.3 nmol m<sup>-3</sup> h<sup>-1</sup> calculated by *Moore and Zafiriou* (1994). This may be due to the short incubation times of 0.5 to 2 hours used in their experiments. They stated that the production rate tends to decrease with increasing irradiation time and in our incubation experiments the irradiation by sunlight was from sunrise till sunset and therefore much longer than in their experiments. In the experiments done during M55 the incubation time included parts of the night without sunlight, because results as close to reality as possible were wanted. Thus the production rates have been calculated for a full day without respect for irradiation time. If only the irradiation time is used in calculating production rates, their value would be about twice the ones in Table 9 and well within the range of the values from *Moore and Zafiriou* (1994).

In order to assess the importance of the estimated photochemical production this source and the sinks of methyl iodide in the mixed layer, which is the upper, well mixed part of the ocean and the only part which exchanges with the atmosphere, have to be estimated. The mixed layer depth during the eastern part of M55, where the incubation experiments were done, was about 30 m (B. Quack, personal communication). The layer of photoproduction is dependent of the depth which is reached by a sufficient amount of light, which is dependent on the wave length. During the M55 cruise overall light intensities have been measured at several depths, but there was no possibility of measuring light depth profiles for different wave lengths. The mean intensity was 29 ± 18.7 % of the initial value at 10 m depth and 12 ± 9.2 % at 20 m depth (K. Lochte, personal communication). The 1 % level was reached at depths between 20 and 80 metres. *Faust* (1999) defines the “photochemical zone” as the maximum depth for the light level corresponding to 0.1 % of the incident light for the wavelength range of interest and gives an average depth of 6 – 30 metres for marine waters and a wavelength of 400 nm. The result for incubation 2 with reduced light levels indicated that the photochemical production of methyl iodide is already very low at light intensities of about 50 % of the initial value, but from this single experiment alone no quantitative



**Figure 38: Simplified model of the sources and sinks of methyl iodide in the mixed layer.**

information about the light dependence of the photochemical methyl iodide production can be derived. For the following calculations a depth for the layer of photochemical production of 5 m and 10 m was guessed. The losses of methyl iodide from the mixed layer are the flux to the atmosphere, reaction with chloride and diffusion into deeper water (see Figure 38).

Calculating the source strength from mean rate of  $0.12 \text{ nmol m}^{-3} \text{ h}^{-1}$  from the incubation experiments for the whole mixed layer (30 m) gives  $0.02 \text{ nmol m}^{-3} \text{ h}^{-1}$  with a photoproductive layer of 5 m and  $0.04 \text{ nmol h}^{-1} \text{ m}^{-3}$  with a photoproductive layer of 10 m. The mean flux to the atmosphere during M55 was calculated with  $0.95 \text{ nmol m}^{-2} \text{ h}^{-1}$  (chapter 3.4.5, calculated with W92), which corresponds to a methyl iodide loss of  $0.032 \text{ nmol m}^{-3} \text{ h}^{-1}$  with a mixed layer depth of 30 m. The methyl iodide loss due to the reaction with chloride is calculated with  $0.053 \text{ nmol m}^{-3} \text{ h}^{-1}$  for the whole mixed layer, according to *Elliott and Rowland* (1993). The mean seawater concentration of  $10.7 \text{ pmol L}^{-1}$  during the eastern part of M55 (see chapter 3.2.2), where the incubation experiments were done, was used in the calculation. The chloride concentration of  $0.546 \text{ mol L}^{-1}$  was used, derived from the mean salinity of 35.0 measured during M55, together with the measured mean seawater temperature of  $28^\circ\text{C}$  from M55. For the estimate of the diffusive loss methyl iodide concentration gradient is needed. The measured concentration of  $10.7 \text{ pmol L}^{-1}$  for the mixed layer was used together with a concentration of  $0.5 \text{ pmol L}^{-1}$  at 100 m depth, which have been measured during M55 (A. Chuck, personal communication). An estimate of the turbulent diffusion out of the mixed layer was made with following formula (*Bange and Andreae*, 1999)

$$D_d = -\frac{K_D \cdot [(CH_3I)_{ML} - (CH_3I)_{DW}]}{d_{ML} - d_{DW}} \quad (31)$$

where  $K_D$  is the diapycnal diffusivity ( $10^{-5} \text{ m}^2 \text{ s}^{-1}$ , *Polzin et al.*, 1997),  $(CH_3I)$  is the methyl iodide concentration in the mixed layer ( $ML$ ,  $10.7 \text{ pmol L}^{-1}$ ) and in the deep water ( $DW$ ,  $0.5 \text{ pmol L}^{-1}$ ), respectively,  $d_{ML}$  is the mixed layer depth (30 m) and  $d_{DW}$  is the reference depth of 100 m. This gives a diffusive flux of  $1.46 \times 10^{-6} \text{ nmol m}^{-2} \text{ s}^{-1}$  or  $0.0052 \text{ nmol m}^{-2} \text{ h}^{-1}$ , which gives a loss of  $0.17 \times 10^{-3} \text{ nmol m}^{-3} \text{ h}^{-1}$  calculated for the entire mixed layer. This amount is insignificant (about  $1/100^{\text{th}}$ ) compared to the losses from flux and halogen exchange. The calculated strengths of the source and sinks are listed in Table 10.

**Table 10: Calculated source and sinks for methyl iodide to the mixed layer (depth 30 m, calculations explained in the text).**

Source	[ $\text{nmol m}^{-3} \text{ h}^{-1}$ ]	Sinks	[ $\text{nmol m}^{-3} \text{ h}^{-1}$ ]
photochemical production (5 m depth)	0.02	flux to the atmosphere	0.032
photochemical production (10 m depth)	0.04	reaction with chloride	0.053
		diffusion	0.00017

These calculation shows that the combined losses are higher than the photochemical source by a factor of 2 to 4, depending on which photoproducer layer depth is taken. It has to kept in mind that no information about the depth of the photoproducer layer is available, because the reaction pathway leading to the production of methyl iodide is not known. The depth of the productive layer may be more than 10 m, especially in the tropics due to the high light intensity and the clear water. Additionally, the sink due to the reaction with chloride may be overestimated, because the high methyl iodide concentrations from the eastern part of M55 were used, which are not representative for the open ocean. With lower methyl iodide concentrations the loss by this reaction decreases.

*Moore and Zafiriou* (1994) calculated that with a production rate of 0.15 and a loss rate by flux to the atmosphere of  $0.3 \text{ nmol m}^{-2} \text{ h}^{-1}$ , a water layer of 2 m with this production rate would be sufficient to support the flux. During the M 55 cruise we calculated a mean flux to the atmosphere of  $0.95 \text{ nmol m}^{-2} \text{ h}^{-1}$  (chapter 3.3.5, calculated with W92) which would



require a 8.1 m layer with a production rate of  $0.12 \text{ nmol m}^{-3} \text{ h}^{-1}$ , without a correction for the loss due to the reaction with chloride. Including the loss with a rate of  $0.042 \text{ nmol m}^{-3} \text{ h}^{-1}$  according to *Elliott and Rowland* (1993) ( $T = 28 \text{ }^\circ\text{C}$ , methyl iodide concentration of  $8.7 \text{ pmol L}^{-1}$ ,  $S = 35.0$  {mean values from M55}) increases the necessary productive layer depth to about 14 m. These photoproduktive layer depths seem reasonable because the production does not depend on UV light whose intensity decreases very rapidly with depth and the open ocean water is more lucid as the coastal water used by *Moore and Zafiriou*. And the attenuation of sunlight by seawater increases with decreasing wavelengths in the range between 300 to 400 nm (*Faust*, 1999), so longer wavelengths penetrate deeper into the seawater. The results from incubation 8, with the foil blocking light with wavelengths below 400 nm, seem to indicate that short wavelengths below 400 nm are not important for the reaction pathway leading to the formation of methyl iodide. The calculated photoproduktive zone of 14 metres to match the flux of methyl iodide to the atmosphere and the loss by halogen exchange with chloride seems to fit the available data. Further investigation is needed to evaluate the mechanism of photochemical methyl iodide production and its importance outside the tropical regions, where these experiments have been done.

## 5. Discussion

In the previous chapters it has been discussed that the oceans represent a net source of methyl iodide for the atmosphere with a mean flux from all measurements of  $22.0 \text{ nmol m}^{-2} \text{ d}^{-1}$ , if calculated with the transfer velocity of *Wanninkhof* (1992), and  $16.2 \text{ nmol m}^{-2} \text{ d}^{-1}$ , if calculated with the transfer velocity of *McGillis et al.* (2001). It was further noted that the surface water concentration of methyl iodide seems to be greatly influenced by the wind speed. The results from our incubation experiments point to a photochemical pathway for the formation of methyl iodide in the open ocean, rather than direct biological production e.g. by phytoplankton or bacteria.

In this chapter an attempt will be made to calculate a global flux and the uncertainties in the flux estimates will be discussed. Afterwards the results will be placed in the context of the global budget of methyl iodide. The sources of methyl iodide in the ocean will be discussed in the light of a photochemical production as indicated by the incubation experiments. Finally possible directions for future research will be outlined.

### 5.1 Flux calculations

To calculate the global ocean-atmosphere flux of a substance an extensive set of data about the concentration anomaly, wind speed, sea surface temperature and other factors influencing the air sea flux is needed. The data should cover all ocean regions and all times of the year to take into account spatial differences as well as seasonal to diurnal variability. Such data sets exist for the sea surface temperature from satellite images and for wind speed. However, measurements of the concentration anomaly of methyl iodide are limited. Research cruises cover only parts of the global ocean for days or weeks during a cruise, thus missing much temporal variability in the methyl iodide distribution. Some coastal stations can cover the whole year, thus showing diurnal and seasonal cycles at one location, but because of the small number of such stations and their limitation to coastal sites their data are not representative for the whole ocean.

Two different approaches have been used to circumvent these limitations in the methyl iodide data set. One is to measure the concentration anomaly or the flux in different water masses thought to be representative for a certain kind of ocean region, such as upwelling areas, tropical oceans or coastal regions, and calculate from these data the flux for the whole region. The problem is that the measured data may not be representative for the whole region and it is difficult to define the areas for such a region. For example how far from the shore line ends the region of coastal influence? This has led to the definition of a variety of oceanic regions (e.g. *Dietrich et al.*, 1975, *Rasmussen et al.*, 1982, *Longhurst et al.*, 1995) which is seldom consistent between different authors.

A second approach is to calculate a mean flux using data from as many different regions and times as possible and calculate a global flux from this mean value using the area of the whole ocean. Calculating such a mean value loses all information about spatial and seasonal variation and introduces error due to under- or over-representation of methyl iodide saturation anomalies from certain areas with very high or very low values.

A possible solution to the problem of a non representative data set of methyl iodide concentrations or concentration anomalies is the use of proxies which can be readily measured for the whole ocean, at the best with satellites. Such proxies will be discussed in the next section.

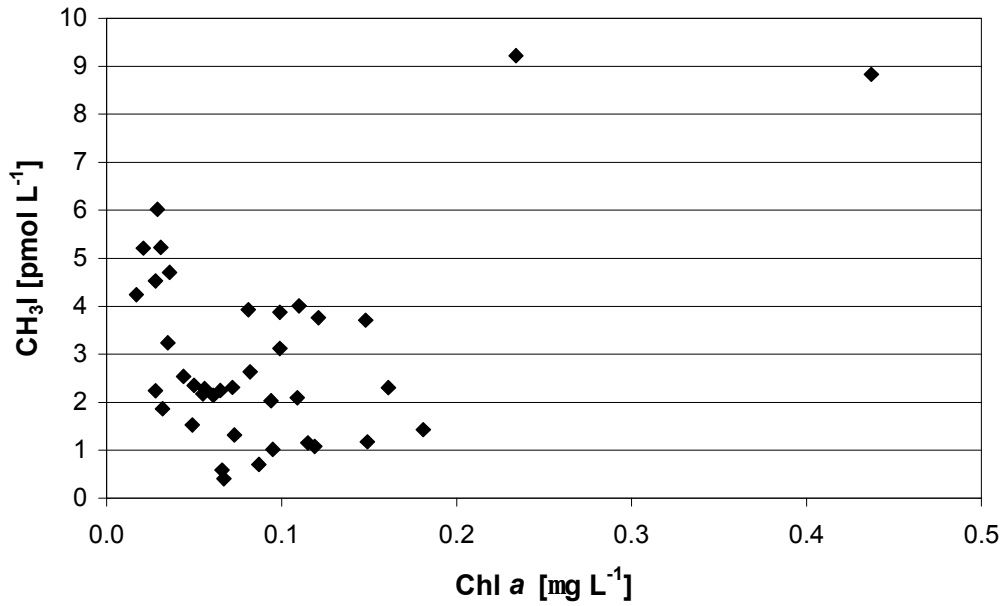
### 5.1.1 Proxies for methyl iodide?

Possible proxies for the surface water concentration of methyl iodide are the chlorophyll concentration and the sea surface temperature, which can both be estimated globally by satellites.

Several authors have tried to find a correlation between chlorophyll or another pigment with the methyl iodide concentration. *Abrahamsson and Ekdahl* (1993) could not detect any correlation between methyl iodide concentration and chlorophyll content in the Skagerrak. *Schall et al.* (1997) found a weak correlation between methyl iodide and chlorophyll *a* concentration in the Atlantic, but at some occasions peaks in the chlorophyll *a* were co-located with very low methyl iodide concentrations. *Moore and Groszko* (1999) found no overall correlation between chlorophyll *a* and methyl iodide concentrations in their data from the eastern Atlantic and Pacific, but found some relationship between these two quantities on short time scales. They stated that the reason may be the production of methyl iodide by specific organisms whose abundance is not well correlated with bulk chlorophyll *a* concentration. The same argument was used by *Hughes* (2001), who found no significant correlation in the entire data set but again an indication of some correlation between methyl iodide and certain pigments over small spatial scales.

During the Pos255 cruise in the north Atlantic some samples for the measurement of chlorophyll *a* were taken. Figure 39 shows a correlation plot of surface water methyl iodide concentrations with chlorophyll *a* concentration. There is no correlation between these two quantities in our data, except that the two highest methyl iodide concentrations fall together with the highest measured chlorophyll *a* concentrations. This is insufficient to postulate a general correlation between them.

These results show that chlorophyll *a* can not serve as a proxy for surface water methyl iodide concentrations or for the concentration anomaly of methyl iodide.

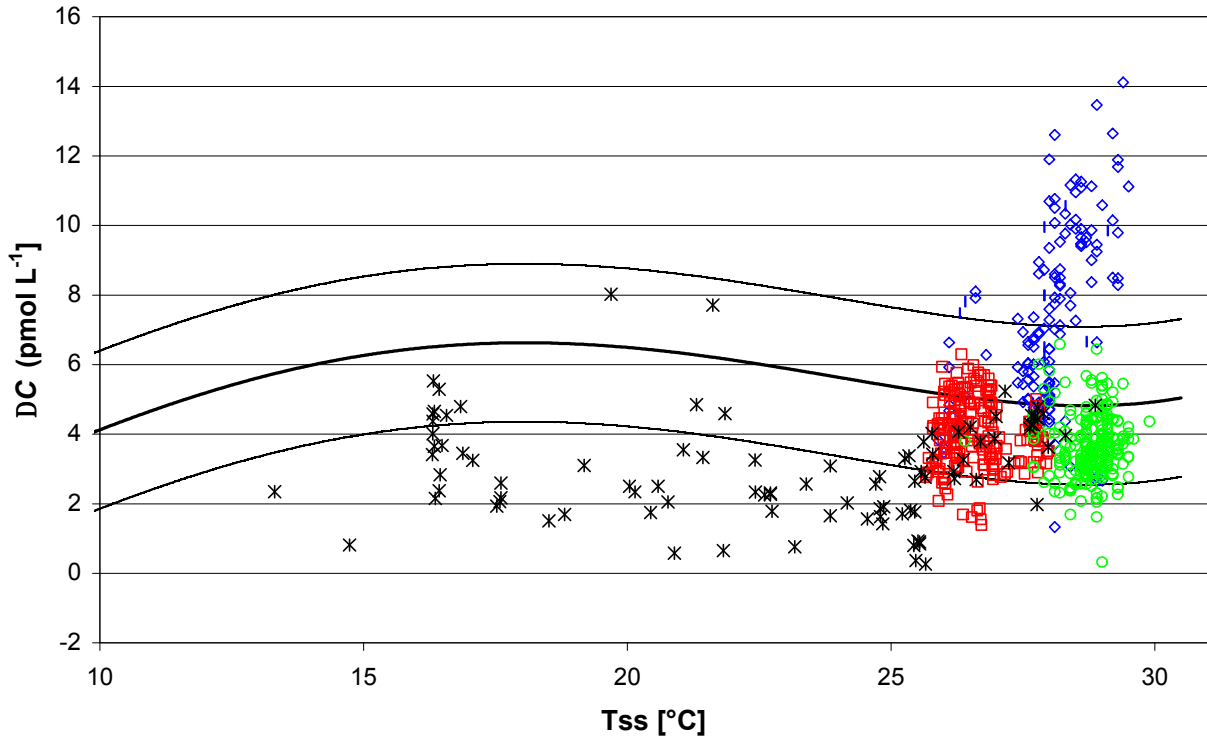


**Figure 39: Correlation between chlorophyll *a* and surface water methyl iodide concentration.**

*Groszko* (1999) proposed an empirical relationship between sea surface temperature and concentration anomaly with a best-fit function for methyl iodide of

$$\Delta C = -0.8770 + 0.01114 \cdot T + 0.09928 \cdot T^2 - 5.998 \cdot 10^{-3} \cdot T^3 + 9.638 \cdot 10^{-5} \cdot T^4 \quad (32)$$

where  $\Delta C$  is the concentration anomaly in  $\text{pmol L}^{-1}$  and  $T$  is the sea surface temperature in  $^{\circ}\text{C}$ . He stated that about 63% of the variance of methyl iodide concentration anomalies is accounted for by this function. But above a temperature of  $15^{\circ}\text{C}$  the variance increased and an arithmetic average would yield the same precision as the best-fit function given by equation (32). Nevertheless *Groszko* (1999) used this function for his flux calculation because it is valid over the whole temperature range. *King et al.* (2000b) presented a linear relationship between sea surface temperature and methyl iodide saturation anomaly. The latter was defined as the difference between the partial pressure in water and the partial pressure in air, given as a percentage. Their data also showed a larger variance in saturation anomalies above  $15^{\circ}\text{C}$  compared to the situation below  $15^{\circ}\text{C}$ . This correlation is derived from observations and not from first principles, and temperature is not the only factor influencing the net flux. They argued that for these reasons their relationship should not be used to estimate net fluxes of methyl iodide.



**Figure 40:** Correlation between sea surface temperature and methyl iodide concentration anomaly. Data from M55 (green diamonds), M47 (blue triangles), So 152 (red squares) and Pos255 (black stars). The black lines indicate the best-fit fourth-order function from *Goszko (1999)* with upper and lower error lines.

My data, which are collected largely in water with a temperature above 15°C, show no correlation between sea surface temperature and concentration anomaly or methyl iodide concentration. Figure 40 shows the results from the four cruises as function of temperature together with the best-fit function from *Goszko (1999)*. As discussed in chapter 3.4 the discrepancies between our data and the best-fit function can be explained by the influence of the wind speed on the flux which in turn strongly impacts the concentration anomaly assuming a constant source. This underlines the necessity for a better understanding of sources and reactions of methyl iodide in the ocean and of the factors influencing the flux of methyl iodide.

*Bell et al. (2002)* calculated the oceanic source strength of methyl iodide in their model as a function of dissolved organic carbon (DOC, monthly average fields taken of *Six and Maier-Reimer, 1996*) and the solar radiation flux at the surface (RAD, monthly average values from GEOS fields from 1994) by

$$P = \mathbf{b} \cdot [\text{RAD} \cdot \text{DOC}] \quad (33)$$

where  $\mathbf{b}$  is a scaling parameter ( $0.1 \text{ m}^2 \text{ W}^{-1} \text{ h}^{-1}$ , by least-squares fit of model results). If the photochemical production is the main source of methyl iodide to the ocean and all sinks excluding the flux are known, the flux can be estimated by balancing the source and the sinks.

For the use of proxies the sources and sinks and the factors influencing their strength have to be understood. Neither chlorophyll concentration or surface water temperature can serve as a useful proxy for the methyl iodide concentration or concentration anomaly. A better basic understanding of the processes controlling the oceanic cycling of methyl iodide will give a better choice of proxies for its ocean-atmosphere flux.

## 5.1.2 Global ocean atmosphere flux

Several attempts have been made to calculate the global ocean-atmosphere flux. Most investigators agree that the ocean-atmosphere flux is in the range of  $10^{11}$  grams per year or gigamoles per year. The global flux estimates from some authors are listed in Table 11, together with the estimates from this thesis.

**Table 11:** Comparison of different calculated fluxes. W92 means the relationship from *Wanninkhof (1992)* and McG01 the relationship from *McGillis et al. (2001)*. Literature value have been converted to  $\text{Gmol a}^{-1}$ .

Flux [ $\text{Gg a}^{-1}$ ]	Flux [ $\text{Gmol a}^{-1}$ ]	relationship used for the calculation of k	source
270	1.90	$k = 10.6 \text{ cm h}^{-1}$	<i>Liss and Slater (1974)</i>
1300	9.16	$k = 11 \text{ cm h}^{-1}$	<i>Rasmussen et al. (1982)</i>
300 - 500	2.11 – 3.52	$k = 10.6 \text{ cm h}^{-1}$	<i>Singh et al. (1983)</i>
800	5.64	$k = 10.2 \text{ cm h}^{-1}$	<i>Reifenhäuser and Heumann (1992)</i>
344	2.42	W92	<i>Groszko (1999)</i>
225 – 330	1.59 – 2.32	W92	<i>Moore and Groszko (1999)</i>
210	1.48	#	<i>Bell et al. (2001)</i>
214	1.51	$k = 0.23u^2 + 0.1u$ ‡	<i>Bell et al. (2002)</i> (from model calculations)
410	2.89	W92	this work
189	1.33	McG01	

# Calculation of k is not stated

‡ taken from *Nightingale et al. (2000a)*

The global flux estimate from *Rasmussen et al.* (1982) is extremely dependent on the high methyl iodide concentrations measured by *Lovelock* (1975) in coastal areas with high biomass productivity. From these data *Rasmussen et al.* calculated a net flux of  $7.0 \text{ Gmol a}^{-1}$  for high biomass productive areas, albeit they only contribute about 10% of the total ocean area in their calculation. In the light of subsequent measurements this high global flux seems to be an overestimate. The other literature values are all comparable within the uncertainties in the calculations. The global flux data from this thesis are shown in Table 11 twice, one time calculated using the relationship from *Wanninkhof* (1992) for the calculation of the transfer velocity and another time calculated with the relationship from *McGillis et al.* (2001). In both cases the value is the mean of all flux estimates from the different cruises. It may be favourable to calculate a mean concentration anomaly and then using this together with meteorological wind data to calculate the global flux as proposed by *Groszko* (1999), but from our data sets, especially from the M55 cruise, it seems the concentration anomaly may be strongly influenced by the wind speed as discussed in chapter 3.4, leading to higher concentration anomalies at low wind speeds and vice versa. This can result in comparable fluxes from areas with very different concentration anomalies. To highlight this point in Figure 41 the measured concentration anomalies and fluxes from the M55 cruise are plotted together along the cruise track. The fluxes do not change despite an along-track increase in the concentration anomalies.

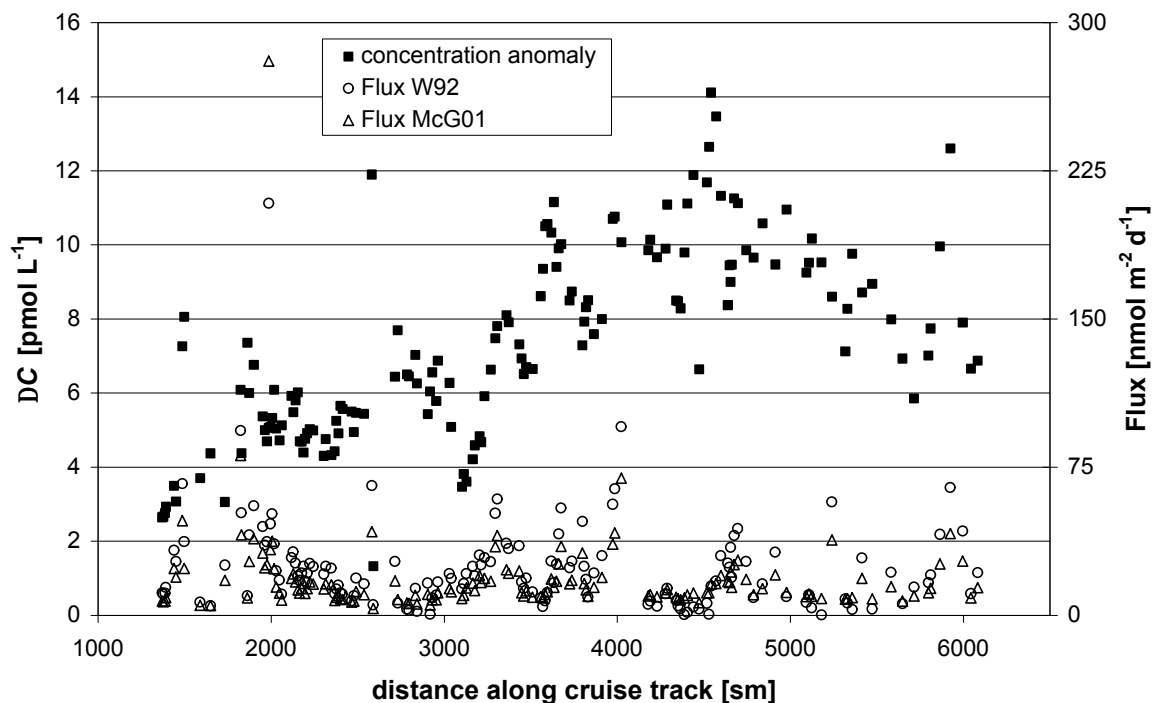


Figure 41: Concentration anomalies (solid squares) and calculated fluxes (open circles for W92 and open triangles for McG01 calculation) from M55.

Calculating the global flux from single flux measurements causes an uncertainty, because the measured single flux may not be representative since it is sensitive to short term changes in the wind speed. This may lead to over- or under-estimations of the compared to the real flux. Averaging over many single flux measurements should reduce the uncertainty, but the error introduced in the calculation by this problem is quite difficult to estimate. Despite this uncertainty the global flux was calculated in this thesis as the mean of the individual flux calculations instead of the mean concentration anomaly, because of the relatively big discrepancy in the trend between the measured concentration anomaly and the flux shown in Figure 41.

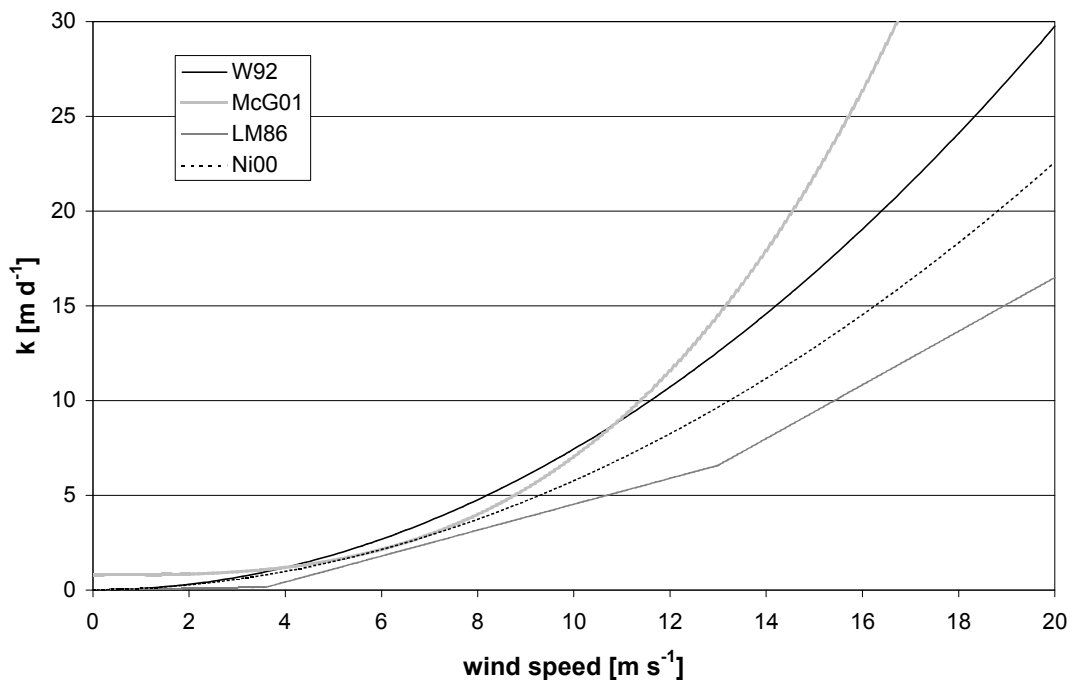
There are a variety of uncertainties in the calculated global flux which are difficult to assess. First there are the analytical uncertainties in the measurement of the surface water and especially air concentrations of methyl iodide due to its low concentration. With the instruments used today and good standards the precision is normally better than 10 %. On additional error may be introduced by the fact that most measurements of the surface water concentration are done with water from 2 to 10 m depth, because either submersible pumps located at the bottom of a ship are used to collect sample water or the sample water is taken from the topmost Niskin-bottle of a station. In both cases the concentration of methyl iodide may not represent the situation at or very close to the air-sea interface. It is the interfacial concentration that determines the air-sea flux.

*Yokouchi et al.* (2001) introduced a new model with photochemical production of methyl iodide very close to the water surface, which would lead to a subsurface maximum in the methyl iodide concentration located only centimetres below the surface. So far no sampling procedure has sampled methyl iodide with such fine depth resolution, making it impossible to test this model with data. Until a sampling procedure capable of a depth resolution in the centimetre range is developed, and/or a better understanding of the processes responsible for methyl iodide formation is achieved, this possible mechanism can not be confirmed or excluded. The potential influence of such a near-surface production and maximum is high, since it directly changes the concentration anomaly and hence the flux.

Another uncertainty is caused by the lack of a data set covering the whole ocean and all seasons. Calculating the global flux as the mean of measured fluxes results in variances depending on the data set used. For example, calculating the global flux from the mean of all cruises in this thesis gives a result of  $2.89 \text{ Gmol a}^{-1}$ . Excluding the flux measurements from the So152 cruise which are generally higher than the results from all other cruises and the literature values results in a global flux of  $2.27 \text{ Gmol a}^{-1}$ . This is a difference of 27 %. Calculating the global flux from every individual cruise gives 2.15, 1.75, 4.36 and  $2.98 \text{ Gmol a}^{-1}$  for Pos255, M47, So152 and M55, respectively. This is a variance of -40 to +51 % from the mean. A slightly lower range of -25 to + 11 % of the mean of  $2.10 \text{ Gmol a}^{-1}$  was given by *Moore and Groszko* (1999). This highlights the necessity of a data set with better spatial and seasonal coverage to reduce the uncertainty associated with undersampling.



The major uncertainty in flux calculations is caused by the different values for the transfer velocities  $k$  from different models. The global flux in this thesis was calculated twice, one time with the transfer velocity calculated following *Wanninkhof* (1992) and a second time with transfer coefficient from *McGillis et al.* (2001). The resulting global flux calculated with the W92 relationship is about 54 % higher than that calculated with the McG01 relationship. Use of other relationships from in the literature, would result in even higher differences. This is illustrated in Figure 42 where the dependence of the transfer velocity on the wind speed is shown for relationships from several different authors, and in Table 12 where the resulting transfer velocities from these different relationships are shown for four different wind speeds. The variance between the different values exceeds 50 % and is therefore the limiting factor which determines the precision and accuracy of the global flux calculations.



**Figure 42:** Wind speed dependence of the transfer velocity  $k$  after *Wanninkhof* (1992, marked W92), *McGillis et al.* (2001, marked McG01), *Liss and Merlivat* (1986, marked LM86) and *Nightingale et al.* (2000, marked Ni00). All calculations are for a Schmidt number of 660 (which is the one for  $\text{CO}_2$  at  $20^\circ\text{C}$ ).

**Table 12:** Calculated transfer velocities [ $\text{m d}^{-1}$ ] at certain wind speeds. The notations used are same as in Figure 42. All calculations are for a Schmidt number of 660 (which is the one for  $\text{CO}_2$  at  $20^\circ\text{C}$ ).

wind speed [ $\text{m s}^{-1}$ ]	LM86	W92	Ni00	McG01
2	0.07	0.30	0.22	0.83
5	1.10	1.86	1.50	1.57
10	4.52	7.44	5.76	7.03
15	9.41	16.74	12.78	21.85

Taking into account the different sources of variance and error in the global flux calculations the overall uncertainty is at least 50 %. To improve this uncertainty an improvement in calculating the transfer velocity is most urgently needed. To achieve this all the factors influencing the transfer velocity have to be fully understood. The data set of methyl iodide concentrations in the ocean needs to be extended in spatial coverage and for the possibility of seasonal variations. The use of more rigorous proxies would improve the data base, if such proxies can be found. Another way to improve the flux estimates can be the better understanding of sources and sinks in the ocean, since the production rate should be equal to all sinks including the flux, assuming a steady state.

Within these uncertainties the mean flux from this thesis is in reasonable agreement with the previously calculated fluxes.

## **5.2 Global budget of methyl iodide**

The known sources of methyl iodide and there strengths are listed in Table 13 together with estimates of the photolytic loss which is believed to be the only important sink for methyl iodide in the atmosphere. The most important source of methyl iodide for the atmosphere is the flux from the oceans, contributing about 90 % of the total. From the land biota, rice paddies contribute another 10 %, but only a few investigations have been done with other plants. *Dimmer et al.* (2001) measured methyl iodide fluxes from a peatland ecosystem which represented a small contribution of  $< 1$  % to the overall source strength. Similar small contributions come from biomass burning and vulcanism. *Amachi et al.* (2001) showed in incubation experiments that several species of soil bacteria are capable of methylating iodine but because of the unknown distribution of bacteria in the different environments and the

difference in physiological conditions between the laboratory and environment, no attempt was made to calculate a global flux from this source. Another source from the soil may be the reaction of halide ions when organic matter is oxidized in the presence of a redox partner like Fe(III)-ions, as proposed by *Kepler et al.* (2000). Again no estimate of the source strength from this reaction has been made since the laboratory experiments do not represent environmental conditions. Higher plants have been shown to have the ability to produce methyl iodide, too (*Saini et al.*, 1995), but the results are also from laboratory experiments and no investigation has been done to evaluate the possible importance of this reaction in the environment. Hence no flux estimate from higher plants is possible.

**Table 13: Overview of sources and sinks of methyl iodide in the atmosphere.**

<b>Sources:</b>	[Gmol a <sup>-1</sup> ]	
Ocean	1.33 – 2.89	this work
Rice paddies	0.18 0.50 0.30 – 0.66	<i>Muramatsu and Yoshida</i> (1995) <i>Redeker et al.</i> (2000) <i>Redeker et al.</i> (2002)
Biomass burning	0.024 – 0.060 0.014 – 0.028	<i>Andreae et al.</i> (1996) <i>Blake et al.</i> (1996)
Volcanic emissions	< 0.018	<i>Jordan et al.</i> (2000)
Peatland ecosystems	0.010	<i>Dimmer et al.</i> (2001)
<b>total:</b>	<b>1.53 – 3.64</b>	
<b>Sinks:</b>		
Photolysis	(10.57) ~ 2.11 2.14	<i>Chameides and Davis</i> (1980) <i>Chameides and Davis</i> (1980) <sup>#</sup> <i>Bell et al.</i> (2002) (from model calculations)
<b>total:</b>	<b>~ 2.1</b>	

<sup>#</sup> corrected following *Groszko* (1999) to atmospheric methyl iodide concentrations of 1 – 2 pmol mol<sup>-1</sup>.

The sources and sinks in Table 13 balance within the uncertainties, but the great range, especially in the oceanic source, makes it difficult to address this question. The high photolytic loss from *Chameides and Davis* (1980) is based on atmospheric methyl iodide concentrations of 10 pmol mol<sup>-1</sup> in the tropics between 30°N and 30°S and 5 pmol mol<sup>-1</sup> in the rest of the atmosphere, which is most likely too high. The second value for these authors is accordingly corrected to concentrations of 2 and 1 pmol mol<sup>-1</sup> in and outside the tropics, respectively, as done by *Groszko* (1999). In the light of the higher measured air concentrations in this thesis the true photolytic loss seems to be between these two values. The absorption cross section for methyl iodide used by *Chameides and Davis* was taken from *Porret and Goodeve* (1938) and is confirmed by the more recent study from *Roehl et al.* (1997).

An additional loss mechanism for atmospheric methyl iodide is the reaction with OH radicals. But the loss by this process was found to be of minor importance and accounting for only about 2 % compared to the photolytic loss (*Brown et al.*, 1990, *Cotter et al.*, 2003).

Another possible loss of methyl iodide is to aerosol particles in the atmosphere and subsequent deposition. *Baker et al.* (2000b) measured iodine concentrations in atmospheric aerosol and found a significant difference between total iodine and inorganic iodine concentrations. They concluded that this difference is caused by organic iodine species. However, they argued since this organic iodine has a low volatility, it is unlikely that it is methyl iodide or another low molecular weight organoiodine compound. Thus atmospheric aerosol seems not to be a significant sink of atmospheric methyl iodide, albeit until now the loss by this pathway has not been estimated.

From these calculations the global budget of methyl iodide may be balanced, but due to the uncertainties it is still possible that the sources exceed the sinks or vice versa. Unless the estimates of sources and sinks are more precise the balance or imbalance of the global budget can not be decided.

### 5.2.1 Sources and sinks of oceanic methyl iodide

The sources of methyl iodide in the ocean must at least equal the flux to the atmosphere, additional production would be needed to account for any additional oceanic sinks. The sinks are known to a certain extent, but the sources of methyl iodide to the ocean are less well understood. In this chapter the sinks and sources of oceanic methyl iodide will be discussed in the light of the photochemical production from the incubation experiments presented in chapter 4.

The flux to the atmosphere is fairly well known to be in the range of 1.3 – 5.6 Gmol a<sup>-1</sup> (see last chapter). A second important sink of methyl iodide is the halogen exchange reaction with chloride and, to a lesser extent, with bromide. The rate of these reactions was

measured by *Zafiriou* (1975) and *Elliott and Rowland* (1993). Using this reaction rates, *Bell et al.* (2002) estimated the resulting sink from the reaction with chloride ions during their model runs and found a methyl iodide loss of  $1.85 \text{ Gmol a}^{-1}$ . This reaction thus contributes about same amount to the overall loss for oceanic methyl iodide as the flux to the atmosphere. The loss due to the reaction with bromide is insignificant, since the concentration of bromide is three orders of magnitude lower in sea water than the chloride concentration, and the reactivity of bromide is lower than the reactivity of chloride (*Zafiriou*, 1975). Another loss of oceanic methyl iodide is due to hydrolysis, but its rate is typically an order of magnitude slower than the reaction with chloride (*Moelwyn-Hughes*, 1938) and the loss rate was too low to be measured in the experiments done by *Elliott and Rowland* (1993). Since methyl iodide is easily destroyed by photolysis in the atmosphere the photolytic loss in seawater was measured by *Zika et al.* (1984) and was found to be insignificant, because the necessary UV radiation is extinguished quickly in the water.

The loss of methyl iodide from the ocean by the sum of all this sinks is about  $3.3 \text{ Gmol a}^{-1}$  to  $7.1 \text{ Gmol a}^{-1}$ . This amount must be accounted for by the sources in order to maintain the measured seawater concentrations.

The sources of methyl iodide in the ocean are not well known. Several investigations have been done to evaluate the role of algae and phytoplankton in producing methyl iodide. Macroalgae have been shown to produce methyl iodide in incubation experiments, and the methyl iodide concentrations in seawater and atmosphere are elevated around fields of macroalgae (e.g. *Manley et al.*, 1992, *Carpenter et al.*, 1999). The estimated source strengths are listed in Table 14 together with the estimated strength of other sources. The contribution by macroalgae is very small compared to the loss rates, due to the limited spatial distribution of the algae, but it may dominate locally at coastal sites with large algae beds. Microalgae and phytoplankton have a similar low contribution to the overall source, despite their widespread occurrence in the ocean, due to the low production rates observed in the experiments (*Manley and de la Cuesta*, 1997). Both the production rates for algae and phytoplankton have been measured in incubation experiments and the results may not be representative for environmental conditions. But even with a high uncertainty about the actual amount released from algae and phytoplankton their contribution to the overall source is almost insignificantly small on the global scale.

Bacteria are another possible source of methyl iodide and they are abundant everywhere on the world. Marine bacteria have been shown to produce methyl iodide in some incubation experiments (*Amachi et al.*, 2001). The estimates of a global methyl iodide production by bacteria range from insignificantly low to about 13 gigamoles per year. The higher values in Table 14 represent potential source strengths instead of measured ones. *Manley and Dastoor* (1988) calculated that if 80 % of the annual global kelp production is degraded microbially every year, and all the iodide contained in the kelp is converted to methyl iodide, the global production could be  $2.11 \text{ Gmol a}^{-1}$ . They stated that this value is an upper limit

**Table 14: Estimated sources of methyl iodide to the ocean.**

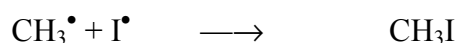
Source	[Gmol a <sup>-1</sup> ]	
Macroalgae	4 • 10 <sup>-3</sup> 0.3 • 10 <sup>-3</sup> (kelps) 0.006 • 10 <sup>-3</sup> (non kelps) ≤ 0.078 • 10 <sup>-3</sup>	<i>Manley and Dastoor</i> (1988) <i>Nightingale et al.</i> (1995) <i>Giese et al.</i> (1999)
Phytoplankton	8.45 • 10 <sup>-3</sup> (mean)	<i>Manley and de la Cuesta</i> (1997)
Bacteria	2.11 0.0042 – 13.33 (0.007 – 0.07) • 10 <sup>-3</sup>	<i>Manley and Dastoor</i> (1988) <i>Manley</i> (1994) <i>Amachi et al.</i> (2001)
Photochemical production	# 5.30	this work
<b>total:</b>	<b>5.31 – 18.64</b>	

which is most likely not reached, because not all iodide is converted to methyl iodide and some iodide may be lost from the tissue during the decay. *Manley* (1994) gave potential production rates of 0.01 to 3 ng L<sup>-1</sup> h<sup>-1</sup> from the lysis of bacterial cells when the methylcobalamin from the cells reacts with iodide from the sea salt. The stated rate is from the initial reaction rate with seawater iodide concentrations and a methylcobalamin concentration equal to that found in living bacterial cells. Once again this represents a potential production rate rather than a real one found in the environment. The results from incubation experiments with bacteria give a far lower global production rate which is insignificantly small compared to the losses (*Amachi et al.*, 2001).

In the recent literature the possibility of photochemical production has been proposed. Either observantly by higher methyl iodide concentrations in incubation experiments with filtered seawater exposed to sunlight compared to incubations kept in the dark (*Moore and Zafiriou*, 1994). Or by correlation between measured concentration anomalies and photosynthetically active radiation (*Happell and Wallace*, 1996). Further by correlation of an estimated source strength to support measured atmospheric concentrations with biological productivity (*Li et al.*, 2001, *Yokouchi et al.*, 2001), and from modelling studies (*Bell et al.*, 2002). But so far there is no direct evidence for a photochemical production and hence no estimate of the possible source strength by this mechanism. The incubation experiments from *Moore and Zafiriou* (1994) are the most direct evidence for photochemical production so far, but because they cleaned the seawater only by filtering it through a 0.45 µm silver filter the presence of bacteria was not excluded and the observed production

could possibly have been due to bacterial activity. The goal for the incubation experiments in this thesis was to provide evidence for photochemical production of methyl iodide under environmental conditions. Methyl iodide was produced in all incubations kept in the light and the measured production rates were not influenced by the treatment of the seawater prior to the incubation (either filtering through 0.1  $\mu\text{m}$  membrane filters, poisoning with mercury(II)chloride or no treatment, see chapter 4.2.2 and 4.3 for details). These observations give evidence that the observed production is via a photochemical pathway. The filtering removes all phytoplankton and some of the bacteria from the seawater and the poisoning inactivates both phytoplankton and bacteria. Thus any observed methyl iodide production is from a pathway which is independent of the presence of living cells and therefore not directly biological. The production rate calculated from the measured methyl iodide production is the net production. It was not corrected for the losses during incubation, because the rates of these losses are not known. Thus the measured production is the real photoproduction minus the losses due to halogen exchange and photolysis. This is important when estimating the balance of production and losses of methyl iodide in the ocean.

The reaction mechanisms leading to the formation of methyl iodide remains unknown from these experiments. *Moore and Zafiriou (1994)* discussed a radical recombination reaction to yield methyl iodide as follows



and estimated that the concentrations of both radicals in surface water may be sufficient to sustain the production rate of 0.2 to 0.3  $\text{nmol m}^{-3} \text{h}^{-1}$  observed in their experiments. The production rate measured during M55 was 0.24  $\text{nmol m}^{-3} \text{h}^{-1}$ , when using only the time with sunlight for the calculation. This rate fits well with the rate from *Moore and Zafiriou (1994)*. If methyl iodide is produced by this radical recombination mechanism, the production should be dependent on the concentrations of iodine atoms, methyl radicals and light intensity. As already discussed in chapter 4.4, iodine atoms are formed readily and their availability seems to be sufficient to sustain the calculated production rates, but the availability of methyl radicals is rather limited. They react very fast with oxygen (*Zafiriou et al., 1990*) and with other methyl radicals (*Mezyk and Madden, 1996*), therefore the in situ concentrations seem to be rather low. It is likely that the concentration of methyl radicals is limiting the methyl iodide production, at least in areas with sufficient light like the tropics.

Further research is needed to evaluate the mechanism for the photochemical production of methyl iodide. Maybe the production of methyl iodide is not by the proposed radical recombination mechanism, but by another, so far unknown, reaction pathway. With the knowledge of the exact production pathway for methyl iodide it might be possible to find a new tracer for its production, for example light intensity or dissolved organic carbon as used by *Bell et al. (2001)* for their model calculations, and possibly even an tracer for the ocean-atmosphere flux.

A rough estimate of the global methyl iodide production was made based on the measured production rates despite the uncertainties arising from estimating global rates from a spatial and seasonal limited set of measurements. The rates have been measured in the tropics where the solar radiation is more intense than at higher latitudes and different cloud coverage can also change the intensity of the radiation. Another uncertainty is the depth up to which photochemical production will occur. In chapter 4.4.2 we discussed that a productive layer of about 14 m is necessary to get a methyl iodide production of the same amount than the combined losses by the mean flux to the atmosphere and the reaction with chloride in the mixed layer. This productive layer depth corresponds to a decrease of ~75 % of the overall sunlight intensity during M55 (K. Lochte, personal communication). Using this depth of 14 m and the mean production rate of  $0.12 \text{ nmol m}^{-3} \text{ h}^{-1}$ , a global photochemical production of  $5.30 \text{ Gmol a}^{-1}$  is estimated. This is an upper limit because it is not corrected for lower light intensities outside the tropics. The initial incubation experiments of *Moore and Zafiriou* (1994) were done in the North Sea instead of the tropics, and they estimated a similar production rate of 0.2 to  $0.3 \text{ nmol m}^{-3} \text{ h}^{-1}$ . Thus it seems possible that the photochemical production is similar in the tropics and at mid latitudes, despite different light intensities, or that another factor than light intensity is controlling the photochemical production of methyl iodide. For a better estimate of the global production it is necessary to know the reaction pathway leading to the formation of methyl iodide, and the factors controlling the reaction like light intensity, wavelength, and/or necessary precursors (e.g. dissolved organic carbon, methyl radicals etc.). Without this knowledge it is not possible get a better and more precise estimate of the global photochemical production of methyl iodide in the ocean.

Following this estimate the photochemical production seems to be able to account for most if not all of the source strength needed to match the loss of  $3.3 \text{ Gmol a}^{-1}$  to  $7.1 \text{ Gmol a}^{-1}$  via halogen exchange reaction with chloride, hydrolysis, photolysis and flux to the atmosphere (see Table 14). Because the incubation experiments done so far are restricted to the tropics, and the resulting uncertainty in the global source estimate, it is impossible to decide if the photochemical production accounts alone for the missing amount of methyl iodide production, or if there are other so far unidentified sources. To reduce the uncertainty in the global rate of photochemical production a better understanding of the involved reaction mechanisms is needed to know the influencing and limiting factors. And a more extensive data base is needed with evaluation of production rates for a variety of regions and seasons to minimise uncertainties resulting from the calculation with a insufficient data set. Nevertheless the photochemical production of methyl iodide is likely the major source of methyl iodide for the ocean.



### **5.3 Future research**

The most important tasks for a better understanding of the global cycle and budget of methyl iodide are to reduce the uncertainties in the sea-air flux and to identify the oceanic sources of methyl iodide. The best approach is likely to get a better understanding of the factors influencing production and loss of methyl iodide in the ocean. As discussed above it seems that the surface water concentration of methyl iodide is strongly influenced by the wind speed, and hence the concentration anomaly. This can be easily explained if the production of methyl iodide in the ocean is the limiting factor. With nearly constant sources and also nearly constant sinks in the ocean despite the flux to the atmosphere (e.g. halogen exchange reaction with chloride and hydrolysis), the flux is driven by the net production, defined in this case as the difference between these oceanic sources and sinks. If the wind speed changes, and therefore the transfer velocity, the flux increases or decreases. Since the net production stays the same, the surface water concentration will decrease or increase, and hence the concentration anomaly. This changing concentration anomaly will in turn change the flux, until the steady state between net production and ocean-atmosphere flux is reached again. This explains why the flux seems to be independent from the measured concentration anomalies, as encountered during the M55 cruise.

At this point it seems that the estimates of the global ocean-atmosphere flux of methyl iodide can not be improved by collecting more data about the concentration anomaly. The future research should instead focus on the mechanisms of methyl iodide production in the ocean. With the identification of photochemical production of methyl iodide the missing source in the ocean is possibly found. The magnitude of the source must still be evaluated in other regions besides the tropics to calculate its contribution to the total source strength in the ocean. Therefore incubation experiments like the ones in this thesis should be repeated in different regions at different times of the year. In addition similar experiments under controlled conditions (e.g. light intensity, temperature and added photochemical active substances) should be carried out to investigate which factors influence and/or control the production and evaluate the reaction mechanism leading to the formation of methyl iodide. This may lead to the possibility to find a proxy like the incident radiation or the dissolved organic carbon concentration for the production of methyl iodide and for its surface water concentration.

Further the role of bacteria as a source of methyl iodide, both on land and in the ocean, needs to be investigated to complete our knowledge of the methyl iodide cycle. Again incubation experiments in the laboratory with controlled conditions and during research cruises seem an appropriate way to get more information about this source of methyl iodide.

Next to the sources of methyl iodide the oceanic sinks need to be evaluated in more detail. The reaction rates of hydrolysis and the halogen exchange reaction with chloride and

bromide have been measured, but the loss due to photolysis in the surface water and due to bacteria and/or plankton are not well known.

With the knowledge about sources and sinks of methyl iodide in the ocean and the factors influencing its production and destruction, a model of the methyl iodide cycle in the ocean can be developed. This may even help to refine the air-sea exchange models. With the exact knowledge of oceanic sources and oceanic sinks except the ocean-atmosphere flux, it is possible to calculate this flux from the difference between the sources and sinks more precisely as today with the air-sea exchange models. This flux can then be used to calculate the transfer velocity, thus refining the models for the air-sea exchange. At this point it can only be speculated if it is possible to evaluate the sources and sinks of methyl iodide in the ocean detailed enough for such a calculation, but it seems to me that the possible result justifies the effort.

## **5.4 Conclusions**

The main conclusions from this thesis are:

- The ocean is the main source of methyl iodide for the atmosphere.
- The surface water concentration and hence the concentration anomaly are influenced by the wind speed, so as to maintain a relatively constant air-sea flux.
- Methyl iodide is produced in the ocean by a photochemical pathway without direct biological influence.
- The photochemical production of methyl iodide is higher than the production by algae and plankton and is probably the most important source in the ocean, but the reaction mechanism remains unknown.

## 6. Literature

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## Abbreviations and symbols

a	year (as time unit)
A	Ampere
atm	atmosphere (as pressure unit)
°C	degree Celsius
$c_a$	concentration in the air at equilibrium
$C_D$	drag coefficient
CFC	chlorofluorocarbon
CFC 11	trichloroflouromethane (CCl <sub>3</sub> F)
CFC 113	trichlorotrifluoroethane (CCl <sub>2</sub> FCClF <sub>2</sub> )
Chl <i>a</i>	chlorophyll <i>a</i>
cm	centimetre (10 <sup>-2</sup> metres)
$c_w$	concentration in the water at equilibrium
d	day (as time unit)
D	molecular diffusivity of a gas in seawater
$D_c$	diffusion coefficient [cm <sup>2</sup> s <sup>-1</sup> ]
°	degree (unit for positions)
$d_{ML}$	mixed layer depth [m]
DMS	dimethylsulfide
DMSP	dimethylsulfoniopropionate
DOC	dissolved organic carbon
ECD	electron captor detector
e.g.	for example
$F$	Flux between ocean and atmosphere [nmol m <sup>-2</sup> d <sup>-1</sup> ]
$F_a$	instrument reading at fluorometer after acidification (for Chl <i>a</i> measurements)
FID	flame ionisation detector
$F_o$	instrument reading at fluorometer before acidification (for Chl <i>a</i> measurements)
GC	gas chromatograph
Gg	gigagram (10 <sup>9</sup> grams)
Gmol	gigamole (10 <sup>9</sup> moles)
h	hour (as time unit)
$H$	dimensionless solubility constant
$H'$	solubility of a gas in seawater [pmol L <sup>-1</sup> patm <sup>-1</sup> ]
“	inch
hPa	hecto pascal (10 <sup>2</sup> pascal)
$k$	exchange velocity [m d <sup>-1</sup> ]
$k_{Cl}$	rate constant for the reaction of methyl iodide with chloride ions
$K_D$	diapycnal diffusivity [m <sup>2</sup> s <sup>-1</sup> ]
kJ	kilojoule (10 <sup>3</sup> joule)
kPa	kilopascal (10 <sup>3</sup> pascal)
$K_x$	calibration factor for the fluorometer (for Chl <i>a</i> measurements)
L	litre
m	metre

M47	the cruise on board RV Meteor from Salvadore, Brasil, to Recife, Brasil, in March and April 2000
M55	the cruise on board RV Meteor from Curacao to Douala, Cameroun, in October and November 2002
mbar	millibar ( $10^{-3}$ bars)
McG01	relationship for the calculation of $k$ from <i>McGillis et al.</i> (2001)
mg	milligram ( $10^{-3}$ grams)
min	minute (as time unit)
'	minute (unit for positions)
mL	millilitre ( $10^{-3}$ litres)
mm	millimetre ( $10^{-3}$ metres)
mmol	millimole ( $10^{-3}$ moles)
Mmol	megamole ( $10^6$ moles)
mol	mole
MS	mass spectroscopy
n	number of samples or data points (for t-test calculations)
N	north
ng	nanogram ( $10^{-9}$ grams)
NH	northern hemispheric
nm	nanometre ( $10^{-9}$ metres)
nmol	nanomole ( $10^{-9}$ moles)
$p$	barometric pressure [mbar or hPa]
$P$	production rate per unit volume
$P_a$	net production of methyl iodide [ $\text{nmol m}^{-2} \text{d}^{-1}$ ]
$p_{H_2O}$	saturated partial pressure of water
Pa	pascal (pressure unit)
patm	picoatmospheres ( $10^{-12}$ atmospheres, or $1.01325 \cdot 10^{-7}$ Pa)
pmol	picomole ( $10^{-12}$ moles)
Pos255	the cruise on board RV Poseidon from Bremerhaven, Germany to Brest, France, in August to October 1999
R	resistance towards flux ( $R = k^{-1}$ )
RAD	solar radiation flux at the surface
RV	research vessel
s	second (as time unit)
S	south
$S$	salinity
$Sc$	Schmidt number
$s_d$	standard deviation
sm	nautical miles
SAM	S-adenosyl-L-methionine
SH	southern hemispheric
So152	the cruise on board RV Sonne from Recife, Brasil, to Guadeloupe, France, in November and December 2000
t	time
$T$	temperature [ $^{\circ}\text{C}$ ]
$T_D$	turbulent diffusion
$T_K$	temperature [ $^{\circ}\text{K}$ ]
$T_{SS}$	sea surface temperature [ $^{\circ}\text{C}$ ]
$t_t$	test value for comparing data sets (t-test)



$u$	wind speed [ $\text{m s}^{-1}$ ]
$U$	content per unit area [ $\text{nmol m}^{-2}$ ]
$u_{10}$	wind speed in 10 m height [ $\text{m s}^{-1}$ ]
$u^*$	friction velocity
UV	ultraviolet radiation
$V_b$	molar volume of a substance at its normal boiling point
$V_{ex}$	extraction Volume for Chl <i>a</i> measurements [L]
$V_S$	sample Volume [L]
W	west
W92	relationship for the calculation of $k$ from <i>Wanninkhof</i> (1992)
$\bar{x}$	mean value of a data set
$z$	height above sea surface [m]
$z_0$	roughness length
$\alpha$	confidence level (usually 5 %, if not stated otherwise)
$\Delta C$	concentration anomaly [ $\text{pmol L}^{-1}$ ]
$c_a$	atmospheric dry gas mole fraction of methyl iodide [ $\text{pmol mol}^{-1}$ ]
$c_w$	dry gas mole fraction of methyl iodide from a equilibrator sample [ $\text{pmol mol}^{-1}$ ]
$c_{ww}$	gas mole fraction of methyl iodide from a equilibrator sample (not corrected for water vapour) [ $\text{pmol mol}^{-1}$ ]
$h_w$	dynamic viscosity of pure water
$\mu\text{g}$	microgram ( $10^{-6}$ grams)
$\mu\text{L}$	microlitre ( $10^{-6}$ litres)
$\mu\text{m}$	micrometer ( $10^{-6}$ meters)
$\mu\text{mol}$	micromole ( $10^{-6}$ moles)
$\nu$	kinematic viscosity of seawater
<b>K</b>	Kármán constant (= 0.41)

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# Lebenslauf

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## Erklärung

Ich erkläre, dass die Abhandlung „Factors influencing methyl iodide production in the ocean and its flux to the atmosphere“ nach Inhalt und Form meine eigene Arbeit ist, abgesehen von der üblichen Beratung durch den Betreuer, Prof. Dr. D.W.R. Wallace. Diese Arbeit hat bisher, weder ganz noch in Teilen, einer anderen Stelle im Rahmen eines Prüfungsverfahrens vorgelegen. Ein Teil der Arbeit, namentlich der Teil mit der Beschreibung und den Ergebnissen der Inkubationsversuche (Kapitel 4), ist als Artikel mit dem Titel „Photochemical versus biological production of methyl iodide in the tropical ocean“ bei der Zeitschrift „Geochemical Research Letters“ eingereicht worden.

Uwe Richter

Kiel, den 15.03.2004