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Air-sea flux of bromoform: Controls, rates, and implications

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[1] Bromoform ($CHBr_3$) is the largest single source of atmospheric organic bromine and therefore of importance as a source of reactive halogens to the troposphere and lower stratosphere. The sea-to-air flux, originating with macroalgal and planktonic sources, is the main source for atmospheric bromoform. We review bromoform's contribution to atmospheric chemistry, its atmospheric and oceanic distributions and its oceanic sources and sinks. We have reassessed oceanic emissions, based on published aqueous and airborne concentration data, global climatological parameters, and information concerning coastal and biogenic sources. The goals are to attempt an estimate of the global source strength and partly to identify key regions that require further investigation. The sea-to-air flux is spatially and temporally variable with tropical, subtropical and shelf waters identified as potentially important source regions. We obtain an annual global flux of bromoform of $\sim$10 Gmol Br yr^{-1} (3–22 Gmol Br yr^{-1}). This estimate is associated with significant uncertainty, arising from data precision and coverage, choice of air-sea exchange parameterizations and model assumptions. Anthropogenic sources of $\sim$0.3 (to 1.1) Gmol Br yr^{-1} (as $CHBr_3$) can be locally significant, but are globally negligible. Our estimate of the global oceanic source is three to four times higher than recent estimates based on the modeling of atmospheric sinks. The reasons for this discrepancy could lie with the limited regional and temporal data available and the broad assumptions that underlie our flux calculations. Alternatively, atmospheric sink calculations, often made on the basis of background $CHBr_3$ levels, may neglect the influence of strong but highly localized sources (e.g., from some coastal and shelf regions). The strongly variable and poorly characterized source of $CHBr_3$, together with its short atmospheric lifetime, complicates model-based estimation of the distribution of reactive Br resulting from its atmospheric degradation. An integrated program of marine and atmospheric observations, atmospheric modeling and mechanistic studies of oceanic bromoform production is required to better constrain present and future Br delivery to the atmosphere. *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 4820 Oceanography: Biological and Chemical: Gases

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1. Introduction

[2] Brominated organic compounds are major carriers of bromine to the atmosphere. These compounds are photo-dissociated to form reactive radical species BrO_x (Br + BrO), which participate in catalytic ozone depletion in the troposphere and stratosphere [*World Meteorological Organization*, *WMO*, 1999]. Key bromine-carriers include the long-lived anthropogenic halons and methyl bromide [*Yokouchi et al.*, 2000; *Lee-Taylor et al.*, 1998; *Wamsley et al.*, 1998; *Butler and Rodriguez*, 1996]. A variety of

short-lived trace gases with predominantly natural sources also contribute to atmospheric BrO_x, including bromoform ($CHBr_3$), dibromomethane (CH_2Br_2), bromochloromethane (CH_2BrCl), dibromochloromethane ($CHBr_2Cl$), and dichlorobromomethane ($CHBrCl_2$). To date, the longer-lived compounds with anthropogenic sources have received most attention because they are abundant and measurable in the troposphere and stratosphere and are believed to be the primary carriers of bromine to the stratosphere. Of all these compounds, methyl bromide has the highest tropospheric background concentration of $\sim$10 ppt. It has been suggested that CH_3Br represents the largest supply of organic bromine to the stratosphere, and numerous studies have focused on its distribution and global budget [*Lovelock*, 1975; *Yung et*

al., 1980; *Singh et al.*, 1983; *Lobert et al.*, 1997; *Wamsley et al.*, 1998; *King et al.*, 2000; *Butler*, 2000]. Until recently, short-lived brominated compounds have received comparatively little attention, partly due to their low tropospheric concentration and because they are generally not detectable within the stratosphere. On the other hand, the low background concentrations, which are the consequence of short atmospheric lifetimes, may have diverted attention from a potentially large input of bromine to the atmosphere carried by such species. Recent modeling studies and measurements suggest significant contributions (30 to >60%) of such short-lived trace gases, especially of bromoform to inorganic bromine levels within the upper troposphere (UT)-lower stratosphere (LS) region [*Dvortsov et al.*, 1999; *Nielsen and Douglass*, 2001; *WMO*, 1999; *Schauffler et al.*, 1998; *Sturges et al.*, 2000]. The modeling studies reproduce background atmospheric concentrations of bromoform by atmospheric sink processes and distribute the required sea-to-air flux of $3.5-5.6$ Gmol Br yr^{-1} uniformly across the ocean surface. An alternative estimate of an atmospheric sink, based on a mean atmospheric $CHBr_3$ concentration of 0.4 ppt and a globally and seasonally averaged lifetime of 36 days at 5 km height yields 2.5 Gmol Br yr^{-1} [*Kurylo et al.*, 1999]. An earlier source estimate [*Penkett et al.*, 1985] based on a lifetime of two weeks and higher average atmospheric background concentrations was correspondingly higher at 12 Gmol Br yr^{-1}. *Penkett et al.* [1985] identified bromoform as the greatest single source for atmospheric bromine. These atmosphere-based estimates generally rely on "background" concentrations. Hence they likely underestimate the global source, since they "miss" the influence of strongly localized sources that, in the case of short-lived bromoform, could contribute significantly to the global budget. The oceanic production and hence the ocean-to-atmosphere flux of this short-lived trace gas is spatially and temporally variable. Highest concentrations are found in coastal waters, where bromoform is believed to have predominantly natural sources [*Carpenter et al.*, 2000]. Given bromoform's mean atmospheric lifetime of two to four weeks [*DeMore et al.*, 1997; *Moortgat et al.*, 1993], this nonuniform source will inevitably create variations in the atmospheric distribution of bromoform and corresponding variations in its atmospheric degradation rate. Recently the global bromoform flux from macroalgal sources, in combination with emissions of polar microalgae and water chlorination has been estimated to be 2.6 $(0.6-4.6)$ Gmol Br yr^{-1}, which is close to recent atmospheric sink calculations [*Carpenter and Liss*, 2000].

[3] Prior estimates of the global source strength based on saturation anomalies of very few isolated spot data range from 10 to 20 Gmol Br yr^{-1} and are therefore three to six times larger than the recent atmospheric sink calculations [*Liss*, 1986; *Fogelqvist and Krysell*, 1991]. The strongly variable and obviously poorly characterized source is the largest source of uncertainty for atmospheric modeling studies and model-based estimation of the distribution of reactive Br resulting from its atmospheric degradation [*Dvortsov et al.*, 1999; *Nielsen and Douglass*, 2001]. Variability of bromoform emissions must be related directly to oceanic production and degradation. In section 2 we

therefore review the literature concerning oceanic source and sink pathways.

[4] We suspect that strong geographical variability of the oceanic source of atmospheric bromoform (e.g., strong emissions from coastal regions and warm surface waters) may be of considerable importance for its global atmospheric budget and hence for the budget of amospheric BrO_x. In section 3, we present a reassessment of emissions, based on all published aqueous and airborne concentration data, global climatological parameters, and informations concerning coastal and biogenic sources.

[5] We interpret this conglomerate of widely but sporadically distributed data within a framework of biogeochemical provinces [*Longhurst et al.*, 1995] to account for variations in biogenic production, and within climatologically similar latitudinal bands to account for wind speed related variation in transfer-coefficients and surface water properties. We also reassess the anthropogenic source and identify several issues that warrant further research.

[6] The potential for short-term (e.g., subdecadal) variability in processes such as ozone destruction arising from variability in the supply of short-lived trace gases to the atmosphere should be considered, particularly in the context of global atmospheric monitoring. Related to this, the possibility of long-term changes in the emission of naturally produced, halogenated trace gases owing to biological or physical changes at the Earth's surface should also be considered as a possible consequence of global environmental change. For short-lived species emission changes can translate almost directly into altered rates of atmospheric processes. On the other hand, even radical and sudden changes in emissions of long-lived species require years or decades before they have a significant effect on atmospheric processes, since the large atmospheric reservoirs of long-lived species buffer the atmosphere with respect to short-term changes in emissions.

2. Background
2.1. Bromoform in Atmospheric Chemistry
2.1.1. Fate of Bromoform in the Atmosphere

[7] Atmospheric bromoform is mainly destroyed by photolysis (lifetime: $\sim$35 days) and also by reaction with OH and Cl (lifetime: $\sim$100 days) [*McGivern et al.*, 2002]. Its atmospheric lifetime varies, depending on temperature, zenith angle actinic flux, and oxidant concentrations in the region of interest. Bromoform and its degradation products are photolysed and oxidized in the lower troposphere as well as in upper atmospheric layers and likely deliver three reactive bromine species (BrO_x: Br + BrO) to the atmosphere (Figure 1) [*Barrie et al.*, 1988; *Moortgat et al.*, 1993; *DeMore et al.*, 1997; *Kurylo et al.*, 1999; *McGivern et al.*, 2000, 2002]. The lifetime of $CHBr_3$-photooxidation products and their washout coefficients, which are critical for the reactive bromine contribution, are however, not available from the literature.

2.1.2. Bromoform and its Relative Contribution to Tropospheric Br-Chemistry

[8] The rapid episodic destruction of boundary layer ozone in the Arctic at polar sunrise was initially linked to
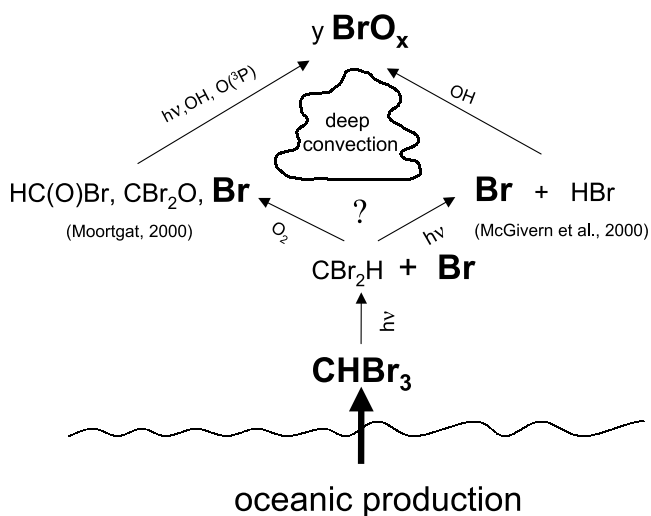
Figure 1. Primary and secondary processes in the photodissociation of bromoform, yielding reactive bromine species BrO_x ($Br + BrO$) [*McGivern et al.*, 2000; G. K. Moortgat, Max-Planck-Institut, Mainz, personal communication, 2000]. Oxidation pathways of bromoform degradation, initiated by OH and Cl, have recently been examined by *McGivern et al.* [2002].

the observed simultaneous photochemical removal of bromoform from 10 to 2 ppt [*Berg et al.*, 1984; *Cicerone et al.*, 1988; *Barrie et al.*, 1988]. Later it was determined that the tropospheric ozone loss in the Arctic and Antarctic is caused by autocatalytic cycles on the snowpack, involving Br^- and HOBr (aq) derived from sea-salt, which lead to massive Br_2-releases [*Bottenheim et al.*, 1990; *Tuckermann et al.*, 1997; *Kreher et al.*, 1997]. Although bromoform's photolysis is considered too slow to explain the observed rate of ozone destruction by BrO_x [*Hausmann et al.*, 1993, *Moortgat et al.*, 1993, *McConnell et al.*, 1992], it was suggested to be the initial source of reactive bromine that starts the autocatalytic cycle [*Tang and McConell*, 1996].

[9] Tropospheric BrO_x in midlatitudes and the tropics may also be derived from the autocatalytic release of bromine from sea-salt aerosol, which needs to be acidic, to start the autocatalytic cycles [*Vogt et al.*, 1996; *Abbatt and Nowak*, 1997; *Sander et al.*, 1997; *Wagner et al.*, 2001]. Marine aerosol is considered to be the globally most important source for tropospheric reactive bromine BrO_x. A global source strength of $40-60$ Gmol Br yr^{-1}, based on a sea-salt production rate of 1785 Tg Cl^- yr^{-1} [*Erickson et al.*, 1999], the mass ratio of Br^-/Cl^- as 0.00348 [*Wilson*, 1975], and a volatilization rate of 50% in the form of Br_2 and BrCl is considered likely (R. Sander, Max-Planck-Institute, Mainz, personal communication, 2002). With a Br-volatilization rate of 80%, as observed over the open ocean and significant recycling of the Br-species through the aerosol, the global marine aerosol source may even account for 100 Gmol of reactive Br yr^{-1} (W. C. Keene, University of Virginia, personal communication, 2001). The contribution of bromoform to BrO_x in localized source regions may be directly comparable or even higher than

the sea-salt source, as often bromoform carries more bromine than the total inorganic bromine (aerosol and gaseous) background of $2-10$ ppt [*Duce et al.*, 1965; *Kritz and Rancher*, 1980; *Berg et al.*, 1983; W. C. Keene, unpublished data, 2001]. For example, close to source regions, bromoform-mixing ratios >300 ppt $CHBr_3$ (~900 ppt Br) have been observed [*Class et al.*, 1986]. Further, the sea-salt aerosol may not be acidic enough to release Br during autocatalytic cycles, especially in tropical and subtropical regions. Hence, short-lived brominated source gases, of which bromoform is a major component, may be large regional and/or global sources for reactive bromine species.

2.1.3. Bromoform and Stratospheric Chemistry

[10] The ozone-depleting effectiveness of bromine is about 50 times greater on a mole-for-mole basis than that of chlorine, since much less bromine resides in inorganic reservoir species. [*WMO*, 1999; *Solomon et al.*, 1994; *Garcia and Solomon*, 1994]. Further, synergistic coupling between atmospheric bromine and chlorine cycles produces additional free bromine and chlorine atoms which can, for moderate mixing ratios of stratospheric bromine, enhance ozone depletion by chlorofluorocarbons by up to 20% [*WMO*, 1999, 1995; *Anderson et al.*, 1989; *McElroy et al.*, 1986; *Yung et al.*, 1980; *Wofsy et al.*, 1975] and is most effective below 25 km height [*Lary*, 1996].

[11] Recent observations and models have identified significant contributions to stratospheric inorganic bromine from short-lived brominated source gases, especially bromoform [*Wamsley et al.*, 1998; *Harder et al.*, 2000; *Pfeilsticker et al.*, 2000; *Ko et al.*, 1997; *Dvortsov et al.*, 1999; *Nielsen and Douglass*, 2001]. In situ release of bromine atoms via degradation of the short-lived parent compound within the lowermost stratosphere, and the upward transport of inorganic bromine, released earlier as a result of degradation of the parent compound within the troposphere, may be equally important [*Pfeilsticker et al.*, 2000]. At ground level, bromoform frequently carries more bromine than all other organobromine compounds combined, which sum to ~20 ppt Br [*Schauffler et al.*, 1999] (Figure 2). If its degradation products reach the stratosphere, it may therefore contribute significantly to the control of stratospheric ozone levels. A potentially important factor for the Br-supply by $CHBr_3$ is fast "pumping" of the trace gas from the marine boundary layer to the upper troposphere and stratosphere by convection [*Kritz et al.*, 1993; *Solomon et al.*, 1994; *Nielsen and Douglass*, 2001; *Ko et al.*, 1997; *Daniel et al.*, 1996]. Observational data of bromoform's atmospheric vertical profile over the remote open Pacific imply potential Br release from this compound of about 1 ppt within the immediate vicinity of the tropopause (Figure 3, redrawn from data in the work of *Schauffler et al.* [1998]). In comparison, Br-release from CH_3Br evidently takes place over a much broader and higher altitude range. Thus bromoform's contribution to reactive bromine may be especially focused within the upper troposphere and lower stratosphere region (UT/LS). Indeed, its contribution to this region was estimated by *Dvortsov et al.* [1999] to be >60%, assuming a uniformly distributed oceanic source on 3.5 Gmol Br yr^{-1}, whereas a subsequent study by *Nielsen and Douglass* [2001] estimated a maximum contribution of 30%, despite their
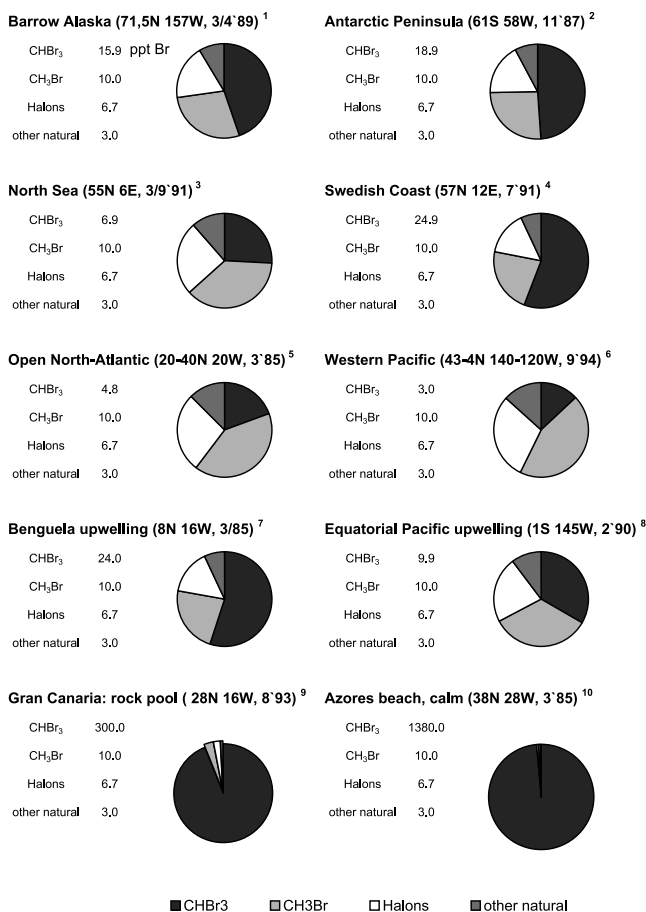
Figure 2. Contribution of various organobromine compounds in ppt Br to total organic bromine in marine surface air at selected locations. Halons comprise CBrClF (Halon 1211), CBrF$_3$ (Halon 1301) and C$_2$Br$_2$F$_4$ (Halon 2402). "Other natural" comprise CH$_2$Br$_2$ (dibromomethane), CH$_2$BrCl (bromochloromethane), CHBrCl$_2$ (bromodichloromethane) as well as CHBr$_2$Cl (dibromochloromethane). Br-contribution of methyl bromide, halons and other natural is constant with 19.7 ppt Br for all locations [*Schauffler et al.*, 1999]; 1, *Berg et al.*, 1984; 2, *Reifenhäuser and Heumann*, 1992; 3, 4, *Quack*, 1994; 5, 7, 10, *Class et al.*, 1986; 6, *Quack and Suess*, 1999; 8, *Atlas et al.*, 1993; 9, *Ekdahl et al.*, 1998.

larger oceanic source of 5.9 Gmol Br yr^{-1}(also uniformly distributed). The differences between these model results arise from differing atmospheric transport characteristics and model resolutions and show a need for further studies. These contrasting modeling studies show clearly the influence of atmospheric transport on CHBr$_3$'s contribution to ozone chemistry. It is likely that the nonhomogeneous surface source of bromoform is also an important factor.

2.2. Sources

[12] Air-sea exchange is the main source for atmospheric bromoform, which is produced in the surface water by macroalgal and planktonic organisms. Spatial and temporal variation in production and in the gas-exchange coefficient will inevitably lead to an inhomogeneous surface source. In this section we review potential within-ocean production pathways, including the factors that may control source variability.

2.2.1. Macroalgal Source

[13] Brown, green and red macroalgae produce variable amounts of bromoalkanes, which they deliver to the aquatic environment or, in inter-tidal regions, directly to the atmosphere. Even though the actual ratios of the bromoalkanes released (CHBr$_3$, CH$_2$Br$_2$, CH$_2$BrCl, CHBr$_2$Cl, CHBrCl$_2$) vary from one study to another, bromoform is always the dominant compound. The macroalgae appear to release the compounds from tissue reservoirs and de novo synthesis, especially from older parts of the plants [*Nightingale et al.*, 1995]. In general, polar species produce the least bromo-compounds, whereas subtropical and tropical species appear to be more efficient producers. Measured production rates range from 4 to 5000 pmol CHBr$_3$ g^{-1} h^{-1} (bromoform per gram fresh weight per hour), with highest release rates (>4000 pmol CHBr$_3$ g^{-1} h^{-1}) being reported for rhodophytae and phaeophyta [*Carpenter et al.*, 2000; *Pedersen et al.*, 1996; *Nightingale et al.*, 1995; *Manley et al.*, 1992; *Gschwend*, 1985]. Brown algae contribute 60% of the global macroalgal bromoform production, which has been estimated to be 1.6 (0.4–2.7) Gmol Br yr^{-1}, because of their large biomass [*Carpenter and Liss*, 2000].

[14] *Klick* [1992] and *Goodwin et al.* [1997a] reported seasonal variation in CHBr$_3$ release from brown macroalgae. Larger emissions in summer months were attributed to visible tissue decay of the algae. *Gschwend and MacFarlane* [1986] however, report higher CHBr$_3$ release rates at a site on the east coast of the USA in early spring. Diurnal variations in CHBr$_3$ release have been observed in subtropical and temperate macroalgal communities, with maximum release rates at midday. CHBr$_3$ production is generally reported to increase with irradiance [*Carpenter et al.*, 2000; *Marshall et al.*, 1999; *Ekdahl et al.*, 1998; *Goodwin et al.*, 1997a; *Pedersen et al.*, 1996]. Higher CHBr$_3$ production in the dark and a temperature-dependent release has, however, been suggested for Antarctic species [*Laturnus*, 1996; *Laturnus et al.*, 1998]. Macroalgal CHBr$_3$ production may be induced by stress, which may increase the release from inter-tidal species [*Mtolera et al.*, 1996]. Overall, release rates are species-specific and sensitive to external physical conditions [*Carpenter et al.*, 2000]. *Manley et al.* [1992] suggested that macroalgae might additionally excrete HOBr, which then reacts in seawater with organic matter to produce bromoform and other brominated compounds.

[15] The oceanic macroalgal source of bromoform is highly variable in space and time, and hence the current best estimate by *Carpenter and Liss* [2000] is necessarily associated with a large uncertainty.

2.2.2. A Phytoplankton Source?

[16] CHBr$_3$ concentrations have consistently been found to decrease with depth in the open ocean [*Fogelqvist*, 1985; *Krysell*, 1991; *Sturges et al*, 1997] (Figure 4). Elevated open ocean surface concentrations may be caused by transport of coastal waters, enriched in bromoform [*Moore and Tokarczyk*, 1993; *Carpenter and Liss*, 2000] or by the existence of local surface sources. Locally elevated concentrations of bromoform, measured in open ocean air and seawater have
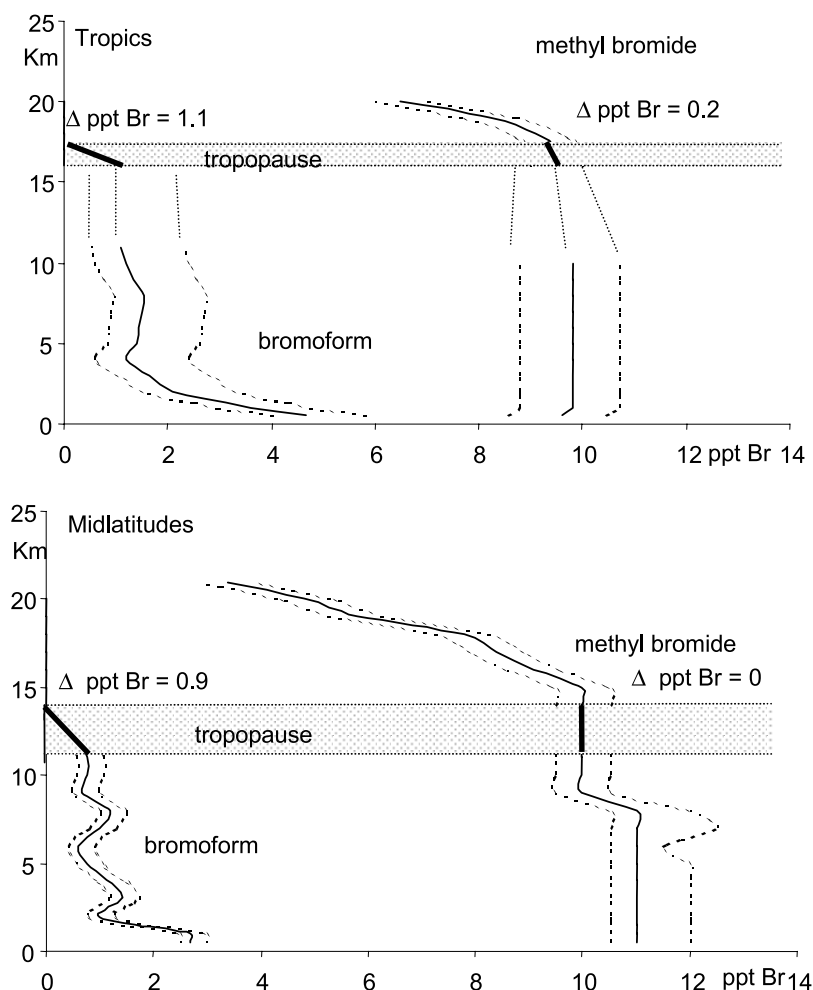
Figure 3. Inferred contribution of reactive bromine (Δ ppt Br) to the upper troposphere/lower stratosphere from bromoform and methyl bromide in (a) the tropical Pacific and (b) the midlatitudes (data from *Schauffler et al.* [1999]). Height of the tropopause was variable among investigations; dashed line range of data; dotted line no data available.

often been attributed to planktonic production associated with upwelling and, most likely, diatom abundance [*Atlas et al.*, 1993; *Baker et al.*, 1999; *Class and Ballschmiter*, 1988; *Klick and Abrahamson*, 1992]. These studies did not however, directly determine which species or processes were responsible. Some studies have found correlations of dissolved $CHBr_3$ and planktonic proxies in the open ocean. For example, *Krysell* [1991] observed an inverse relationship between nitrate and bromoform concentrations at stations within the Arctic Ocean. A correlation between chlorophyll a and bromoform has been observed in several open oceanic regions [*Moore and Tokarzcyk*, 1993; *Baker et al.*, 1999; *Yokouchi et al.*, 1997; *Krysell*, 1991; *Schall and Heumann*, 1993]. Some studies in shelf areas however, did not yield such correlations [*Krysell and Nightngale*, 1994; *Abrahamson and Ekdahl*, 1996], possibly because the biotic correlation is masked by local anthropogenic contamination, due to water chlorination. Ice algae have been identified to produce significant amounts of bromoform, which may partly account for elevated bromoform concentrations in Arctic snowpack and sea-ice [*Sturges et al.*, 1992, 1997;

Sturges and Cota, 1995; *Moore et al.*, 1993]. Experimental fractionation studies found picoplankton (0.4–2 μm) of a polar plankton population as the major bromoform producer [*Ekdahl*, 1997]. Temperate plankton species appear to be poor producers [*Moore et al.*, 1995b]. *Tokarczyk and Moore* [1994] found bromoform production by cold-water diatoms to be dependent on the growth stage of the organisms. Rates ranged from 48.9 to 72 pmol $CHBr_3$ (mg Chla)$^{-1}$ h^{-1} in the exponential growth phases of *Porosira glaciali* and *Nitzschia* sp., decreasing to 6–20.5 pmol $CHBr_3$ (mg Chla)$^{-1}$ h^{-1} during the senescent phase.

[17] The latter studies may be used to estimate a possible magnitude of $CHBr_3$ production by phytoplankton. Assuming a mean $CHBr_3$ production of 30 pmol (mg Chla)$^{-1}$ h^{-1} for 12 hours d^{-1} and 180 d yr^{-1} in all ocean areas and a mean chlorophyll a inventory of 5 mg Chla m^{-2} for the open ocean (area: 270×10^6 km^2), 20–30 mg Chla m^{-2} in the polar ocean (area: 20.8×10^6 km^2 and 130–200 mg Chla m^{-2} for coastal regions (37.4×10^6 km^2), the phytoplankton source could contribute ~0.6 Gmol $CHBr_3$ (~2 Gmol Br yr^{-1}) to ocean surface waters. For compar-
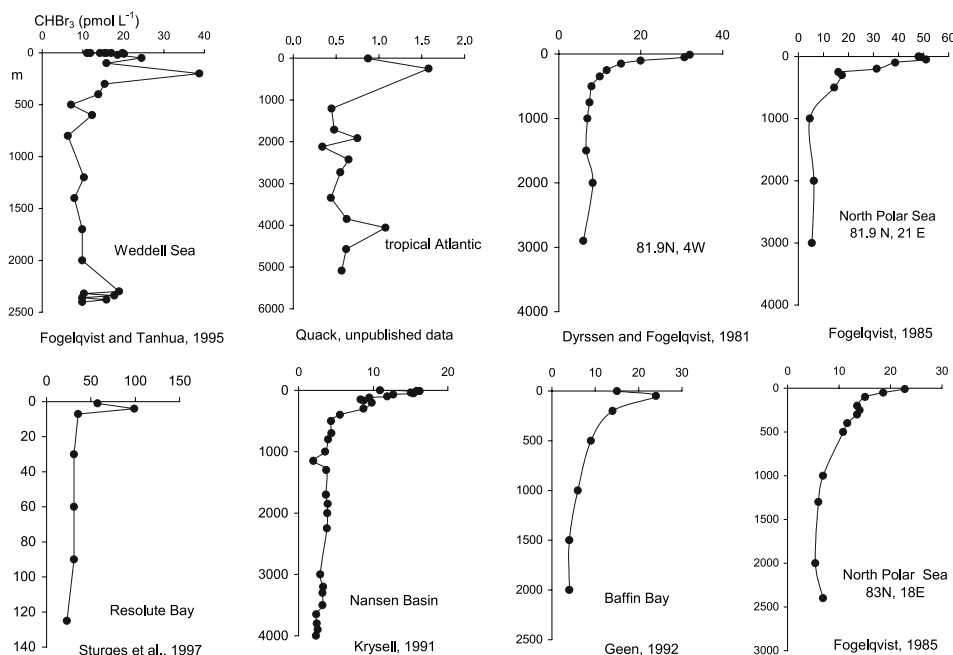
Figure 4. Bromoform depth profiles of the open ocean [*Dyrssen and Fogelqvist*, 1981; *Fogelqvist*, 1985; *Geen*, 1992; *Fogelqvist and Tanhua*, 1995; *Krysell*, 1991; B. Quack, unpublished data, 2001].

ison, *Sturges et al.* [1992] attributed a source strength of 0.04–0.6 Gmol $CHBr_3$ (0.1–2 Gmol Br yr^{-1}) to ice algal communities. Obviously, such calculations are exceedingly rough, but indicate that planktonic and macroalgal sources may be of comparable magnitude globally. Additional bacterial production in the marine environment and in phytoplankton cultures cannot be excluded. Possible pelagic sources of $CHBr_3$ should therefore be considered and better defined in future work [*Sturges et al.*, 1992, *Sturges*, 1993; *Tokarczyk and Moore*, 1994; *Moore et al.*, 1995b, 1996; *Harper*, 1995].

2.2.3. Pathways of CHBr₃ Synthesis

[18] The principle of bromoform production resembles the common haloform reaction [*Morrison and Boyd*, 1992]:

$$(R1) \qquad R-CO-CH_3 \xrightarrow{OX^-} R-COO^- + CHX_3$$
$$(X : Cl^-, Br^-, J^-)$$
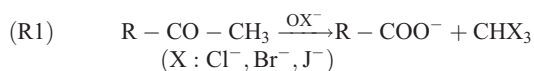
where methylketones are easily oxidized by means of hypohalite. The production of bromoform requires oxidation of bromide to hypobromite in the first step. In the second step, many different organic substrates, especially those with activated terminal methyl groups (CH_3-CO-R; CH_3-HCOH-C-R, after oxidation; HO_2C-CH_2-CO-R, after decarboxylation) such as ketones, diketones, phenols and β-keto acids as well as alkenes and alkynes, can be brominated. Complex oxidation and substitution reactions yield unstable intermediates, which hydrolyze to dibromomethane and mainly bromoform (R2) [*Fenical*, 1981, 1982; *Theiler et al.*, 1978; *Gribble*, 2000]

$$(R2) \qquad \xrightarrow{(OH^-)} CH_2Br_2, CHBr_3$$
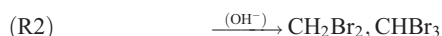
Bromide, being an abundant anion in seawater, is the obvious ultimate source for oxidized bromine.

[19] Oxidation of bromide in the marine environment occurs most commonly via hydrogen peroxide in the presence of haloperoxidases [*Beissner et al.*, 1981; *DeBoer and Wever*, 1987; *Wever et al.*, 1991; *Butler*, 1999].

$$(R3) \qquad Br^- \xrightarrow{bromo-and\ chloroperoxidases\ (H_2O_2)} Enz - Br^+, BrO^-$$
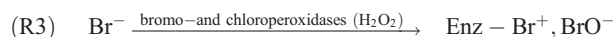
Substrates may then either bind to the enzyme or possibly be brominated by free oxidized bromine [*Wever et al.*, 1991; *Butler*, 1999]. *Theiler et al.* [1978] were the first to demonstrate bromoform production by a peroxidase in a marine red alga, and this pathway has subsequently been confirmed for several other macroalgae [*Wever et al.*, 1993; *Itoh and Shinya*, 1994; *Goodwin et al.*, 1997a]. Bromoform production by phytoplankton also involves peroxidases [*Moore et al.*, 1996]. The volatile compounds are most likely arbitrary cleavage products of the manifold halogenating activities of marine organisms [*Gribble*, 1999], produced while eliminating toxic hydrogen peroxide from inside and outside their cells [*Collen et al.*, 1994; *Pedersen et al.*, 1996; *Manley and Barbero*, 2001].

[20] Screening of marine macroalgae and bacteria shows that many organisms contain haloperoxidases (e.g., 75% of the macroalgae) [*Hewson and Hager*, 1980; *Moore and Okuda*, 1996]. *Bacillus firmus* and *Bacillus* ssp. isolated from decaying seaweed, beach sand and salt brines also produced haloperoxidases [*Hunter-Cevera et al.*, 1992]. Many phytoplankton species, as well as marine animals such as sponges, nudibranchs, pteropods, worms and bryozoans, contain bromo- and chloroperoxidases with either iron (heme) or vanadium as the prosthetic group [*Gribble*, 1999, 2000; *Moore et al.*, 1996; *Klick*, 1993; *Wever et al.*, 1991, 1993; *Soedjak and Butler*, 1991; *Neidleman and Geigert*, 1986]. The pathways of bromoform synthesis and

Table 1. Anthropogenic Sources of Bromoform

|	$CHBr_3$ in Effluents, nmol L^{-1}	Global Capacity, Mega Watts Electricity (MWE)	Water Use, $m^3 s^{-1}$ (1000 MWE)$^{-1}$	Water Use, km^3	$CHBr_3$ Emission, Mmol Br yr^{-1}
Coastal power plants	80 (60–200)	100,000	45	142	34 (25–85)
Inland nuclear power	4 (1–80)	250,000	45	355	4 (1–85)
Coastal fossil fuel plants[a]	80 (60–200)	1,125,000	30	1167	280 (210–700)
Inland fossil fuel plants[a]	4 (1–80)	1,125,000	30	1167	14 (3–280)
Desalination/power plants	4 (1–80)			3	2 (including atmospheric release from dearation process)
Desinfection of waste water, drinking water and recreational water	4 (1–80)			1000	12 (3–240)
Total		2,600,000			346 (245–1393)

[a]Assumed localization of capacity (50% coastal, 50% inland).

the overall abundance of peroxidases in the marine environment make many organisms possible candidates for bromoform (and dibromomethane) release. The excretion of halogenated metabolites from peroxidase-containing organisms can reach environmentally significant amounts, as in the case of the acorn worm [*Higa and Sakemi*, 1983; *Gribble*, 2000]. Additionally, free peroxidases in the water column [*Wever et al.*, 1993] may also be involved in bromoform production. Free peroxidases appear to be responsible for bromoform production in bromide-rich soils [*Hoekstra et al.*, 1998], and thus could also be a significant biotic pathway for bromoform production in coastal waters.

[21] In addition to the biotic bromoform production, abiotic chemical and photochemical bromoform production may also be significant in certain situations. A variety of halocarbons including bromoform can be formed during UV-irradiation of seawater [*Class and Ballschmiter*, 1987]. Bromide can be photochemically oxidized in oxygenated and acidified seawater [*Halmann and Porat*, 1988; *Gratzel and Halmann*, 1990; *True and Zafiriou*, 1987; *Zafiriou et al.*, 1987].

$$(R4) \qquad Br^- \xrightarrow{\text{sunlight (H}^+,O_2)} BrO^-, BrO_3^-$$

Bromide can also be naturally oxidized by chlorine and hypochlorite (OCl$^-$, produced from chloroperoxidase reaction with Cl$^-$). Ozone and hydrogenperoxide, occurring in the natural oceanic environment, may also serve as abiotic oxidants [*Jolley et al.*, 1990].

$$(R5) \qquad Br^- \xrightarrow{\text{chlorination (OCl}^-)} BrO^-$$
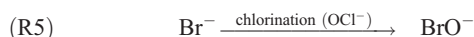
Abiotic reactions with organic material (e.g., DOM - Dissolved Organic Matter) as well as other peroxidase containing organisms thus may be additional natural bromoform sources and require investigation.

2.2.4. Anthropogenic Sources

[22] Disinfection of seawater, freshwater, and wastewater by chlorination and ozonation leads to the production of a wide range of halogenated organic compounds. Hypochlorite and hypobromite (bromine oxidized by chlorine) react with organic material, forming trihalomethanes (THM). Bromoform production in fresh water ranges from 1 to 80 nmol CHBr$_3$ L^{-1}, typically 4–40 nmol CHBr$_3$ L^{-1} [*Rook*, 1974; the Agency for Toxic Substances and Disease Registry

(ATSDR) at http://www.atsdr.cdc.gov]. Production of bromoform increases during the chlorination of seawater due to its large bromide content [*Jolley et al.*, 1980, 1990; the World Health Organization (WHO) site at http://www.who.int]. Concentrations between 60 and 200 nmol CHBr$_3$ L^{-1} (median: 80 nmol L^{-1}) have been measured in effluents of coastal power plants. Bromoform concentrations are particularly elevated in this disinfected seawater during summer months and variations are most likely related to the nature of the natural organic matter in the water [*Jenner et al.*, 1997; *Allonier et al.*, 1999; *Wu and Chadik*, 1998]. Generally, the relative production of different THM via water chlorination is dependent on temperature, organic loading, radiation and salinity [*Jolley et al.*, 1980], which complicates any assessment of the source strength. A previous estimate of this source attributed 57 Mmol organic Br yr^{-1} to the chlorination of natural waters [*Gschwend*, 1985]. We have reassessed this anthropogenic source as follows (Table 1).

[23] Coastal power plants may discharge 0.15–0.5 Mmol Br annually per plant in the form of bromoform, based on published discharge concentrations, cooling water amount, and power plant capacity (Table 1) [*Jenner et al.*, 1997; *Fogelqvist and Krysell*, 1991; *Allonier et al.*, 1999]. We estimate a global source of 34 Mmol Br (CHBr$_3$) yr^{-1} from coastal nuclear facilities. Inland nuclear power (70% of the total nuclear capacity) adds 4 Mmol Br (CHBr$_3$) yr^{-1}. Data on coastal nonnuclear facilities have not been assessed separately, since we have no data on the installed coastal fossil fuel generating capacity. If we consider half of the fossil fuel generating capacity to be situated at coastlines, we obtain ~290 Mmol Br (CHBr$_3$) yr^{-1} from this source. Desalination/power plants also show elevated levels of bromoform in their effluents [*Saeed et al.*, 1999]. Based on 3 km^3 water globally processed per year (according to the World Resources Institute at http://www.wri.org), they represent a source of only 0.04 Mmol Br (CHBr$_3$) yr^{-1}. However, 98% of the bromoform production at such plants may be discharged directly to the atmosphere [*Ali and Riley*, 1986, 1989], and this may add an additional ~2 Mmol Br yr^{-1}. Disinfection of wastewater, drinking water, and recreational water may add ~12 Mmol Br yr^{-1}, assuming ~1000 km^3 of global water withdrawal for domestic and industrial purposes (data from the World Resources Institute site at http://www.wri.org). These anthropogenic bromoform sources due to water chlorination total ~0.35 Gmol Br yr^{-1} (0.25–1.4 Gmol Br yr^{-1}), which is a minor

contribution in comparison with natural sources [*Krysell and Nightngale*, 1994; *Nightingale*, 1991; *Fogelqvist and Krysell*, 1986, 1991; *Amy et al.*, 1985; *Fogelqvist et al.*, 1982; *Helz and Hsu*, 1978]. However, industrial bromoform emissions are locally very significant and should be carefully evaluated during investigations in coastal regions.

2.3. Within-Ocean Sinks

[24] Degradation pathways for bromoform in seawater include hydrolysis, biotic and abiotic reductive dehalogenation, halogen-substitution, and photolysis. Sea-to-air exchange represents the most important process, and is discussed separately in section 3.
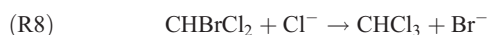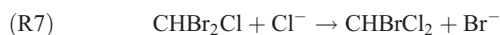
2.3.1. Hydrolysis

[25] Bromoform hydrolysis is a slow process in cold water, where the bromoform half-life is $\sim$680–1000 years at 2–4°C. The reaction rate increases with increasing temperature, the half-life being only 30–50 years at 25°C [*Mabey and Mill*, 1978; *Vogel et al.*, 1987]. Assuming mean concentrations of 1 pmol $CHBr_3$ L^{-1} for the deep ocean and 10 pmol $CHBr_3$ L^{-1} for near-surface seawater (mixed-layer depth of 75 m), the inventory of global oceanic bromoform can be estimated to be $\sim$1.5 Gmol (ocean volume: 1349.93×10^6 km^3 [*Dietrich et al.*, 1975]). At the mean temperatures of 3.5°C for the deep ocean and 15°C for the mixed layer, the overall loss due to hydrolysis would amount to only 3.4–5.5 Mmol $CHBr_3$ yr^{-1}.

2.3.2. Reductive Dehalogenation

[26] Reductive dehalogenation of brominated organic compounds occurs through microbial activity and also under sterile anaerobic conditions [*Bouwer et al.*, 1981; *Bouwer and McCarthy*, 1983; *Goodwin et al.*, 1997b]. In suboxic seawater from the Black Sea, the concentrations of several volatile bromocarbons declined with decreasing oxygen concentration, most likely because of chemical reduction [*Tanhua et al.*, 1996]. Although bromoform data were not reported, it may also be degraded, since the redox-potential for this compound is higher than those of the other investigated mixed bromochloro-compounds. The rapid vertical decline of bromoform concentrations in coastal and open ocean sediments indicates that bromoform is degraded either by anaerobic microorganisms or due to its redox-potential [*Geen*, 1992]. The reductive dehalogenation of bromoform would initially yield CH_2Br_2, which is itself an important vector of atmospheric bromine. Removal of halocarbons by abiotic processes is generally considered to be slower than removal by biotic, mainly microbial, processes [*Vogel et al.*, 1987], but may certainly be important on the time-scale of oceanic circulation. At present it is not possible to estimate the losses due to such processes.

2.3.3. Halogen Substitution

[27] Halogen substitution, due to nucleophilic attack by chloride ion may be an important degradation pathway for bromoform in the ocean. A hypothetical reaction sequence is proposed by *Class and Ballschmiter* [1988]:

(R6) $$CHBr_3 + Cl^- \rightarrow CHBr_2Cl + Br^-$$

(R7) $$CHBr_2Cl + Cl^- \rightarrow CHBrCl_2 + Br^-$$

(R8) $$CHBrCl_2 + Cl^- \rightarrow CHCl_3 + Br^-$$

The end product of this reaction chain is chloroform ($CHCl_3$), which at 9 Gmol Cl yr^{-1} is the second largest supplier of organic chlorine from the ocean to the atmosphere (after methyl chloride which contributes $\sim$13 Gmol Cl yr^{-1}) [*Khalil and Rasmussen*, 1999; *Khalil et al.*, 1999]. Based on limited laboratory experiments, the half-life for the conversion from bromoform to dibromochloromethane is reported to range from 5 (25°C) to 74 (2°C) years [*Geen*, 1992]. Thus halogen substitution appears to be 1–2 orders of magnitude faster than hydrolysis, implying a loss of $\sim$20–100 Mmol $CHBr_3$ yr^{-1}. Whereas bromoform concentrations decrease with depth in the open ocean, $CHBr_2Cl$ and $CHBrCl_2$ concentrations increase with depth, suggesting that halogen substitution is indeed an important source and sink mechanism [*Moore and Tokarczyk*, 1993]. Although direct production of $CHBr_2Cl$ and $CHBrCl_2$ from organisms has been reported, the main oceanic source of these compounds in the deep ocean is expected to be progressive substitution of chlorine into bromoform [*Moore and Tokarczyk*, 1993; *Fogelqvist and Tanhua*, 1995; *Krysell*, 1991; *Sturges et al.*, 1997].

2.3.4. Photolysis

[28] An additional sink for bromoform in the ocean surface layer is photolysis. *Carpenter and Liss* [2000] calculated the lifetime of bromoform due to photolysis to be $\sim$40 times longer than the lifetime due to gas exchange for a midlatitude open ocean mixed layer. In other words, the photolytic sink could amount to about 2% of the air-sea flux. As a result, photolysis may be the largest internal ocean sink for $CHBr_3$. Subsurface maxima of bromoform, located from 5 to 10 and 50 to >200 m, have sometimes been found in polar and tropical open ocean water columns (Figure 4). These subsurface maxima may be created by surface-loss due to photolysis and air-sea exchange loss pathways.

[29] The most significant loss process for bromoform with respect to seawater is the sea to air flux of the compound, which is the subject of the remainder of this article.

3. The Air-Sea Exchange of Bromoform

3.1. Distribution of Bromoform in Marine Air and Seawater

[30] The literature concerning bromoform concentrations in marine air and seawater comprises approximately 60 publications; split evenly between atmospheric and oceanic studies, and is based on different campaigns to several oceanic regions. Few campaigns included both marine boundary layer and ocean surface water measurements, which, given that concentrations in both boundary layers are spatially and temporally variable, is unfortunate for estimates of air-sea exchange. The studies also vary greatly in the spatial resolution of reported bromoform concentrations and in the detail with which ancillary data, such as sampling location, date, water temperature, etc. are reported. For the various campaigns and areas of investigation (Figure 5) we report about 100 separate mean values for both airborne observations (Table 2) and surface water measurements (Table 3). Missing ancillary data, such as
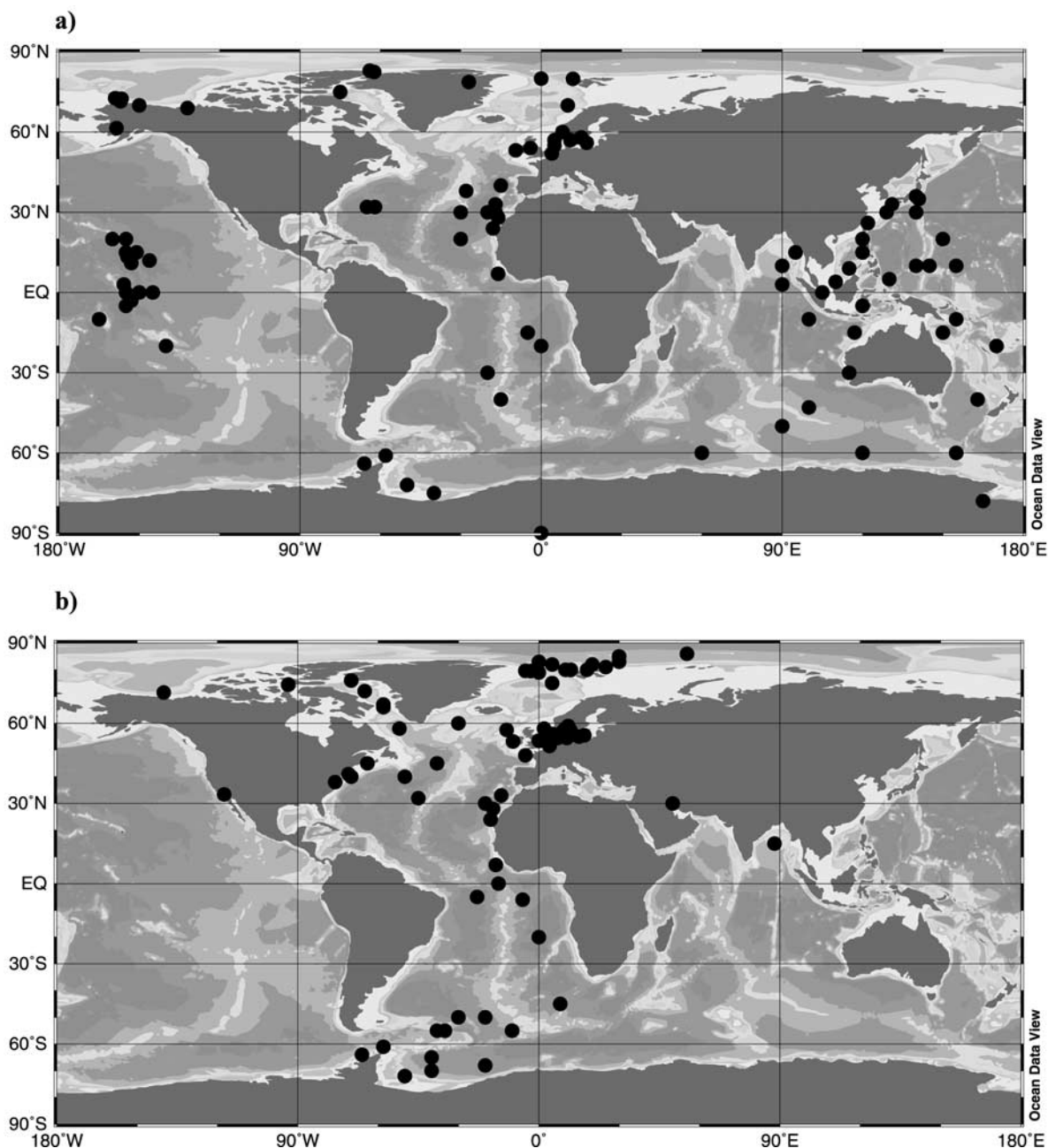
Figure 5. Geographical sample coverage of published bromoform measurements. Representative locations of reported CHBr$_3$-data in (a) air and (b) seawater [*Abrahamsson et al.*, 1995; *Abrahamsson and Ekdahl*, 1996; *Allonier et al.*, 1999; *Atlas et al.*, 1992, 1993; *Barrie et al.*, 1988; *Berg et al.*, 1984; *Carpenter et al.*, 1999; *Carpenter and Liss*, 2000; *Cicerone et al.*, 1988; *Class et al.*, 1986, ; *Dyrssen and Fogelqvist*, 1981; *Ekdahl et al.*, 1998; *Ekdahl*, 1997; *Eklund et al.*, 1982; *Fogelqvist and Krysell*, 1986, 1991; *Fogelqvist et al.*, 1982; *Fogelqvist*, 1984, 1985; *Fogelqvist and Tanhua*, 1995; *Gschwend and MacFarlane*, 1986; *Helz and Hsu*, 1978; *Rasmussen and Khalil*, 1984; *Klick and Abrahamson*, 1992; *Klick*, 1992; *Krysell and Nightngale*, 1994; *Krysell*, 1991; *Kuß*, 1993; *Li et al.*, 1994; *Manley et al.*, 1992; *Moore and Tokarczyk*, 1993; *Moore et al.*, 1993; *Nightingale et al.*, 1995; *Nightingale*, 1991; *Penkett et al.*, 1985; *Quack and Suess*, 1999; *Quack*, 1994; *Reifenhäuser and Heumann*, 1992; *Saeed et al.*, 1999; *Schall and Heumann*, 1993; *Sharp et al.*, 1992; *Sturges and Cota*, 1995; *Sturges et al.*, 1997; *Sturges*, 1993; *Wakeham et al.*, 1983; *Yamamoto et al.*, 2001; *Yokouchi et al.*, 1994, 1997, 1999; B. Quack, unpublished data, 2001].

Table 2. Published Atmospheric Mixing Ratios of Bromoform

	Date	Latitude	Longitude	$CHBr_3$ mean pptv	$CHBr_3$ min pptv	$CHBr_3$ max pptv	Reference[a]	Domain	Region
Alert	spring 1986–1987	83°N	64°W	3.6			3	>80°N	shelf
Alert	summer 1986–1987	83°N	64°W	5.5			3	>80°N	shelf
Alert	Jan.–April 1992	83°N	64°W				12	>80°N	shelf
Arctic	Alert	83°N	64°W	1.6			21	>80°N	shelf
Arctic flights	April 1986	>80°N		4.9			3	>80°N	open ocean
Canadian arctic	April 1986	82.5°N	62.3°W	8	<1	12	3	>80°N	open ocean
Arctic	Aug.–Sept. 1991	53°–57°N	0°–20°E	1.71			16	>80°N	open ocean
Arctic flights	March–April 1983	60°–80°N		16.5	2	46	4	80°–60°N	shelf
Barrow, Alaska	March–April 1983	72°N	157°W	15	13 (sd)		4	80°–60°N	shelf
Anchorage	Aug. 1983	61.5°N	149.5°W	32			4	80°–60°N	shelf
Anchorage	Sept. 1983	61.5°N	149.5°W	6			4	80°–60°N	shelf
Barrow, Alaska	Nov. 1983	72.7°N	159°W	5			4	80°–60°N	shelf
Barrow, Alaska	March 1983	72.5°N	156.9°W	5			4	80°–60°N	shelf
Barrow, Alaska	March 1983	71.19°N	156.37°W	29			4	80°–60°N	shelf
Barrow, Alaska	March 1983	71.19°N	156.37°W	8			4	80°–60°N	shelf
Barrow, Alaska	April 1983	71.19°N	156.37°W	18			4	80°–60°N	shelf
Bodo, Norw	April 1983	70.19°N	10.33°E	5			4	80°–60°N	shelf
Barrow, Alaska	spring 1985–1987	71.5°N	157°W	6.6			7	80°–60°N	shelf
Barrow, Alaska	summer 1985–1987	71.5°N	157°W	3.3			7	80°–60°N	shelf
Alaska	na	70°N	150°W	6.3	2	11	7	80°–60°N	shelf
Tuktuyaktuk	na	69°N	132°E	1.85	0.95	3.34	13	80°–60°N	shelf
Svalbard	Sept. 1992	79.93°N	11.95°E	0.45	0.02	1.19	18	80°–60°N	shelf
Barrow	March–April 1989	71.5°N	157°W	5.3			20	80°–60°N	shelf
Barrow	March–April 1990	71.5°N	157°W	2.3			20	80°–60°N	shelf
Resolute	May 1991	75°N	95°W	2.6			20	80°–60°N	shelf
Resolute	May 92	75°N	95°W	1.4			20	80°–60°N	shelf
Svalbard	March 1983	79.93°N	11.95°E	26			4	80°–60°N	shore
Ny Alesund	April 1983	78.75°N	27.14°E	26			4	80°–60°N	shore
Southern Baltic	March 1992	53°–57°N	0°–20°E	2.32			16	60°–40°N	shelf
Kiel Bight	July 1992	53°–57°N	0°–20°E	2.12			16	60°–40°N	shelf
Middle Baltic	July 1992	53°–57°N	0°–20°E	1.66			16	60°–40°N	shelf
Middle Baltic	March 1991	53°–57°N	0°–20°E	2.13			16	60°–40°N	shelf
Northeastern Baltic	March 1991	53°–57°N	0°–20°E	2.22			16	60°–40°N	shelf
Southern Baltic	March 1991	53°–57°N	0°–20°E	2.27			16	60°–40°N	shelf
Kattegatt, Skaggerak	April 1991	53°–57°N	0°–20°E	2.27			16	60°–40°N	shelf
Norwegian Trench	April 1991	53°–57°N	0°–20°E	2.46			16	60°–40°N	shelf
Central North Sea	April 1991	53°–57°N	0°–20°E	2.11			16	60°–40°N	shelf
Southern North Sea	April 1991	53°–57°N	0°–20°E	2.28			16	60°–40°N	shelf
Elbe Delta	April 1991	53°–57°N	0°–20°E	1.68			16	60°–40°N	shelf
Central North Sea	Sept. 1991	53°–57°N	0°–20°E	2.48			16	60°–40°N	shelf
Central North Sea	Sept. 1991	53°–57°N	0°–20 °E	1.55			16	60°–40°N	shelf
North Sea	Sept. 1991	53°–57°N	0°–20°E	1.66			16	60°–40°N	shelf
North Sea, Baltic	1991–1992	53°–57°N	0°–20°E	2.38			16	60°–40°N	shelf
Mace Head	Sept. 1998	53.19°N	9.54°W	6.6	5	10	5	60°–40°N	shore
Mace Head	Sept. 1998	53.19°N	9.54°W	15	10	23	5	60°–40°N	shore
Mace Head	May 1997	53.19°N	9.54°W	6.27	1.9	16.3	6	60°–40°N	shore
Baltic (Kiel Fjord)	winter 1990–1991	53°–57°N	0°–20°E	3.52			16	60°–40°N	shore
Baltic (Kiel Fjord)	May 1991	53°–57°N	0°–20°E	1.61			16	60°–40°N	shore
Baltic (Kiel Fjord)	June 1991	53°–57°N	0°–20°E	0.75			16	60°–40°N	shore
Baltic (Kiel Fjord)	Aug. 1991	53°–57°N	0°–20°E	1.86			16	60°–40°N	shore
Baltic (Kiel Fjord)	March 1992	53°–57°N	0°–20°E	3.09			16	60°–40°N	shore
Baltic (Kiel Fjord)	March 1991	53°–57°N	0°–20°E	1.3			16	60°–40°N	shore
North Sea (Sylt)	Sept. 1991	53°–57°N	0°–20°E	2.16			16	60°–40°N	shore
North Sea (Wadden)	Sept. 1991	53°–57°N	0°–20°E	2.94			16	60°–40°N	shore
North Sea (Sylt)	June 1991	53°–57°N	0°–20°E	0.74			16	60°–40°N	shore
North Sea (Sylt)	July 1991	53°–57°N	0°–20°E	2.29			16	60°–40°N	shore
North Sea (Sylt)	Aug. 1991	53°–57°N	0°–20°E	2.39			16	60°–40°N	shore
North Sea (Sylt)	April 1992	53°–57°N	0°–20°E	1.99			16	60°–40°N	shore
North Sea (Sylt)	May 1992	53°–57°N	0°–20°E	1.91			16	60°–40°N	shore
North Sea (Sylt)	June–July 1992	53°–57°N	0°–20°E	3.45			16	60°–40°N	shore
Swedish coast	July 1991	53°–57°N	0°–20°E	8.27			16	60°–40°N	shore
Western Pacific	Sept. 1994	36°–35°N	142°–144°W	3.86			15	40°–10°N	shelf
Hawaii	1985–1987	20°N	155°W	3.1	1	6	7	40°–10°N	shelf
Madeira	March 1984–Aug. 1984	33°N	17°W	6			9	40°–10°N	shore
Teneriffa	Oct. 1985	28°N	16°W	6.6		20	9	40°–10°N	shore
Azores	June 1982	38°N	28°W	460			9	40°–10°N	shore
Bermuda	July 1985	32°N	65°W	24			9	40°–10°N	shore
Gran Canaria	Aug. 1993	30°N	17°W	100	25	300	10	40°–10°N	shore
Tsukuba, Japan	April 1990	36°N	140°W		0.91	2.18	19	40°–10°N	shore
Central Pacific	May–June 1984	10°–40°N		0.94			1	40°–10°N	open ocean

Table 2. (continued)

	Date	Latitude	Longitude	$CHBr_3$ mean pptv	$CHBr_3$ min pptv	$CHBr_3$ max pptv	Reference[a]	Domain	Region
Equatorial Pacific	Feb. 1990	13.36°N	154.37°W	0.97			2	40°–10°N	open ocean
Equatorial Pacific	Feb. 1990	12.69°N	154.99°W	0.9			2	40°–10°N	open ocean
Equatorial Pacific	Feb. 1990	12.38°N	154°W	1.24			2	40°–10°N	open ocean
Equatorial Pacific	Feb. 1990	12.11°N	154.98°W	1.01			2	40°–10°N	open ocean
Equatorial Pacific	Feb. 1990	11.97°N	146.22°W	1.41			2	40°–10°N	open ocean
Equatorial Pacific	Feb. 1990	15°–10°N	152.9°W	1.47	0.9	1.41	2	40°–10°N	open ocean
Central Pacific	March 1990	15°N		2.7			2	40°–10°N	open ocean
Atlantic	March 1985	40°N		3			8	40°–10°N	open ocean
Atlantic	March 1985	20°–40°N		2			8	40°–10°N	open ocean
Atlantic	March 1985			2			8	40°–10°N	open ocean
North Atlantic	March 1985	0°–40°N	20°W	1.6			9	40°–10°N	open ocean
North Atlantic	March 1985	24°N	18°W	8			9	40°–10°N	open ocean
Western Atlantic	July 1985	32°N	64°W	0.6			9	40°–10°N	open ocean
Atlantic	1982–1983	0°–40°N		0.85	0.2	1.5	14	40°–10°N	open ocean
Atlantic	1982–1983	20°N		5.96			14	40°–10°N	open ocean
Western Pacific	Sept. 1994	4°–43°N	110°–145°W	1.2	0.38	10.67	15	40°–10°N	open ocean
Western Pacific	Sept. 1994	36°–43°N	140°–145°W	1.01			15	40°–10°N	open ocean
Western Pacific	Sept. 1994	31°–35°N	130°–140°W	0.76			15	40°–10°N	open ocean
Western Pacific	Sept. 1994	30°–31°N	125°–132°W	0.98			15	40°–10°N	open ocean
Western Pacific	Sept. 1994	24°–30°N	125°W	0.62			15	40°–10°N	open ocean
Western Pacific	Sept. 1994	19°–24°N	120°–125°W	0.82			15	40°–10°N	open ocean
Western Pacific	Dec. 1995–Jan. 1996, Jan.–Feb. 1997	15°–30°N	140°–120°E	0.7	0.4	1	22	40°–10°N	open ocean
Western Pacific	Nov. 1997–March 1998	15°–30°N	140°–120°E	0.4	0.2	0.7	22	40°–10°N	open ocean
Western Pacific	Jan.–Feb. 1991	15°–30°N	140°–150°E	0.8	0.6	1.3	23	40°–10°N	open ocean
Western Pacific	Sept.–Oct. 1992	15°–30°N	140°–150°E	0.2	0.1	0.4	23	40°–10°N	open ocean
Southeast Asia	Jan. 1994	3°–40°N	80°–140°E	1.2	0.32	7.1	23	40°–10°N	open ocean
Hawaii	May–June 1988	20°N	156°W	0.25			1	40°–10°N	shelf
Equatorial Pacific	Feb. 1990	5°–10°N	153.45°W	1.44	1.2	2.16	2	10°N–10°S	open ocean
Equatorial Pacific	Feb. 1990	0°–5°N	155.75°W	2.37	1.69	2.78	2	10°N–10°S	open ocean
Equatorial Pacific	Feb. 1990	0°–5°S	153°W	2.47	1.78	3.28	2	10°N–10°S	open ocean
Equatorial Pacific	Feb. 1990	5°–11°S	158.6°W	1.14	0.68	1.32	2	10°N–10°S	open ocean
NH (10°N)	March 1985	10°N		8	3	14	8	10°N–10°S	open ocean
7°N	March 1985	7°N	16°W	14			8	10°N–10°S	open ocean
SH (0°–20°S)	March 1985	0°–20°S		1			8	10°N–10°S	open ocean
Western Pacific	Sept. 1994	4°–19°N	110°–120°W	1.12			15	10°N–10°S	open ocean
Western Pacific	Dec. 1995–Feb. 1997	0°–15°N	130°–100°E	1.8	0.5	2	22	10°N–10°S	open ocean
Western Pacific	Dec. 1995–Feb. 1997	10°N	90°E	1.5	1	2	22	10°N–10°S	open ocean
Western Pacific	Dec. 1995–Feb. 1997	0°–15°S	120°E	1	0.4	1.5	22	10°N–10°S	open ocean
Indian Ocean	Dec. 1995–Feb. 1997	0°–15°S	100°–90°E	0.4	0.2	0.5	22	10°N–10°S	open ocean
Western Pacific	Dec. 1995–Feb. 1997	0°–15°N	130°–100°E	2	0.7	3.8	22	10°N–10°S	open ocean
Western Pacific	Jan.–Feb. 1991	0°–10°N	145°–155°E	1	0.7	1.5	22	10°N–10°S	open ocean
Western Pacific	Sept.–Oct. 1992	0°–10°N	145°–155°E	0.4	0.2	0.6	23	10°N–10°S	open ocean
Western Pacific	Jan.–Feb. 1991	0°–10°S	150°–155°E	0.7	0.7	1	23	10°N–10°S	open ocean
Western Pacific	Sept.–Oct. 1992	0°–10°S	150°–155°E	0.6	0.5	0.8	23	10°N–10°S	open ocean
South China Sea	Jan. 1994	0°–15°N	115°W	2			23	10°N–10°S	open ocean
Equatorial Pacific	Feb. 90	15°N–10°S	144°–165°W	1.8			2	10°N–10°S	open ocean
Pacific	May–June 1984	10°–40°S		0.74			1	10°–40°S	open ocean
Pacific	Feb. 1990	15°S		1.3			2	10°–40°S	open ocean
Atlantic	March 1985			2.5			8	10°–40°S	open ocean
Atlantic	March 1985			1.4			8	10°–40°S	open ocean
South Atlantic	March 1985	0°–30°S	5°W	1			9	10°–40°S	open ocean
South Atlantic	1982–1983	0°–75°S		0.58	0.2	1.5	14	10°–40°S	open ocean
Indian Ocean	Dec. 1995–Feb. 97	30°–60°S	30°–120°E	1.5	0.4	2	22	10–40°S	open ocean
East Australia	Jan.–Feb. 1991	20°S	155°E	2.5	2	3	23	10°–40°S	open ocean
East Australia	Sept.–Oct. 1992	20°S	155°E	1.2	0.4	1.6	23	10°–40°S	open ocean
South Atlantic	1982–1983	0°–75°S		0.58	0.2	1.5	14	40°–60°S	open ocean
Indian Ocean	Dec. 1995–Feb. 1997	40°–45°S		1.5	1	1.5	22	40°–60°S	open ocean
Indian Ocean	Dec. 1995–Feb. 1997	30°–60°S	30°–120°E	1.5	0.4	2	22	40°–60°S	open ocean
Indian Ocean	Dec. 1995–Feb. 1997	60°S		1.5	1.2	3	22	40°–60°S	open ocean
South Pole	na	90°S		1			11	60°–80°S	shelf
Antarctic	Oct.–Dec. 1987	62°–66°S	54°–70°W	6.3	1	37.4	17	60°–80°S	shelf
Mc Murdo Sound	Nov. 1989	78°S	165°E	1.2			20	60°–80°S	shelf
South Atlantic	1982–1983	72°S		1			14	60°–80°S	open ocean
Antarctic peninsula	Oct.–Dec. 1987	62°–66°S	54°–70°W	6.3	0.1	12.5	17	60°–80°S	open ocean

[a]References: 1, *Atlas et al.* [1992]; 2, *Atlas et al.* [1993]; 3, *Barrie et al.* [1988]; 4, *Berg et al.* [1984]; 5, *Carpenter and Liss* [2000]; 6, *Carpenter et al.* [1999]; 7, *Cicerone et al.* [1988]; 8, *Class and Ballschmiter* [1988]; 9, *Class et al.* [1986]; 10, *Ekdahl et al.* [1998]; 11, *Khalil and Rasmussen* [1999]; 12, *Li et al.* [1994]; 13, *Moore et al.* [1993]; 14, *Penkett et al.* [1985]; 15, *Quack and Suess* [1999]; 16, *Quack* [1994]; 17, *Reifenhäuser and Heumann* [1992]; 18, *Schall and Heumann* [1993]; 19, *Sharp et al.* [1992]; 20, *Sturges* [1993]; 21, *Yokouchi et al.* [1994]; 22, *Yokouchi et al.* [1999]; 23, *Yokouchi et al.* [1997].

Table 3. Published Surface Seawater Measurements of Oceanic Bromoform (n = Number of Observations)

	Date	Latitude	Longitude	n	CHBr$_3$[a] mean pmol L^{-1}	CHBr$_3$ (Minimum), pmol L^{-1}	CHBr$_3$ (Maximum), pmol L^{-1}	Reference[b]	Domain	Region
Arctic Ocean	Aug. 1991	86.4°N	55.3°E		13.50	7.00	19.80	1	>80 °N	open ocean
North of Svalbard	Aug.–Sept. 1980	82°N	20°E		29.68	23.74	51.44	8	>80 °N	open ocean
Arctic Ocean	1979–1980	83°N		26	25.72	11.87	11.87	12	>80°N	open ocean
Arctic Ocean	Aug.–Sept. 1980	>80°N			40.36	11.08	11.08	15	>80°N	open ocean
Nansen Basin	July–Aug. 1987	82–87°N	30°E		15.83	11.87	27.70	24	>80°N	open ocean
Greenland Sea	Oct. 1995	75°N			44.00	0.40	180.02	9	80°–60°N	shelf
Baffin Bay	April–May 91	67°N	58°W		79.15	15.83	118.72	27	80°–60°N	shelf
Svalbard	Sept. 1992	79.93°N	11.95°E	10	77.05	34.43	157.89	34	80°–60°N	shelf
Svalbard	Sept. 1992	79.93°N	11.95°E	13	66.32	18.52	197.07	34	80°–60°N	shelf
Resolute Bay	March–April	74.39,9°N	94.55,2°W		59.36	59.36	79.15	35	80°–60°N	shelf
Resolute Bay	March–April	74.39,9 °N	94.55,2°W		79.15			35	80°–60°N	shelf
Svalbard	Aug.–Sept. 1980	80°N	10°E		277.01			8	80°–60°N	shore
Polar, coastal	na	>80°N			1000.00	7.90	2000.00	9	80°–60°N	shore
Svalbard	Aug.–Sept. 1980	80°N	18°E		1187.18	1206.96	1483.97	15	80°–60°N	shore
Svalbard	Sept. 1992	79.93°N	11.95°E	11	650.18	203.44	1309.38	34	80°–60°N	shore
West of Svalbard	Aug.–Sept. 1980	79°N	0°E		25.72	19.79	31.66	8	80°–60°N	open ocean
Baffin Bay	Aug.–Sept. 1980	76°N	70°W	4	12.27	5.54	5.54	13	80°–60°N	open ocean
Arctic Ocean	Aug.–Sept. 80				17.81			15	80°–60°N	open ocean
Atlantic water	Aug.–Sept. 1980	79.5°N	3°W		23.74			15	80°–60°N	open ocean
Arctic Ocean	Aug.–Sept. 1980	79.6°N	5°W		31.66			15	80°–60°N	open ocean
Arctic Ocean	Aug.–Sept. 80				27.31	9.89 (sd)	9.89	15	80°–60°N	open ocean
Arctic Ocean	Aug.–Sept. 1980				37.99	18.99	18.99	15	80°–60°N	open ocean
Arctic Ocean	Aug.–Sept. 1980				22.56	9.50	9.50	15	80°–60°N	open ocean
Baffin Bay	na	72°N	65°W	1	7.91			17	80°–60°N	open ocean
Beaufort Sea	March 91	71.5°N	140°W		7.91	6.33	11.48	27	80°–60°N	open ocean
Resolute Bay	April–May 1992	74.5°N	94.5°W		32.45	15.83	31.66	27	80°–60°N	open ocean
Resolute Bay	April–May 1992				55.40	39.57	71.23	27	80°–60°N	open ocean
Davis strait	April–May 91	66°N	58°W		23.74			28	80°–60°N	open ocean
Resolute Bay	April–May 1992	74.39,9°N	94.55,2°W		79.15			36	80°–60°N	open ocean
Resolute Bay	April–May 1992	74.39,9°N	94.55,2°W		27.70			36	80°–60°N	open ocean
Skaggerak	Sept. 1990–March 1993	57°N	9°E		7.52	5.14	9.89	3	60°–40°N	shelf
Central North Sea	Sept. 90–March 93	57°N	9°E		9.10	8.31	10.29	3	60°–40°N	shelf
South. North Sea	Sept. 1990–March 1993	57°N	9°E		15.04	12.27	18.60	3	60°–40°N	shelf
Skagerrak coast	Sept. 90–March 93	57°N	9°E		13.85	12.27	14.64	3	60°–40°N	shelf
Kattegatt	1979–1980	57°N	11°E	15	91.02			12	60°–40°N	shelf
Skagerrak	na	57°N	11°E	8	25.33			13	60°–40°N	shelf
Baltic	na	55°N	11–13°E	20	21.37			13	60°–40°N	shelf
North. North Sea	na	57°N	8–0°E	7	9.50			13	60°–40°N	shelf
North Sea	na	56°N	8–0°E	12	33.24			13	60°–40°N	shelf
Biscaya-Engl. Ch.	na	44–50°N	0–8°W	16	39.97			13	60°–40°N	shelf
Kattegatt	May–June 1980	57.5°N	12°W		11.87			16	60°–40°N	shelf
Kattegatt	May–June 1980	57.5°N	12°W		47.49			16	60°–40°N	shelf
Swedish coast	Sept. 1989, 1990	58°N	10°E		134.55	6.33	478.83	21	60°–40°N	shelf
Swedish coast	April–June 90	58°N	10°E		182.03	13.85	585.67	21	60°–40°N	shelf
Humber estuary	May 1990	53.5°N	0°W	10	31.66	31.66	237.44	23	60°–40°N	shelf
Rhine estuary	Oct. 1990	51.5°N	4°E	11	11.87	11.87	300.75	23	60°–40°N	shelf
Central North Sea	March 1991	55.5°N	2.5°E		65.29			25	60°–40°N	shelf
Central North Sea	Sept. 1991	55.5°N	2.5°E		39.97			25	60°–40°N	shelf
SE North Sea	March 1991	54.5°N	7°E		55.01			25	60°–40°N	shelf
SE North Sea	Sept. 1991	54.5°N	7°E		344.28			25	60°–40°N	shelf
SW Baltic	March 1991	54.5°N	10.5°E		56.19			25	60°–40°N	shelf
SW Baltic	July 1992	54.5°N	10.5°E		153.15			25	60°–40°N	shelf
SE Baltic	March 91	55.5°N	17°E		19.79			25	60°–40°N	shelf
SE Baltic	July 1992	55.5°N	17°E		124.26			25	60°–40°N	shelf
Nova Scotia	Jan.–June	45°N	64°W		391.77			27	60°–40°N	shelf
Labrador shelf	April–May 1991	58°N	52°W	12	31.66	11.87	118.72	28	60°–40°N	shelf
North Sea	Feb.–March	53–57°N	0°–10°E	780	33.64	1.78	601.50	29	60°–40°N	shelf
North Sea	Feb. 1989	53–57°N	0°–10°E		118.72			29	60°–40°N	shelf
North Sea	March 1989	53–57°N	0°–10°E		39.57			29	60°–40°N	shelf
North Sea	April 1989	53–57°N	0°–10°E		31.66			29	60°–40°N	shelf
North Sea	May 1989	53–57°N	0°–10°E		23.74			29	60°–40°N	shelf
North Sea	June. 1989	53–57°N	0°–10°E		27.70			29	60°–40°N	shelf
North Sea	July. 1989	53–57°N	0°–10°E		27.70			29	60°–40°N	shelf
North Sea	Aug. 1989	53–57°N	0°–10°E		19.79			29	60°–40°N	shelf
North Sea	Sept. 1989	53–57°N	0°–10°E		11.87			29	60°–40°N	shelf
North Sea	Oct. 1989	53–57°N	0°–10°E		15.83			29	60°–40°N	shelf
Humber estuary	April–May	53.5°N	1°E	8	48.28	15.04	90.23	30	60°–40°N	shelf
Humber estuary	May–June	53.5°N	1°E	10	56.59	34.03	83.50	30	60°–40°N	shelf
Humber estuary	June–July	53.5°N	1°E	11	61.73	34.43	101.31	30	60°–40°N	shelf

Table 3. (continued)

	Date	Latitude	Longitude	n	CHBr$_3$[a] mean pmol L^{-1}	CHBr$_3$ (Minimum), pmol L^{-1}	CHBr$_3$ (Maximum), pmol L^{-1}	Reference[b]	Domain	Region
Humber estuary	July–Aug.	53.5°N	1°E	8	50.26	17.81	70.83	30	60°–40°N	shelf
Mace Head	Sept. 1998	53.19°N	9.54°W		104.50			5	60°–40°N	shelf
Mace Head	Sept. 1998	53.19°N	9.54°W		395.73	100.00	700.00	4	60°–40°N	shore
Mace Head	Sept. 1998	53.19°N	9.54°W		2770.08			4	60°–40°N	shore
Swedish Coast	na	57°N			500.00	19.79	791.45	11	60°–40°N	shore
Idefjorden	May 1985	59°N	11°E		79.15	39.57	118.72	14	60°–40°N	shore
Sweden	April–June 1990	58.5°N	11°E		945.79	490.70	1392.96	21	60°–40°N	shore
Swedish Coast	Nov.–April	58.5°N	11°E		197.86	79.15	791.45	22	60°–40°N	shore
Swedish Coast	May–Sept.t	58.5°N	11°E		989.32	791.45	1978.63	22	60°–40°N	shore
Labrador shelf	April–May 1991	58°N	52°W	1	1582.90			28	60°–40°N	shore
Cumbrae island	May 90	56°N	5°W		1187.18	672.73	1820.34	30	60°–40°N	shore
Narragansett Bay	Aug. 1979–Feb. 1981	41°N	71°W		1978.63	39.57	7914.52	37	60°–40°N	shore (ind)
Mace Head	Sept. 1998	53.19°N	9.54°W		388.00			5	60°–40°N	shore
North Atlantic	na	60°W	30°W	27	5.54			13	60°–40°N	open ocean
Labrador Current	April–May 91	40°N	50°W	10	60.94	3.96	60.94	28	60°–40°N	open ocean
NW Atlantic	April–May 1991	45°N	38°W	18	5.94	3.96	7.91	28	60°–40°N	open ocean
Cape Cod Canal	Jan.–March	40°N	70°W		237.44	79.15	316.58	19	40°–10°N	shelf
Chesapeake Bay	Feb.–May 1977	38°N	76°W			87.06	4590.42	20	40°–10°N	shelf
California coast	Aug.–Sept. 1990	33.20°N	117.5°W		170.16	170.16	518.40	26	40°–10°N	shelf
California coast	Aug.–Sept. 1990	33.20°N	117.5°W		87.06	43.53	87.06	26	40°–10°N	shelf
Cape Cod Coast	Sept. 1983–Dec. 1984	40°N	70°W		158.29	118.72	197.86	19	40°–10°N	shelf
Gran Canaria	Aug. 93	28°N	17°W		2000.00	400.00	4500.00	10	40°–10°N	shore
California	Aug.–Sept. 1990	33.35°N	117.5°W		1187.18	490.70	2041.95	26	40°–10°N	shore
Kuwait	na	30°N	50°E		403.64	3.96	7914.52	33	40°–10°N	shore (ind)
Kuwait	na	30°N	50°E		35.62	3.96	2144.84	33	40°–10°N	shore (ind)
Atlantic	March 1984				3.17			6	40°–10°N	open ocean
North Atlantic	March 1985	33°N	14°W		3.17			7	40°–10°N	open ocean
Upwelling	March 1985	24°N	18°W		23.74			7	40°–10°N	open ocean
NW Atlantic	April–May 1991	32°N	45°W	6	5.94	3.96	7.91	28	40°–10°N	open ocean
Canary Current	March 1984	7°N	16°W		19.79			6	10°N–10°S	open ocean
South Atlantic	March 85	6°S	6°W		3.17			7	10°N–10°S	open ocean
Equatorial Atlantic	na	10°N–10°S	10°W	4	4.35	2.77	5.93	15	10°N–10°S	open ocean
Equatorial Atlantic	April 2000	5°S	23°W	1	0.87			31	10°N–10°S	open ocean
Equatorial Atlantic	April 00	11°S	31.9°W	1	0.40			31	10°N–10°S	open ocean
South Atlantic	na	10°–40°S		5	10.68	5.93	15.43	13	10°–40°S	open ocean
South Atlantic	March 1984	10°–30°S	0°–10°E		3.16			6	10°–40°S	open ocean
South Georgia	Nov. 1989	55°S	140°W		32.00	19.70	87.85	21	40°–60°S	shelf
Antarctic	Nov. 1989	55°S	10°E–60°W	5	10.68	5.94	87.85	21	40°–60°S	open ocean
South Atlantic		55°S	10°E–60°W	1	17.81			2	40°–60°S	open ocean
Weddell Sea	1993	60°–80°S	40°–50°W	3	54.20	48.30	56.90	18	60°–80°S	open ocean
Weddell Sea	1993	60°–80°S	40°–50°W	9	15.40	11.80	19.80	18	60°–80°S	open ocean
Weddell Sea	1993	60°–80°S	40°–50°W		7.91			13	60°–80°S	open ocean
Antarct. Penins.	Oct.–Dec. 1987	64°S	64°W		24.54	5.42	186.86	32	60°–80°S	open ocean

[a]The mean was taken from the literature or calculated from the min and max values. All data were converted to pmol L^{-1}.

[b]References: 1, *Abrahamsson et al.* [1995]; 2, *Abrahamson and Klick* [1990]; 3, *Abrahmsson and Ekdahl* [1996]; 4, *Carpenter and Liss* [2000]; 5, *Carpenter et al.* [2000]; 6, *Class and Ballschmiter* [1988]; 7, *Class et al.* [1986]; 8, *Dyrssen and Fogelqvist* [1981]; 9, *Ekdahl* [1997]; 10, *Ekdahl et al.* [1998]; 11, *Eklund et al.* [1982]; 12, *Eklund et al.* [1980]; 13, *Fogelqvist and Krysell* [1991]; 14, *Fogelqvist and Krysell* [1986]; 15, *Fogelqvist* [1985]; 16, *Fogelqvist et al.* [1982]; 17, *Fogelqvist* [1984]; 18, *Fogelqvist and Tanhua* [1995]; 19, *Gschwend and MacFarlane* [1986]; 20, *Helz and Hsu* [1978]; 21, *Klick and Abrahamson* [1992]; 22, *Klick* [1992]; 23, *Krysell and Nightngale* [1994]; 24, *Krysell* [1991]; 25, *Kuß* [1993]; 26, *Manley et al.* [1992]; 27, *Moore et al.* [1993]; 28, *Moore and Tokarczyk* [1993]; 29, *Nightingale* [1991]; 30, *Nightingale et al.* [1995]; 31, B. Quack, unpublished data, 2001; 32, *Reifenhäuser and Heumann* [1992]; 33, *Saeed et al.* [1999]; 34, *Schall and Heumann* [1993]; 35, *Sturges and Cota* [1995]; 36, *Sturges et al.* [1997]; 37, *Wakeham et al.* [1983].

exact location and date of sampling, were inferred from the publications.

3.1.1. Distribution in Air

[31] Background concentrations of bromoform in marine boundary layer air are generally in the range 0.5–1.5 ppt Mean background concentrations seem to be slightly higher in the Northern Hemisphere with 0.85 ppt [*Penkett et al.*, 1985] and 0.94 ppt [*Atlas et al.*, 1993], compared to 0.58 and 0.74 ppt, respectively, in the Southern Hemisphere. The short atmospheric lifetime of bromoform implies clearly that there are sources in both hemispheres. The apparent interhemispheric gradient may

partly be due to a seasonality of sources and sinks in both hemispheres.

[32] According to these measurements, the marine boundary layer (<1000 m height) contains ~0.02 Gmol of CHBr$_3$. Taking an average reported concentration for the entire troposphere of 0.4 ppt [*Kurylo et al.*, 1999] yields a tropospheric inventory of 0.08 Gmol CHBr$_3$ (i.e., 0.24 Gmol Br in the form of CHBr$_3$). Little or no bromoform has been detected above the tropopause (Figure 3) [*Schauffler et al.*, 1998; *Sturges et al.*, 2000]. The marine boundary layer therefore contains as much as 25% of the global atmospheric bromoform inventory. This global inventory
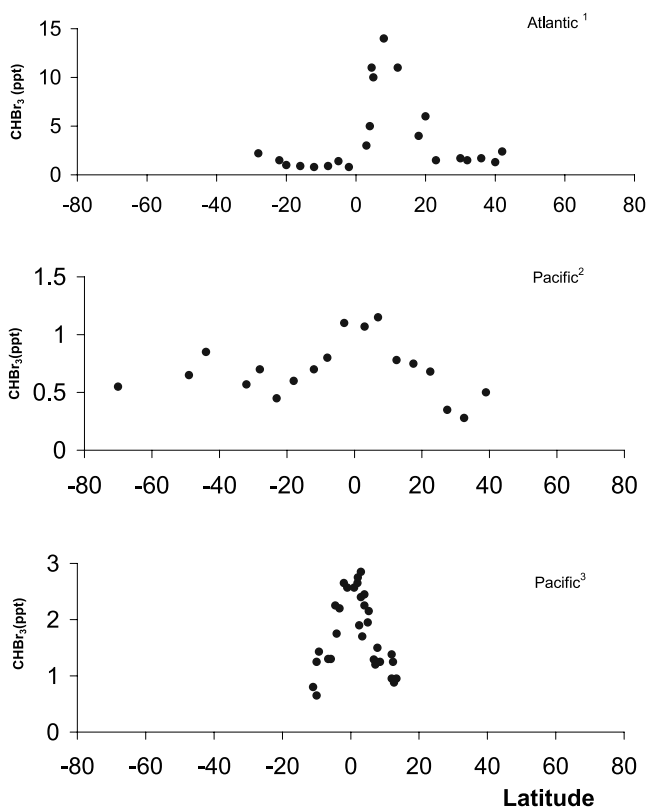
Figure 6. Observations of the tropical maximum of bromoform in the marine boundary layer over the Atlantic (1, $\sim 20° - 10°$W [*Class and Ballschmiter*, 1988]) and Pacific (2, $80° - 160°$W [*Schauffler et al.*, 1999]; 3, $145° - 165°$W [*Atlas et al.*, 1993]).

calculation is very uncertain, because it is based on 'background' concentration measurements, performed in remote locations. The atmospheric bromoform concentration, however, is regionally variable, ranging from 0.2 to $\gg 100$ ppt $CHBr_3$ (0.6 to $\gg 300$ ppt Br), with 'background' values falling at the low end of measured levels. In the following we prefer to report $CHBr_3$ generally as Br, which reflects the actual amount of reactive bromine from this compound. Bromoform contributes approx. 10 to 20% of the total organic bromine near the sea surface in remote locations and $\sim 3\%$ in the entire troposphere [*Schauffler et al.*, 1999]. Highest atmospheric concentrations have been reported from nearshore regions in the vicinity of extensive beds of macroalgae, where they range from 18 ppt Br in the Antarctic, 90 ppt Br in the Arctic to >300 ppt over subtropical coastal areas. Hence bromoform's contribution to total organic bromine may rise to more than 50% or even 90% near strong source regions (Figure 2) [*Class and Ballschmiter*, 1988; *Reifenhäuser and Heumann*, 1992; *Berg et al.*, 1984]. Coastal atmospheric bromoform concentrations have been observed to reach a maximum at low tide, presumably when macroalgae are exposed to air. This maximum is more pronounced at night [*Carpenter et al.*, 1999]. Elevated coastal bromoform concentrations, even in the absence of large

beds of macroalgae have been detected at sandy beaches in the eastern North Sea, as well as above salt marshes and the Wadden Sea [*Quack*, 1994].

[33] Meridional surveys over both the eastern Atlantic and the western Pacific Oceans have revealed maximum concentrations in the tropical marine boundary layer with $9 - 50$ ppt Br from bromoform (Figure 6) [*Schauffler et al.*, 1999; *Atlas et al.*, 1993; *Class and Ballschmiter*, 1988; *Quack and Suess*, 1999; *Yokouchi et al.*, 1997]. The cause of this maximum remains unclear but has generally been attributed to enhanced regional biogenic production associated with enhanced upwelling and diatom abundance [*Moore and Tokarczyk*, 1993; *Klick and Abrahamsson*, 1992; *Yokouchi et al.*, 1997; *Baker et al.*, 1999].

[34] Seasonal cycles of bromoform have been observed in the Arctic and over Hawaii [*Yokouchi et al.*, 1996; *Cicerone et al.*, 1988]. Highest concentrations were observed in the winter months December, January, and February (Point Barrow: 30 ppt Br, Kumukahi: $15 - 18$ ppt), and lowest in June, July, and August (Point Barrow: $6 - 9$ ppt, Kumukahi: $3 - 6$ ppt), with a mean of 18.9 ppt Br for Alaska and 9.3 ppt Br for Hawaii [*Cicerone et al.*, 1988]. However, in the temperate North Sea, where the mean mixing ratio is $6 - 9$ ppt Br, no clear seasonal cycle of airborne bromoform was detected during 2 years of observation [*Quack*, 1994]. The highest variations of bromoform mixing ratios in this variable North Sea environment were found within one season and were related most strongly to the choice of sampling location.

3.1.2. Distribution in Water

[35] Most seawater data originate from the Atlantic Ocean (Figure 5). Means and ranges of reported bromoform concentrations differ strongly between oceanic surface waters inshore, shelf and open ocean regions (Table 3). Open ocean concentrations are in the range of $0.6 - 60$ pmol $CHBr_3$ L^{-1}, with $7 - 60$ pmol L^{-1} in the surface layer of the open polar oceans, decreasing to $0.4 - 30$ pmol L^{-1} in subtropical and tropical open ocean regions of both hemispheres [*Klick and Abrahamsson*, 1992; *Schall and Heumann*, 1993; *Moore and Tokarczyk*, 1993; B. Quack, unpublished data, 2001]. Elevated concentrations of >20 pmol L^{-1} bromoform have occasionally been measured in tropical upwelling regions, strongly implying that there are significant open ocean sources [*Class et al.*, 1986; *Class and Ballschmiter*, 1988]. Coastal and shelf concentrations are however, up to 100 times higher than open ocean concentrations. The highest bromoform concentrations are generally found along coastlines with extensive beds of macroalgae. Temperate and subtropical coastal waters tend to show higher concentrations than those in polar regions (the reverse of the open ocean distribution). Seasonally varying water concentrations have been related to macroalgal sources in both Californian and Baltic Sea nearshore waters, where elevated concentrations have been observed during summer [*Goodwin et al.*, 1997a; *Kuß*, 1993; *Klick*, 1992].

3.2. Air-Sea Flux Calculation for Bromoform

[36] We attempt a first approximation of the global oceanic bromoform emissions, with published air and seawater concentrations, based on known factors affecting
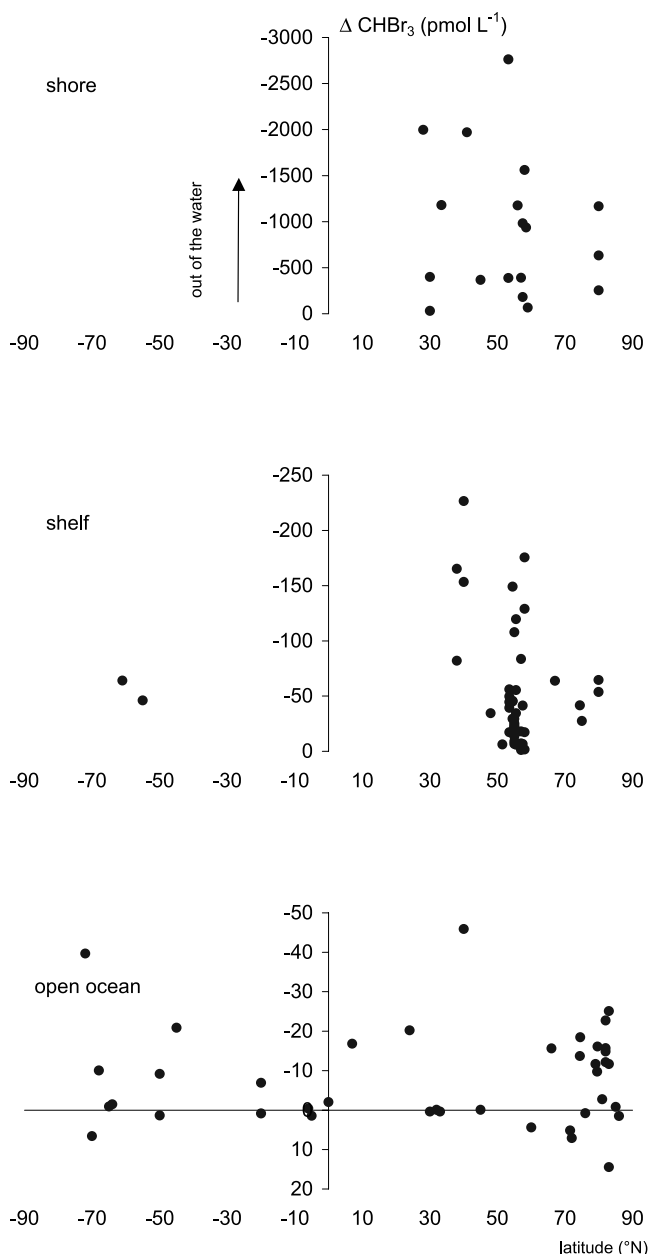
Figure 7. Δc CHBr$_3$[pmol L^{-1}], as a function of latitude of oceanic bromoform for near shore, shelf and open ocean regimes (Δc CHBr$_3$ = actual water concentration-concentration in equilibrium with air).

its distribution. The goal is partly to estimate the global source strength, independent of atmosphere-based estimates and partly to identify key regions that may contribute bromoform to the atmosphere and hence require further investigation. We have therefore calculated annual integrated fluxes of bromoform with global climatological parameters for different latitudes and oceanic biogeochemical provinces.

3.2.1. Air-Sea Exchange Parameterization

[37] Fluxes F (pmol m^{-2} h^{-1}) of bromoform across the air-sea interface were calculated as the product of a gas transfer-coefficient k_W and the air-sea concentration difference (driving force):

$$F = k_w\left(C_w - C_a H^{-1}\right) \qquad (1)$$

[38] Atmospheric mixing ratios were converted to equilibrium water concentrations (pmol L^{-1}) at 1 atm and the air temperature at the air-sea interface, which we took to be the same as the water temperature, assuming 100% relative humidity at the interface. Concentration gradients (Figure 7) and saturation anomalies (Table 4) between ocean and atmosphere were then calculated for each reported aqueous bromoform concentration.

[39] H, the dimensionless Henry's law constant, was found to be in general agreement among various estimates within the literature [*Mackay and Shiu*, 1981; *Moore et al.*, 1995a; *Banerjee et al.*, 1980], and was calculated here according to *Moore et al.* [1995a, 1995b]:

$$H_{(CHBr_3)_T} = \exp(13.16 - 4973/T[K]) \qquad (2)$$

[40] A major uncertainty in estimating the flux of a compound between the atmosphere and ocean is the parameterization of the air-sea transfer-coefficient. Several equations that express k_W as a function of wind speed give a wide range of transfer-velocities, especially at high wind speeds and are all supported to some degree by field or laboratory data. The parameterizations of *Liss and Merlivat* [1986] and *Wanninkhof and McGillis* [1999] represent an upper and lower range of transfer velocities and show the range and uncertainty of the flux calculations, according to this parameter (Figure 8). We selected the quadratic parameterization of *Wanninkhof* [1992] for climatological winds for our subsequent calculations of the transfer velocity, recognizing however, that our flux estimate is dependent on this choice. We chose this parameterization, since it is compatible with global average gas exchange, based on ^{14}C, and we are attempting a global flux estimate and second because it reproduces the air-sea flux under oceanic conditions at medium wind speeds reasonably well [*Keeling et al.*, 1998; *Yvon-Lewis and Butler*, 1997].

[41] The transfer velocity is dependent on the diffusivity of the compound and the viscosity of the solvent, often described by the Schmidt number (Sc), which is the quotient of the kinematic viscosity of the solvent (ν) and the diffusion coefficient (D) of the compound. These are directly dependent on temperature and, to a lesser extent, salinity. We have converted *Wanninkhof*'s, [1992] parameterization, derived for $Sc = 660$ (CO$_2$ at 20°C and $S = 35$), to a parameterization suitable for CHBr$_3$ using a power law dependence of -0.5 at wind speeds above 3.6 m s^{-1} [*Nightingale et al.*, 2000]:

$$kw_{CHBr_3} = 0.39\bar{u}^2(660/Sc_{CHBr_3})^{0.5} \qquad (3)$$

[42] The diffusion coefficient of bromoform in seawater, which is needed for the calculation has not been measured, but can be estimated from the empirical formulae of *Hayduk and Laudie* [1974] and *Wilke and Chang* [1955].

Table 4. Bromoform Concentrations in Marine Boundary Layer Air and Seawater, Saturation Anomalies and Concentration Gradients[a]

	$CHBr_3$ in Surface Water Range (Obs.) (Mean; Median), pmol/L	Water Temp. Range, °C	$CHBr_3$ in Air Range (Mean; Median), ppt	Saturation Anomaly Range (Mean; Median), %	Concentration Gradient Δc Range (Mean; Median), pmol L^{-1}
		Near-Shore			
80–60N	277–1187 (3)	0–3			
60–40N	79–2770 (11)	−1−18			
40–10N	36–2000 (4)	17−25			
Global near-shore			0.7–460 (25; 3.3)	538 to 43,840 (10,420; 6,590)	−2762 to −31(−913; −784)
		Shelf			
80N–60N	44–79 (5)	−2−3			
60N–40N	7.5–182 (39)	1−20.7			
40N–10N	87–237 (4)				
40S–60S	60 (1)	1.5			
60S–80S	80 (1)	−0.5			
Global shelf			0.5 − 32 (5.4; 2.2)	−3.7 to 3760 (733; 395)	−227 to 0.3 (−50.4; −34.5)
		Atlantic open ocean			
>80N	0.6–40.4 (10)	−1.2−4.3		−96 to 165 (66.3; 97.7)	−25 to14 (−9; −12)
80N–60N	7.9–32 (9)	−1.5−8		−47.4 to 193 (65.9; 83.6)	−18 to 7 (−8; −11.7)
60N–40N	5.5–5.9 (2)	5−13		−44 to 1.6 (−21; −21)	−0.1 to 4.4 (2.1; 2.1)
40N–10N	3.2–60.9 (5)	−1−21		−10.5 to 570 (171; 1.7)	−45.9 to 0.4(−13; −0.1)
10N–10S	0.8–19.8 (4)	24−28		−63 to 570 (152; 50)	−16.8 to 1.46(−1.2 ; −4.4)
10S–40S	3.2–10.7 (2)	19−20		−21 to 184 (81; 81)	−6.9 to 0.8 (−3; −3)
40S–60S	10–28 (3)	3−10		−12 to 294 (123; 86)	−21 to 1.4 (−3)
60S–80S	7.9–54.2 (5)	−0.5−−0.3		−45 to 273 (62.7; 10.4)	−37 to 6.6 (−9.1; 1.5)
Atlantic (all latitudes)			0.6 − 14 (3.7; 2.0)		
Pacific open ocean			0.2 − 6.3 (1.3; 1.14)		
Global near-shore	35.6–2,770.1 (934; 946)		(25; 3.3)	538 to 43,840 (10,420; 6,590)	−2,762 to −31(−913; −784)
Global shelf	7.5–237.4 (71.7;40)		(5.4; 2.2)	−3.7 to 3760 (733; 395)	−227 to 0.3 (−50.4; −34.5)
Global open ocean	0.6–61 (18.3; 16.6)		(1.9; 1.2)	−96 to 570 (88; 69)	−46 to 14 (−8.0;−4.8)
Global ocean	0.6–2770		0.2 to 460 (8.1; 2)	−96 to 43,840	−2,762 to 14

[a]Ranges, means and medians of shore, shelf and open ocean regimes (data from Table 2 and 3).

Both approaches use the viscosity of the solvent and the molar volume of the gas at its boiling point. The molar volume of bromoform also needs to be estimated for this purpose, as it, too, has not been measured. The additive methods of Schroeder and Le Bas [*Poling et al.*, 2000] can be applied and yield 108.5 and 99.5 cm^3 mol^{-1}, respectively. For our calculations, we took the mean molar volume and calculated mean *Sc*s of bromoform for differ-
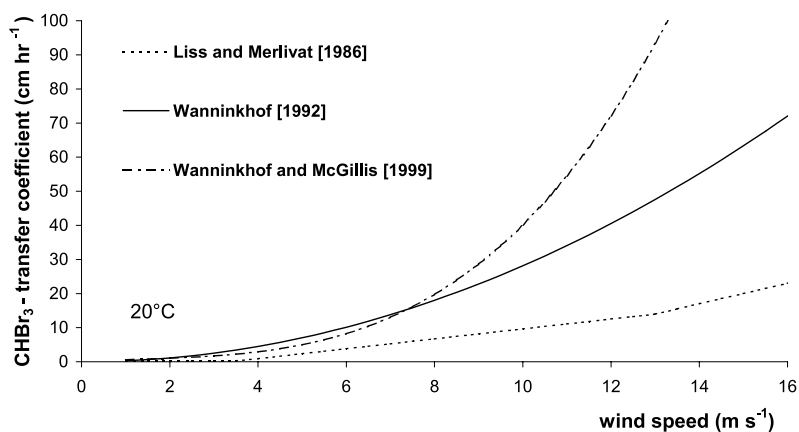

Figure 8. Air-sea exchange transfer-coefficients for bromoform (20°C, $S = 35$) for three different air-sea exchange parameterizations (based on mean Schmidt-numbers according to the diffusion-coefficients from the work of *Hayduk and Laudie* [1974] and *Wilke and Chang* [1955] (see Table 5)).

Table 5. Diffusion-Coefficients (D), Molar Volumes and Schmidt-Numbers (Sc = $\nu * D^{-1}$) of Bromoform

	Units	Temperature, °C				
		−1	0	10	20	30
Dynamic viscosity (η)[a] of seawater ($S = 35$)	centipoises, g m^{-1} s^{-1}	1.95	1.88	1.39	1.07	0.86
Kinematic vicosity (ν)[a] of seawater ($S = 35$)	10^{-2} cm^2 s^{-1}	1.90	1.83	1.35	1.05	0.84
Molar volume of CHBr$_3$ at boiling point (see text)[b]	cm^3 mol^{-1}	104	104	104	104	104
	D (CHBr$_3$)					
Hayduk and Laudie [1974]	cm^2 s^{-1}	3.4E-06	3.5E-06	5.4E-06	7.8E-06	1.1E-05
Wilke and Chang [1955]	cm^2 s^{-1}	4.4E-06	4.5E-06	6.4E-06	8.5E-06	1.1E-05
	Sc (ν D^{-1})[c]					
Hayduk and Laudie [1974]		5615	5173	2479	1341	793
Wilke and Chang [1955]		4354	4052	2118	1226	766
Mean[d]		4985	4613	2299	1283	779
Range of mean Sc	%	12.6	12.1	7.9	4.5	1.7

[a]*Pilson* [1998].
[b]Mean of 108.5 cm^3 mol^{-1} and 99.5 cm^3 mol^{-1} [*Poling et al.*, 2000]: 104 cm^3 mol^{-1} (±4%).
[c]Error of Schmidt-number: 2.5% (due to mean molar volume).
[d]Polynomal fit for mean $Sc_{CHBr3} = 4662.8 - 319.45T + 9.9012T^2 - 0.1159T^3$.

ent temperatures (T in °C) and a salinity of 35 (Table 5), which can be represented as:

$$Sc_{CHBr_3} = 4662.8 - 319.45T + 9.9012T^2 - 0.1159T^3 \quad (4)$$

[43] Although the estimated error of Sc_{CHBr_3} due to our procedure is around 10%, the estimates must be treated tentatively until measurements are available. The actual diffusivities could conceivably lie outside this range.

3.2.2. Data Processing

[44] Oceanic and atmospheric bromoform concentrations, which mostly represent means from several different stud-

ies, were divided among the three regimes; (1) shore (<2 km off coast), (2) shelf, and (3) open ocean, to account for the obvious differences in concentrations between these regimes noted above (Tables 2 and 3). It would not be appropriate to attempt to derive an estimate of the oceanic flux by the usual statistical parametric techniques, because the data are widely scattered and do not approach a normal distribution. Rather, we chose to base our estimates of global fluxes on medians, with the 25% and 75% quartiles as ranges, thereby covering 50% of the available data.

[45] The atmospheric bromoform concentrations revealed no obvious latitudinal trends; hence we obtained median

Table 6. Area-Weighted Means of Sea Surface Temperature, Wind Speed and Transfer-Coefficient (k_w) from Oceanic Domains [*COADS*, 2002], and the Air-Sea Exchange of Bromoform Per Unit Area for Different Oceanic Regimes

Latitudinal Range	Water Temp., Lat. Mean[a], °C	Wind Speed, Lat. Mean[a], m s^{-1}	k_w, Mean[b], cm h^{-1}	Sea-Air Exchange, Median[c], pmol m^{-2} h^{-1}	Sea-Air Exchange, Quartile 25%[c], pmol m^{-2} h^{-1}	Sea-air exchange, Quartile 75%[c], pmol m^{-2} h^{-1}
Global Near Shore						
Global	20.59	6.72	12.89	−101,083	−151,856	−40,057
Global Shelf						
Global	20.59	6.72	12.89	−4452	−7972	−1991
Open Ocean (Atlantic, 70°W–20°E)						
>80°N	2.08	5.42	4.65	−556		
80°–60°N	5.21	7.46	11.39 (10.09)	−1334	Quartiles of the entire Atlantic	
60°–40°N	11.43	8.42	16.13 (14.78)	345		
40°–10°N	23.34	6.57	13.48 (14.18)	−13	−1331	55
10°N–10°S	26.80	5.47	10.34 (9.93)	−124		
10°–40°S	20.79	6.34	11.7 (12.79)	−356		
40°–60°S	7.82	8.52	14.51 (15.90)	−1330		
60°–80°S	0.20	6.46	7.47(8.95)	−111		
Global near shore	20.59	6.72	12.89	−101,083	−151,856	−40,057
Global shelf	20.59	6.72	12.89	−4452	−7972	−1991
Open ocean (Atlantic)	18.39	6.89	12.81	−377	−1331	55
Global open ocean (Median driving forces[a] mean transfer-coefficients)	20.59	6.72	12.89	−625	−2017	61

[a]Area-weighted means from *COADS* [2002].
[b]Area-weighted transfer-coefficients, [*Wanninkhof*, 1992] for $S = 35$ (area-weighted transfer-coefficients for the global ocean).
[c]According to *Wanninkhof* [1992], sum of the individual products of each concentration gradient and the respective transfer-coefficient.
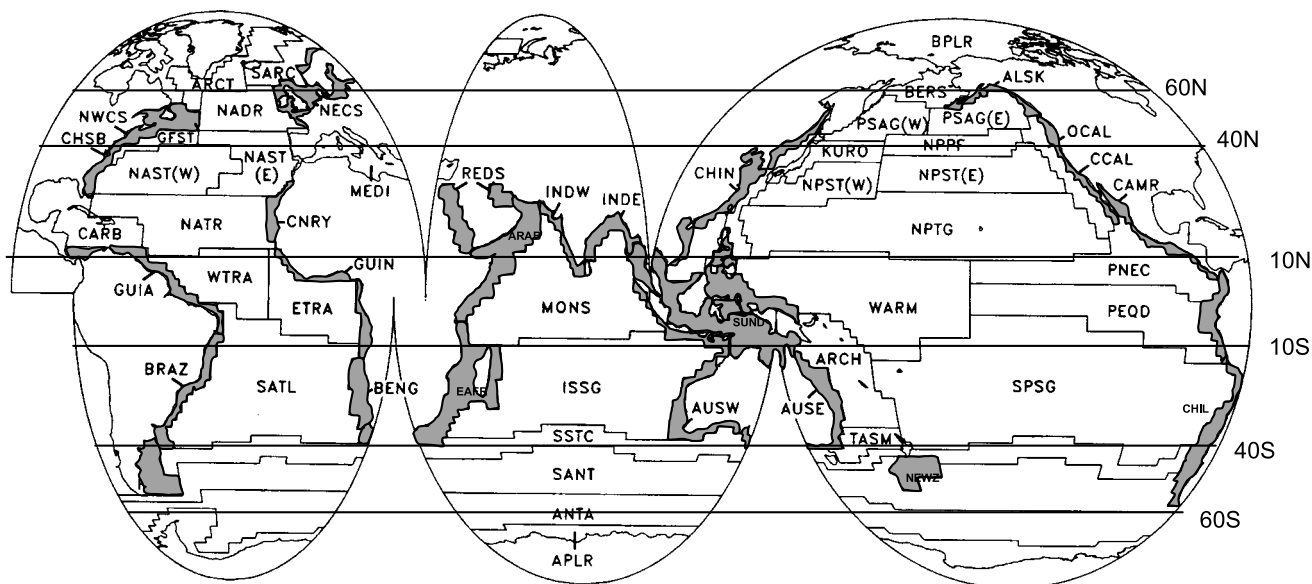
Figure 9. Biogeochemical provinces of the global ocean according to *Longhurst et al.* [1995], including inferred latitudinal bands of similar climatologies. Shaded areas represent Longhurst's coastal provinces, we call shelf regime.

values for the three regimes, which we applied for our flux-calculations (Table 4). For the calculation of individual saturation anomalies and driving forces from each surface water concentration, water temperatures were taken directly from the literature pertaining to the specific study or, if not reported, inferred from cruise locations and dates using the World Ocean Atlas [*Levitus and Boyer*, 1994]. We calculate median global driving forces for shore and shelf regimes, since the data coverage of shelf and shore is very poor (Tables 3 and 4). The median driving forces were combined with the global area-weighted mean transfer-coefficient of $CHBr_3$ of 12.89 cm h^{-1}, to obtain global air-sea fluxes from the shore and shelf regimes. For open ocean waters we chose to calculate air-sea fluxes from the Atlantic, since most published water concentrations for the open ocean regions are from the Atlantic Ocean. Global estimates are based on an extrapolation to the Pacific and Indian Ocean. We try to account for latitudinal variations of the air-sea exchange coefficient in our approach. We therefore, divided the open ocean regime into eight latitudinal bands of similar climatology. Some of the reported data, which were specified only as representative background concentrations for interhemispheric transects had to be assigned to several latitudinal bands. Area-weighted means of sea-surface temperature and wind speed of the Atlantic as well as the global ocean were calculated from comprehensive ocean-atmosphere data set (COADS) data provided by the NOAA-CIRES Climate Diagnostics Center at http://www.cdc.noaa.gov. We calculate median fluxes from the individual latitudinal bands with the resulting area-weighted transfer-coefficients (Table 6).

[46] To infer areas for our shore, shelf, and open ocean regimes within our latitudinal bands, we adopted Longhurst's classification of global biogeochemical provinces, since the correlation between primary and bromoform

production is to our understanding the current best proxy to represent the possible significance of biogenic bromoform production in the global budget. Longhurst specified 57 biogeochemical provinces of different primary production from regional oceanography and examination of chlorophyll fields from the Nimbus7 CZCS (Figure 9) [*Longhurst et al.*, 1995] and differentiated between coastal and open ocean provinces. Coastal provinces generally reveal elevated primary production rates of >300 g C m^{-2} yr^{-1} and open ocean regimes of <200 g C m^{-2} yr^{-1}. The coastal provinces sum up to an area of 41 × 10^6 km^2, which we call the shelf regime (Table 7). To account for the areas of highest primary production and macroalgal sources of bromoform, we assumed a global coastline of 400,000 km and a width of 2 km [*Gierloff-Emden*, 1980; *Lüning*, 1985], resulting in 800,000 km^2 of a highly productive "near-shore" regime.

3.3. Results and Discussion
3.3.1. Bromoform-Flux Estimates for Oceanic Shore, Shelf and Open Ocean Regimes

[47] Shore, shelf, and open ocean regimes are supersaturated with bromoform. Median supersaturations of the shore are two orders and those of the shelf regime one order of magnitude larger than open ocean supersaturations. Median fluxes of 101 (4–430) nmol m^{-2} h^{-1} are calculated for the shore and 4.4 (1–40) nmol m^{-2} h^{-1} are obtained for the shelf regimes (Table 6). Using these fluxes, we obtain global bromoform emissions of 2.3 (0.9–3.4) Gmol Br ($CHBr_3$) yr^{-1} from the shore and 4.7 (3.0–11.7) Gmol Br ($CHBr_3$) yr^{-1} from the shelf regimes, representing 23 and 48% of the entire oceanic bromoform flux (Table 8).

[48] Occasionally, open ocean waters in all latitudinal bands are a sink for bromoform, as noted for Atlantic transects made in the fall [*Chuck*, 2002]. On average,

Table 7. Areas of Inferred Latitudinal Coastal, Shelf and Open Ocean Regimes, According to *Longhurst et al.*'s 1995 Domain Areas[a]

Domain	Ocean	Province	Lat. Range	Province, Area 10^6 km^2	Lat. Range, Area 10^6 km^2	Shore, 0.2% of domain area 10^6 km^2	Shelf, Area 10^6 km^2
Coastal							
Arctic shelf[a]			80°–60°N		3.47	0.07	3.40
Coastal	Atlantic	NECS	60°–40°N	1.36			
Coastal	Atlantic	NWCS	60°–40°N	2			
Coastal	Pacific	ALSK	60°–40°N	0.59	3.95	0.08	3.87
Coastal	Atlantic	CNRY	40°–10°N	0.81			
Coastal	Indian	REDS	40°–10°N	0.56			
Coastal	Indian	INDE	40°–10°N	0.97			
Coastal	Indian	INDW	40°–10°N	0.8			
Coastal	Pacific	CCAL	40°–10°N	0.96			
Coastal	Pacific	CAMR	40°–10°N	1.26			
Coastal	Pacific	CHIN	40°–10°N	0.97	6.33	0.12	6.21
Coastal	Atlantic	GUIN	10°N–10°S	1.42			
Coastal	Atlantic	GUIA	10°N–10°S	1.23			
Coastal	Indian	ARAB	10°N–10°S	2.93			
Coastal	Pacific	SUND	10°N–10°S	6.33	11.91	0.23	11.68
Coastal	Atlantic	BRAZ	10°–40°S	1.2			
Coastal	Atlantic	BENG	10°–40°S	1.13			
Coastal	Indian	EAFR	10°–40°S	3.72			
Coastal	Indian	AUSW	10°–40°S	2.94			
Coastal	Pacific	CHIL	10°–40°S	2.61			
Coastal	Pacific	AUSE	10°–40°S	1.14	12.74	0.25	12.49
Coastal	Atlantic	FKLD	40°–60°S	1.42			
Coastal	Pacific	NEWZ	40°–60°S	1.04	2.46	0.05	2.41
Global shelf + shore					40.86		
Global shore						0.80	
Global shelf							40.06
Open Ocean							
Polar	Arctic	BPLR	>80°N	1.66	1.66		
Polar	Atlantic	ARCT	80°–60°N	2.1			
Polar	Atlantic	SARC	80°–60°N	2.33			
Polar	Pacific	BERS	80°–60°N	3.89	8.32–3.47 = 4.85		
Westerlies	Atlantic	NADR	60°–40°N	3.5			
Westerlies	Atlantic	GFST	60°–40°N	1.1			
Westerlies	Pacific	PSAE	60°–40°N	3.2			
Westerlies	Pacific	PSAW	60°–40°N	2.9	10.7		
Trades	Atlantic	NATR	40°–10°N	8.27			
Trades	Atlantic	CARB	40°–10°N	4.48			
Trades	Pacific	NPTG	40°–10°N	21.09			
Westerlies	Atlantic	NASW	40°–10°N	5.8			
Westerlies	Atlantic	MEDI	40°–10°N	3.08			
Westerlies	Atlantic	NASE	40°–10°N	4.45			
Westerlies	Pacific	KURO	40°–10°N	3.7			
Westerlies	Pacific	NPPF	40°–10°N	3.02			
Westerlies	Pacific	NPSE	40°–10°N	6.83			
Westerlies	Pacific	NPSW	40°–10°N	3.93			
Westerlies	Pacific	OCAL	40°–10°N	2.39	67		
Trades	Atlantic	WTRA	10°N–10°S	5.36			
Trades	Atlantic	ETRA	10°N–10°S	5.34			
Trades	Indian	MONS	10°N–10°S	14.21			
Trades	Pacific	PNEC	10°N–10°S	8.17			
Trades	Pacific	PEQD	10°N–10°S	10.34			
Trades	Pacific	WARM	10°N–10°S	16.78	60.2		
Trades	Atlantic	SATL	10°–40°S	17.77			
Trades	Indian	ISSG	10°–40°S	19.25			
Trades	Pacific	ARCH	10°–40°S	8.84			
Westerlies	Pacific	TASM	10°–40°S	1.65			
Westerlies	Pacific	SPSG	10°–40°S	37.29	84.8		
Westerlies	Southern	SSTC	40°–60°S	16.84			
Westerlies	Southern	SANT	40°–60°S	30.25	47.1		
Polar	Southern	ANTA	60°–80°S	8.87			
Polar	Southern	APLR	60°–80°S	1.93	10.8		
Global open ocean					286		

[a]Area of the arctic shelf was included from the work of *Coachman and Aagard* [1974].

Table 8. Annual Emissions from the Atlantic and the Global Nearshore, Shelf and Open Ocean in Mmol $CHBr_3$ yr^{-1} and Mmol Br yr^{-1} Per Oceanic Domain

Latitudinal Range	Area[a], km^2	Area of Total, %	$CHBr_3$ Emissions, Median[b], Mmol $CHBr_3$ yr^{-1}, Global (Atlantic)	Flux of Total, %	$CHBr_3$ Emissions, Quartile, Mmol $CHBr_3$		$CHBr_3$ Emissions, Median[b], Mmol Br	$CHBr_3$ Emissions, Quartile, Mmol Br	
					25%[b]	75%[b]		25%[b]	75%[b]
Global near shore	8.57×10^5	0.3	−759 (−196)	23	−1140	−301	−2277	−3420	−903
Global shelf	4.01×10^7	12.2	−1.562 (−404)	48	−2789	−699	−4686	−8367	−2097
Open Ocean									
>80°N	1.66×10^6	0.5	−8.1				−24		
80°−60°N	4.85×10^6	1.5	−56.7 (−51.8)				−170		
60°−40°N	1.07×10^7	3.3	32.3 (13.9)				97		
40°−10°N	6.70×10^7	20.4	−7.7 (−3.0)				−23		
10°N−10°S	6.02×10^7	18.4	−65.5 (−11.6)				−197		
10°−40°S	8.48×10^7	25.9	−264.3 (−55.4)				−793		
40°−60°S	4.71×10^7	14.4	−548.8 (−144.5)				−1646		
60°−80°S	1.08×10^7	3.3	−10.5 (−2.6)				−32		
Global open ocean	2.87×10^8	87.5	−929.3 (−263.1)	29	−3348.3	139	−2788	−10,045	417
Global ocean	3.28×10^8	1.0	−3.250 (−863)	100	−7285	−860	−9750	−21,855	−2580

[a]Global shore line [*Gierloff and Emden*, 1974], 2 km area of highest productivity; shelf and open ocean domain areas [*Longhurst et al.*, 1995].
[b]According to the work of *Wanninkhof* [1992], obtained from the sum of the individual products and the respective area.

however, the Atlantic open ocean is a source of atmospheric bromoform (Tables 6 and 8). The largest saturation anomalies have been observed in subtropical and tropical open ocean regions, while polar oceans of the Northern Hemisphere comprise the largest negative saturation anomalies. The overall median flux of bromoform from the Atlantic open ocean is 0.4 nmol m^{-2} h^{-1}. The sum of fluxes from individual latitudinal bands to the atmosphere is 0.79 Gmol Br ($CHBr_3$) yr^{-1}. Extrapolating the Atlantic latitudinal fluxes to the global ocean areas, we yield 3 (−0.4−10) Gmol Br ($CHBr_3$) yr^{-1}. This flux from the open ocean represents 29% of the global oceanic bromoform emission of ∼10 Gmol Br ($CHBr_3$) yr^{-1} (Table 8).

3.3.2. Uncertainties of Flux Estimates

[49] Uncertainties in our flux calculations arise from the overall lack of data, a lack of simultaneous measurements in air and seawater, differing data precision and accuracy of the individual studies, the applied air-sea exchange parameterization, the use of average values, and the error due to spatial and temporal extrapolation of the data. In the following sections, we address uncertainties individually, which need to be considered in future work.

3.3.2.1. Data Availability

[50] Our estimate is limited by a severe lack of field data, including a surprising lack of simultaneous measurements made in both the lower atmosphere and the surface ocean. The database is sparse, scattered and weighted toward temperate and arctic regions. Saturation anomalies from the Atlantic regimes had to be extrapolated to the Indian and Pacific Oceans, for which very few data have been reported (Tables 2 and 3). Thus we are aware that the spatial and temporal extrapolations must be associated with large uncertainties in the global flux. Since bromoform is an ubiquitous compound in the ocean, with significant oversaturations throughout ocean waters, our effort aims mainly at the combination of the available data in order to evaluate the most likely significance of regional and global fluxes of bromoform. In the future, as more

data become available, alternative schemes could certainly be developed and tested.

3.3.2.2. Data Accuracy

[51] Atmospheric bromoform measurements among different groups in the Arctic revealed widely disparate results. Additionally comparison of standards showed a difference of a factor of 2 to 2.5 between data sets [*Sturges*, 1993]. This example shows that measurements of airborne bromoform may be associated with significant uncertainties among the studies. Some studies do not address uncertainties at all and no intercalibrations are performed. Typically, estimates of precision and accuracy for the reactive halocarbons lie in the range of 5−20%. Measurements of aqueous bromoform are additionally hampered by the high solubility of the compound and difficulties in calibration [*Carpenter et al.*, 1999; *Quack and Suess*, 1999]. If we consider the values of measurements being associated with an error of 5% for air and 20% for water concentrations, the flux-calculations yield an uncertainty of 2−8% for the global shore, 17−70% for the global shelf and 40 to 170% for the open ocean. Error-propagation of the flux-equation (Formula 9) reveals that the uncertainty depends highly on the saturation anomaly and is mainly reduced by an increased accuracy of the air measurements.

3.3.2.3. Gas Exchange

[52] The published parameterizations of air-sea gas exchange differ by a factor of 2 for all gases. They do have shortcomings, as surface films, bubbles, and breaking waves, temperature gradients and boundary layer stability influence the exchange in a way, yet not fully understood [*Nightingale et al.*, 2000; *Liss and Merlivat*, 1986; *Wanninkhof and McGillis*, 1999; *Wanninkhof*, 1992]. The relations of gas-exchange measurements to the instantaneous wind speed may cause errors [*Pilson*, 1998], short-term wind variabilities may enhance fluxes by a factor of >2 [*Bates and Merlivat*, 2001], and the use of different global wind regimes also leads to discrepancies on the calculated fluxes [*Boutin and Etcheto*, 1995]. The approximation for
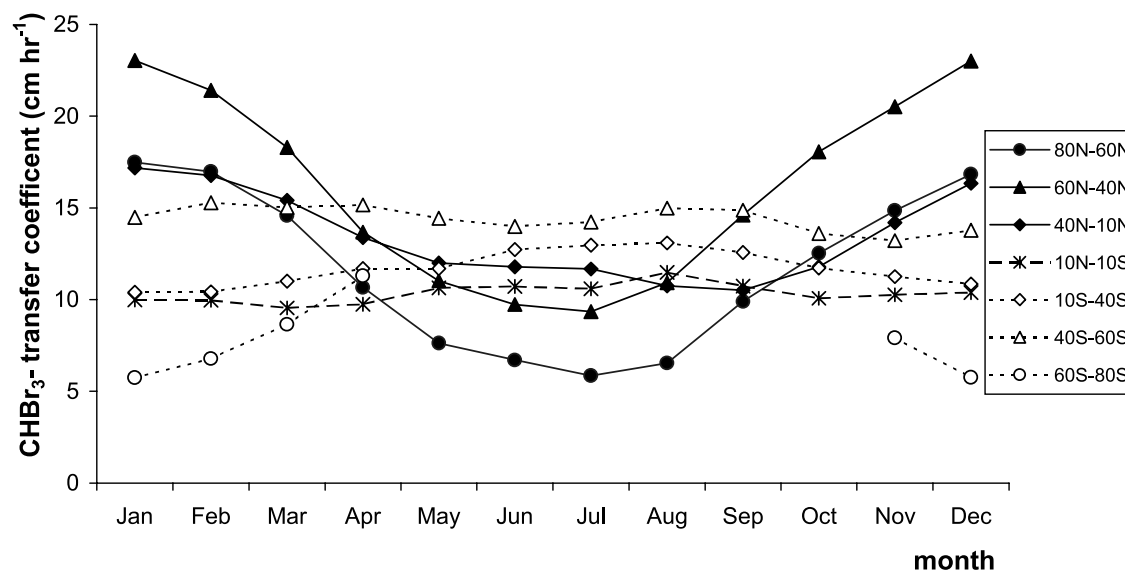
Figure 10. Seasonalitity of the area-weighted air-sea exchange transfer-coefficient from bromoform, calculated according to *Wanninkhof* [1992] for different latitudinal bands of the global ocean.

bromoform's diffusivity and Schmidt number adds additional uncertainty and has to be treated with caution, until actual measurements of bromoform's molar volume and diffusion coefficient are available.

3.3.2.4. Temporal Averaging

[53] The uncertainty due to temporal averaging is most pronounced for Northern Hemispheric latitudes, since seasonality of the air-sea exchange coefficient is largest there (Figure 10). Large transfer-coefficients, along with smaller photolysis rates and lower photochemical oxidant concentration [*Warneck*, 2000], may be the cause of the observed elevated concentrations of airborne bromoform in remote areas of the Northern Hemisphere in winter [*Cicerone et al.*, 1988]. In the North Sea area, no strong seasonal cycles of atmospheric bromoform of its air-sea fluxes could be detected [*Quack*, 1994]. Here, lower transfer-coefficients in summer could be counterbalanced by larger sources during the warm season, which have indeed been observed in coastal waters [*Klick*, 1992]. Decreasing water concentrations toward the warmer season have, however, been observed for the North Sea open waters [*Nightingale*, 1991]. Thus the seasonal variations of air and water concentrations show no clear influence on the flux. We note here that the available data are heavily biased toward the warmer season [Tables 2 and 3].

3.3.2.5. Spatial Extrapolation

[54] The overall lack of data in both atmosphere and ocean, and hence the lack of saturation anomaly estimates, necessitates a large amount of spatial extrapolation. In this section we highlight a few of the major uncertainties associated with this extrapolation.

[55] Our extrapolation approach is based on separating bromoform fluxes into three regimes: near shore, shelf and open ocean. There is an urgent need for transect data that extend from the nearshore out into the open ocean in order to validate and refine this approach. For the atmosphere we applied a constant value of 2 ppt for airborne $CHBr_3$ over open ocean waters. This value appears to be at the low end

of reported polar atmospheric concentrations and at the high end of levels reported for subtropical and tropical open ocean areas (Table 2). The calculated fluxes for the polar oceans might therefore be overestimated with corresponding underestimates for subtropical and tropical oceans. We note that *Li et al.* [1994] and *Moore et al.* [1993] have indicated that Arctic Ocean seawater is most likely in equilibrium with atmospheric $CHBr_3$.

[56] We propose that subtropical coastal and shelf oceans of both hemispheres contribute significantly to global emissions. However there are very few data from these regions and hence the estimated large supersaturations may not necessarily be representative. However elevated atmospheric concentrations [*Yokouchi et al.*, 1999] as well as the distribution of likely producers do imply large fluxes from, for example, the Indonesian and Australian shelf areas for which no oceanic measurement data exist. The best constrained estimate may be for the different latitudinal bands of the Atlantic Ocean (Tables 6 and 8) for which a moderately extensive database exists. Extrapolation of these data to the Indian and Pacific oceans obviously involves additional uncertainty when attempting to derive a global flux estimate. We note however that atmospheric measurements as well as unpublished measurements of bromoform in Pacific surface waters tends to support significant fluxes from equatorial regions and the large southern ocean areas [*Atlas et al.*, 1993; James H. Butler, NOAA, personal communication, 2002]. Relatively high water concentrations of $6-16$ pmol L^{-1} for the Southern Ocean have been applied in our calculations. These levels are significantly higher than 'typical' open ocean concentrations of $3-4$ pmol L^{-1} (Table 3) [*Class and Ballschmiter*, 1988; *Moore et al.*, 1993]. Additional measurements in these waters are therefore a high priority.

3.4. Global Air-Sea Flux of Bromoform

[57] Our calculations yield a global sea-to-air flux of 10 $(3-22)$ Gmol Br ($CHBr_3$) yr^{-1} and thus are in the range of previously reported values. We obtain similar source

Table 9. Global Budgets of Bromoform and Methyl Bromide[a]

	Bromoform, $CHBr_3$ [Reference[b]]	Methyl Bromide, CH_3Br [Reference[b]]
Atmospheric mixing ratios, pptv Br	3 to >1000 [5]	10 [19]
Atmospheric lifetime, year	<0.1	0.7 [9]
Global atmospheric pool, Gmol Br	0.212 [2]	1.596 [1]
Atmospheric sink, Gmol Br yr^{-1}	2.4 [2], 3.5 [3], 11.9 [10]	0.91 (0.69−1.14) [2]
Soil sink, Gmol Br yr^{-1}	(?)	0.45 (0.1−2.28) [2]
Oceanic sink (air to sea flux)	(?)	0.82 (0.39−1.41) [2]
Combined atmospheric sinks; Gmol Br yr^{-1}	2.4−11.7[2, 3, 10]	2.18(1.17−4.79) [2]
Oceanic degradation, Gmol Br yr^{-1}	hydrolysis (30−1000 year): 0.003−0.005 [5] halogen-exchange (5−74 year) [17]: 0.05−0.3 [5] photolysis: 0.03−0.06 [4, 5]	1-100 days hydrolysis average lifetime 100 days [16]
Sinks total, Gmol Br yr^{-1}	2.4−12	
Macro algal source, Gmol Br yr^{-1}	1.6 (0.4−2.7) [4]	
Planktonic source, Gmol Br yr^{-1}	1.05−1.8 [5] 0.12−1.8 [12]	0.07−1.33 [15]
Other natural sources, Gmol Br yr^{-1}	natural haloform [13]	natural oxidation [14]
Combined natural sources, Gmol Br yr^{-1}	0.5−4.5	1.30 (0.46−2.60)[2]
Biomass burning, Gmol Br yr^{-1}	-	0.255 [1] 0.21 (0.11−0.43) [2]
Anthropogenic, Gmol Br yr^{-1}	0.35 (0.25−1.4) [5][c], 0.057 [12]	0.66 (0.29−0.78) [1, 2]
Global oceanic pool, Gmol Br	4.6 [5]	
Oceanic flux, Gmol Br yr^{-1}	10 (3−22) [5], 8.6 [6], (23.73 [11])	−0.8[d] and 0.6 [1, 2.9], net: −0.22[d]
Atmospheric input, Gmol Br yr^{-1}	10 (3−22)	∼1.5

[a]Sinks, sources, inventories and fluxes for bromoform, compared to published informations on methyl bromide, the most abundant atmospheric organic bromine compound.

[b]References: 1, *Lee-Taylor et al.* [1998]; 2, *WMO* [1998]; 3, *Dvortsov et al.* [1999]; 4, *Carpenter and Liss* [2000], 5, this work; 6, *Fogelqvist and Krysell* [1991]; 7, *Moore et al.* [1993]; 8, *Gschwend* [1985]; 9, *Yvon-Lewis and Butler* [1997]; 10, *Penkett et al.* [1985]; 11, *Liss* [1986]; 12, *Sturges et al.* [1992]; 13, *Hoekstra et al.* [1998]; 14, *Keppler et al.* [2000]; 15, *Sæmundsdottir and Matrai* [1998]; 16, *Elliot and Rowland* [1995]; 17, *Geen* [1992]; 18, *Fraser et al.* [1999]; 19, *Butler and Rodriguez* [1996].

[c]Estimated emission due to water chlorination and seawater chlorination.

[d]Negative value: oceanic sink.

strength as the atmospheric-sink calculation of *Penkett et al.* [1985], who estimated 12 Gmol Br ($CHBr_3$) yr^{-1}. Also, the early estimate of 24 Gmol Br ($CHBr_3$) yr^{-1} by *Liss and Slater* [1974], which is based on a rather high mean ocean surface concentration of 40 pmol L^{-1}, is close to the range. Our calculations suggest a 3−4x higher global flux to the atmosphere than the recent global sink-based estimates of 3.5 Gmol Br yr^{-1} [*Dvortsov et al.*, 1999] and 2.49 Gmol Br yr^{-1} [*Kurylo et al.*, 1999]. This might be explicable in terms of strong fluxes from nearshore and coastal regions that may be underrepresented in estimates of atmospheric sink strengths. It is perhaps worth noting that our estimates of the median flux from the open ocean ($\sim$3 Gmol Br ($CHBr_3$) yr^{-1}) closely match the recent estimates of the global sink, which are largely based on measurements over the open ocean. The actual bromoform flux-distribution is highly nonuniform and contradicts model assumptions. We suspect that estimates of bromoform sink strengths in the atmosphere will require more comprehensive sampling of the atmosphere in order to define appropriate temporal and spatial distributions of bromoform. Improved estimates of regional air-sea fluxes will continue to provide an independent means of assessing atmospheric budgets.

[58] Our air-sea flux estimate of 10 (3−22) Gmol Br ($CHBr_3$) yr^{-1} can also be compared with the estimates of within-ocean production and loss. Between our estimate and the combined macroalgal and planktonic bromoform production of 3.1 (0.5−5.1) Gmol Br ($CHBr_3$) yr^{-1} presented above remains an imbalance of 7 (−2 to 22) Gmol Br yr^{-1}. Our air-sea flux estimate thus opens the possibility for additional oceanic sources, which are certainly possible, considering the ease of bromine oxidation and variable

pathways of bromoform production in the marine environment (see section 2.2).

[59] The mean lifetime of bromoform in the marine atmospheric environment, based on our calculated sea to air flux is 7 days, compared to 4 weeks proposed by *Moortgat et al.* [1993]. This lifetime estimate and the imbalance between bromoform's production and flux both seem to contradict our emissions estimates. However, we consider that at present there is a lack of information concerning regional budgets and a serious lack of a quantitative understanding of production pathways, making any decision as to which estimates are more reliable unwarranted. Rather, the discrepancy highlights the uncertainty in our present understanding, which is derived in large part from a lack of suitable observations.

[60] Bromoform sources and calculated fluxes contribute more organic and reactive bromine to the atmosphere than other organobromines, which contribute $\sim$2−3 Gmol Br yr^{-1} including methyl bromide (CH_3Br), the most investigated bromine compound until recently (Table 9).

3.5. Atmospheric Implications of Bromoform's Air-Sea Flux

[61] Marine aerosol, with a most probable source strength of 40−100 Gmol Br yr^{-1}, as described earlier, is the largest source for reactive bromine to the troposphere. If all three bromine atoms of bromoform (10 Gmol Br yr^{-1}) are released in the troposphere, their contribution to the tropospheric reactive Br-budget contributes globally in the range of 10−25%, but with significant regional and possible seasonal variations (see section 2.1). Regional contributions of >50% are likely, since in certain oceanic regions as in the

tropical ocean, the sea-salt aerosol is not acidic enough to maintain autocatalytic cycles and release Br-species. Thus the main source for the reactive bromine BrO_x in these regions of the troposphere are short-lived brominated gases, of which bromoform is likely the most important.

[62] For the lower stratosphere *Nielsen and Douglass* [2001] and *Dvortsov et al.* [1999] calculated a contribution of 30, resp. 60% of reactive bromine from bromoform to the inorganic bromine species. Application of our calculated sources would enhance bromofrom's Br-contribution significantly. Close to source regions, assisted by convection and atmospheric circulation the Br-contribution from bromoform may indeed reach >75%. Analysis of the model approaches, including the neglect of spatial variability of bromofrom sources in both models show a need for further studies.

[63] The strongly variable and poorly characterized source, together with bromoform's short atmospheric lifetime, complicates the model-based estimation of the distribution of reactive Br resulting from its atmospheric degradation. An integrated program of marine and atmospheric observations, atmospheric modeling and mechanistic studies of oceanic bromoform production is required to better constrain present and future Br delivery to the atmosphere.

4. Summary, Conclusion, and Outlook

[64] Based on the available atmospheric and oceanic surface water data, we estimate the global sea-to-air-flux of bromoform to be 10 (3–22) Gmol Br yr^{-1}. Fluxes increase from open ocean waters over shelf to shore regimes by two orders of magnitude. We estimate that the narrow nearshore region, representing only 0.3% of the global ocean area, may be responsible for 23% of the global total emission. Continental shelves (12% of ocean area) are estimated to contribute 48% and the open oceans (88% ocean area) are calculated to contribute 29%. Open ocean waters are generally slightly oversaturated, but may also act as sinks in certain seasons or regions. Subtropical and tropical coastal waters may be important source regions for atmospheric bromoform and therefore for reactive Br-species.

[65] Very rough estimates of marine sources of bromoform including macroalgae and phytoplankton of 3.1 (0.5–5.1) Gmol Br $(CHBr_3)$ yr^{-1} fall short of the calculated sea to-air flux. This leaves room for possible production by other organisms (e.g., those containing haloperoxidases) and processes (e.g., abiotic oxidation).

[66] Natural bromoform sources combined with photochemical Br-release from sea salt may be responsible for most of the bromine-related chemistry in the troposphere and lower stratosphere. Bromoform may contribute 10–25% to the tropospheric reactive Br-budget, with regional contributions of >50% and may also contribute >75% to the lower stratospheric Br-budget. Bromoform's importance for tropospheric and stratospheric bromine chemistry warrants further investigations of the variability of its sources and sinks and of the environmental bromoform distributions.

[67] Based on our literature review and attempts to estimate global fluxes, we identify the following issues for making progress in this area: (1) Additional spatial coverage and time resolution of measurements are needed.

(2) Air and seawater measurements should be made simultaneously, and saturation anomalies should be obtained during field experiments. (3) Simultaneous air and seawater observations during a whole year would be helpful to detect seasonal flux-variations. (4) Suspected source regions without any prior data coverage, such as tropical and subtropical shelf waters and upwelling regimes need to be investigated in detail. (5) Sampling cruises in source regions with active photochemistry and convection, as in the Indonesian Archipelago and the tropical Atlantic and Pacific, may help to quantify the importance of reactive bromine species from bromoform for atmospheric oxidation processes and ozone chemistry. (6) Diffusivity of bromoform in seawater needs to be measured to better constrain the transfer-coefficient. (7) Measurements across gradients of primary production, coupled with process studies may help to identify sources. (8) Sensitivity of sources to environmental forcing needs to be studied and quantified. (9) Nonuniform source of the short-lived bromoform has to be included in atmospheric transport models to evaluate its regional contribution of reactive bromine for tropospheric and stratospheric ozone chemistry.

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