

## Inorganic bromine in the marine boundary layer: a critical review

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**Abstract.** The cycling of inorganic bromine in the marine boundary layer (mbl) has received increased attention in recent years. Bromide, a constituent of sea water, is injected into the atmosphere in association with sea-salt aerosol by breaking waves on the ocean surface. Measurements reveal that supermicrometer sea-salt aerosol is substantially depleted in bromine (often exceeding 50%) relative to conservative tracers, whereas marine submicrometer aerosol is often enriched in bromine. Model calculations, laboratory studies, and field observations strongly suggest that the supermicrometer depletions reflect the chemical transformation of particulate bromide to reactive inorganic gases that influence the processing of ozone and other important constituents of marine air. Mechanisms for the submicrometer enrichments are not well understood. Currently available techniques cannot reliably quantify many Br-containing compounds at ambient concentrations and, consequently, our understanding of inorganic Br cycling over the oceans and its global significance are uncertain. To provide a more coherent

framework for future research, we have reviewed measurements in marine aerosol, the gas phase, and in rain. We also summarize sources and sinks, as well as model and laboratory studies of chemical transformations. The focus is on inorganic bromine over the open oceans outside the polar regions. The generation of sea-salt aerosol at the ocean surface is the major tropospheric source producing about 6.2 Tg/a of bromide. The transport of Br from continents (as mineral aerosol, and as products from biomass-burning and fossil-fuel combustion) can be of local importance. Transport of degradation products of long-lived Br-containing compounds from the stratosphere and other sources contribute lesser amounts. Available evidence suggests that, following aerosol acidification, sea-salt bromide reacts to form Br<sub>2</sub> and BrCl that volatilize to the gas phase and photolyze in daylight to produce atomic Br and Cl. Subsequent transformations can destroy tropospheric ozone, oxidize dimethylsulfide (DMS) and hydrocarbons in the gas phase and S(IV) in aerosol solutions, and thereby potentially influence climate. The diurnal cycle of gas-phase Br and the corresponding particulate Br deficits are correlated. Higher values of Br in the

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gas phase during daytime are consistent with expectations based on photochemistry. We expect that the importance of inorganic Br cycling will vary in the future as a function of both increasing acidification of the atmosphere (through anthropogenic emissions) and climate changes. The latter affects bromine cycling via meteorological factors including global wind fields (and the associated production of sea-salt aerosol), temperature, and relative humidity.

## 1 Introduction

Marchand (1852) reported what were probably the first atmospheric measurements of bromine (in rain). The next data were obtained more than 100 years later (Behne, 1953). Aerosol bromine was first measured by Duce et al. (1963) at Hawaii. Inorganic bromine compounds, especially Br, BrO, and HOBr, are reactive and have the ability to destroy ozone catalytically. It is known that they contribute to the destruction of the stratospheric ozone layer (e.g. WMO, 1998). In addition, bromine may also affect ozone in the troposphere. Zafriou (1974) was the first to notice that halogen atoms in the marine boundary layer (mbl) would rapidly react with ozone. Summaries of these early results were presented by Duce and Hoffman (1976), Berg and Winchester (1978), Cicerone (1981), and Sturges and Harrison (1986b). Today, many new measurements are available which were made subsequent to these reviews. Several field experiments have shown the importance of tropospheric bromine chemistry in polar regions during spring (e.g. Barrie et al., 1988) and near salt lakes (e.g. Hebestreit et al., 1999). Apparently, reactions involving frozen sea water or solid salt crystals play a role there. However, the global role of marine bromine chemistry is still uncertain.

This review focuses on inorganic bromine chemistry over the open oceans, with emphasis on areas outside the polar regions. We have compiled atmospheric measurements of inorganic bromine in marine aerosol, rain drops, and the gas phase. We also review relevant model studies and laboratory measurements. Available data have been assembled and analyzed to gain insight concerning the physical and chemical processes that control inorganic bromine in the mbl. Specific questions that are addressed include:

- How does the chemical composition of the aerosol vary with particle size?
- How does it change with altitude and latitude?
- What are the diurnal and seasonal variations?
- Is particulate bromine in marine air correlated with ambient acids and sea-salt concentrations?
- Are there bromine sources in addition to sea salt?

## 2 Measurement techniques, data quality and analysis

### 2.1 Aerosol measurements

Particulate bromine as well as sea-salt reference species (e.g. Na, Mg) and crustal reference species (e.g. Al) have been measured in marine air using several approaches. The most common techniques involve sampling aerosol over periods of hours to days either in bulk on a single filter (e.g. Kritz and Rancher, 1980) or as a function of size using either a 2-stage stacked filter unit (SFU) (e.g. Raemdonck et al., 1986) or inertial, multi-stage cascade impactors (CI) (e.g. Duce et al., 1965). Samples are then analyzed using various approaches including neutron activation analysis (NAA) for total Br, Na, Mg, and Al (e.g. Arimoto et al., 1987), atomic absorption spectroscopy (AAS, also abbreviated AA) for total Na and Mg (e.g. Galloway et al., 1982), ion chromatography (IC) for Br<sup>-</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> (e.g. Ayers et al., 1999), X-ray fluorescence (XRF) for total Br and Na (e.g. Sturges et al., 1985), and particle-induced X-ray emission (PIXE, also called proton-induced X-ray emission) for total Br, Na, and Mg (e.g. Andreae, 1982). Recently, several aerosol mass spectrometers have been developed to analyze the molecular (or molecular fragment) composition of single particles as a function of size (PALMS = particle analysis by laser mass spectrometry (Murphy et al., 1997); ATOFMS = aerosol time-of-flight mass spectrometry (Gard et al., 1998); AMS = aerosol mass spectrometry (Jayne et al., 2000)).

Bromide (Br<sup>-</sup>) is the dominant form of inorganic bromine in sea water (Stumm and Brauner, 1975). It is therefore tempting to assume that all of the inorganic bromine in sea-salt aerosol samples is also bromide. As described in more detail below, however, other brominated species may be associated with atmospheric aerosols. In addition, different analytical approaches quantify different pools of bromine. For example, NAA detects all chemical forms of bromine whereas IC detects only Br<sup>-</sup>. Consequently, reported measurements of total particulate bromine and particulate bromide may not be directly comparable. In this paper, we use the term ‘bromine’ and the symbol Br to denote the total of all bromine compounds. We only use ‘bromide’ if the ion Br<sup>-</sup> is meant specifically.

In addition to potential differences resulting from species-specific versus non-specific measurement techniques, several other factors can influence the comparability of the resulting data. The geometry of inlets and associated sampling rates impart an effective upper limit for the size of aerosols sampled by different devices. In addition, physical effects such as non-isokinetic flow at sampler inlets (e.g. Rader and Marple, 1988) or wall losses within inlets (e.g. Huebert et al., 1990) may introduce significant bias, particularly in the collection of supermicrometer aerosol from aircraft. Consequently, vertical profiles of sea-salt composition are very poorly constrained. Some cascade impactors may also experience significant internal losses of particles (e.g. Willeke, 1975). Fi-

nally, the current generation of aerosol mass spectrometers is not capable of analyzing larger marine aerosol, which dominate the flux of atmospheric sea salt and related compounds. Reported data from these instruments are limited to the lower end of the sea-salt size distribution (less than about 3  $\mu\text{m}$  diameter). The above limitations in our ability to reliably characterize the upper end of marine aerosol size distributions contribute to the wide range in estimated fluxes of sea salt and associated compounds (e.g. Andreae, 1995; Graedel and Keene, 1995).

In certain techniques, such as NAA, XRF, and PIXE, the filter (or collection substrate) is normally analyzed together with the aerosol deposit. This calls for careful blank corrections. In some filter types, in particular Nuclepore® filters, the blank values of Br can be quite high and they can vary substantially from lot (batch) number to lot number. Blank filters of the same lot as used for the actual aerosol collections should therefore be analyzed. Failure to do so may have given rise to some erroneous (outlier) data in the literature.

Another concern is the possibility of a change in composition during the collection process. Mixing chemically distinct particles on sampling media (e.g. highly acidic sulfate aerosol with sea-salt aerosol on bulk filters) can lead to volatilization of HCl via acid displacement reactions. Fortunately, this is not the case for bromide because the effective solubility of HBr is much larger than that of HCl. For recent paired measurements of particulate Br in size-segregated and bulk aerosol samples collected in coastal air at Hawaii, Br in bulk aerosol samples was found to be conservative (Keene, unpublished). However, gases such as HOBr and  $\text{O}_3$  in air streams may chemically interact with previously sampled aerosols on collection media (as they do in the atmosphere) during the relatively long exposure times (hours) required for most conventional measurement techniques. Such processes could cause significant post-collection artifacts. To our knowledge, the potential magnitudes of such bias in the measurement of particulate Br have not been evaluated experimentally.

Sampling locations and periods may not be regionally or temporally representative, respectively, thereby potentially compromising comparability among reported data. For instance, enhanced turbulence in coastal zones (surf) produces locally high concentrations of sea salt relative to off-shore locations. Sharp altitudinal gradients in sea salt (e.g. Blanchard et al., 1984) lead to substantial variability in measured concentrations as a function of sampling height. Since sea-salt aerosol production strongly depends on wind speed (Gong et al., 2002, 1997, and references therein), temporal variability in wind fields leads to large changes in sea-salt aerosol concentrations (e.g. Erickson et al., 1999). Finally, the relative amounts of sea salt and of acids and bases (both natural and anthropogenic) in the multiphase system vary as functions of proximity to and strengths of their respective up-wind sources. Chemical interactions of this mixture together with ambient relative humidity control aerosol pH (Keene

**Table 1.** Concentrations of selected elements in sea water at 3.5% salinity (Wilson, 1975) and element ratios used to calculate enrichment factors

	based on mass		based on amount of substance	
Cl	19.35	g/kg	0.5459	mol/kg*
Br	0.0673	g/kg	0.000842	mol/kg*
Na	10.77	g/kg	0.4685	mol/kg*
Mg	1.290	g/kg	0.05306	mol/kg*
Ca	0.4121	g/kg	0.01028	mol/kg*
Br/Na	0.00625	kg/kg	0.00180	mol/mol
Br/Cl	0.00348	kg/kg	0.00154	mol/mol
Br/Mg	0.0522	kg/kg	0.0159	mol/mol
Br/Ca	0.163	kg/kg	0.0819	mol/mol
Cl/Na	1.797	kg/kg	1.165	mol/mol

\*Note that this refers to kg of sea water and not to kg of solvent. It thus is not a molality.

and Savoie, 1998, 1999; Erickson et al., 1999; Keene et al., 2002) and related pH-dependent processes involving particulate Br (e.g. Keene et al., 1998; Ayers et al., 1999).

## 2.2 The enrichment factor $EF$

Concentrations of aerosol bromine in the mbl can vary over a large range. The flux of sea-salt Br is mainly a function of wind speed, which drives the generation of sea-salt particles. Thus, it is often useful to interpret bromine data relative to conservative constituents of sea salt. Concentrations of selected elements in sea water are shown in Table 1. In the absence of significant mineral dust, Na and Mg are generally conservative tracers of sea salt in the mbl (e.g. Keene et al., 1986). They are major components of sea salt and stable ions that are not known to undergo chemical reactions in the atmosphere. However, at low concentrations typical of submicrometer marine aerosol, random analytical variability can lead to spurious departures from seawater composition.

Other constituents of sea-salt aerosol including Ca, K, and Cl have also been used as tracers of the sea-salt component. However, these tracers are often not conservative. For example, crustal dust contains significant Ca and K; biomass burning emits particles enriched in K; and Cl is displaced from acidified sea-salt aerosols as HCl. In addition, for some techniques (e.g. AAS), the analytical resolutions for Ca and K are relatively lower than those for Na and Mg. In some of the older Br data sets, paired measurements of Na or Mg were not reported. In such cases, other sea-salt tracers were used (see column 4 in Table 2), which makes the estimates of bromine enrichments less certain. In particular, several early papers used Cl as the reference species. In very remote regions where chlorine deficits relative to sea salt are typically low, errors will be small. However, in polluted regions where

**Table 2.** Bromine depletions measured in marine aerosol samples

data set	Location Date (Campaign <sup>1</sup> )	Sampling <sup>2</sup> Analysis <sup>3</sup>	<i>EF</i> vs.	Result	Reference
AMS9298	Amsterdam Island (38°S, 78°E) Jan 1992-Jul 1998	CI IC	Na	Fig. 3	Baboukas (2000) and Baboukas (unpublished)
ARA95	Arabian Sea cruise May-Aug 1995 (R/V Meteor)	bulk IC	Na	Fig. 2	Johansen et al. (1999)
ATL77	Atlantic cruise Jun 1977 (R/V Capricorne)	bulk NAA	Na	Fig. 2	Kritz and Rancher (1980) and Rancher and Kritz (1980)
ATL7879	Atlantic cruise Sep 1978-Apr 1979 (polyester sailboat)	CI PIXE	K	Fig. 3	Maenhaut et al. (1981b) <sup>4</sup> and Maenhaut et al. (1983)
ATL90	Atlantic cruise Jan-Mar 1990 (R/V Meteor)	SFU NAA	Na	Figs. 2, 5	Maenhaut et al. (unpublished)
ATL94	Atlantic cruise Oct-Nov 1994 (R/V Polarstern)	SFU PIXE	Ca	Figs. 2, 5, 6	Van Dingenen (unpublished)
ATL96	Atlantic cruise Apr 1996 (R/V Seward Johnson)	HVDVI IC	Na	Figs. 2, 5	Johansen et al. (2000)
ATL96b	Atlantic cruise Oct-Nov 1996 (R/V Polarstern)	CI IC	Na	Figs. 2, 3, 5, 6	Baboukas et al. (2000) <sup>4</sup>
BAB8897	Barbados (13°N, 59°W) Aug 1988-Dec 1997 (AEROCE)	bulk NAA	Na	Figs. 2, 11	Arimoto et al. (1995) <sup>4</sup> and Arimoto et al. (unpublished)
BAB94	Barbados (13°N, 59°W) Apr-May 1994 (AEROCE)	CI NAA	Na	Fig. 3	Arimoto et al. (unpublished)
BEM8897	Bermuda (32°N, 64°W) Jul 1988-Dec 1997 (AEROCE)	bulk NAA	Na	Figs. 2, 11	Arimoto et al. (1995) <sup>4</sup> and Arimoto et al. (unpublished)
BEM93	Bermuda (32°N, 64°W) Apr-May, Aug-Sep 1993 (AEROCE)	CI NAA	Na	Fig. 3	Arimoto et al. (unpublished)
BEM96	Bermuda (32°N, 64°W) Apr-May 1996 (AEROCE)	CI NAA	Na	Fig. 3	Keene and Savoie (1998) <sup>4</sup> and Keene and Savoie (1999) <sup>4</sup>
BEM97	Bermuda (32°N, 64°W) May 1997 (AEROCE)	CI + bulk IC <sup>5</sup>	Na	Figs. 2, 3	Keene et al. (2002) <sup>4</sup>
BEM98	Bermuda (32°N, 64°W) Apr-Jun 1998 (AEROCE)	CI + bulk IC <sup>5</sup>	Mg	Fig. 3	Turekian (2000), Turekian et al. (2001), and Turekian et al. (2003)
BIR9196	Birkenes, Norway (58°N, 8°E) Jan 1991-Mar 1996	SFU NAA	Na	Figs. 2, 5, 12	Maenhaut et al. (1996a) <sup>4</sup> and Maenhaut et al. (unpublished)
CGR79	Cape Grim, Australia (41°S, 145°E) Sep 1979	CI + SFU PIXE	K	Fig. 3	Andreae (1982)
CGR94	Cape Grim, Australia (41°S, 145°E) Mar-Jun 1994	CI IC	Na	see note <sup>6</sup>	Ayers et al. (1999)
CGR95	Cape Grim, Australia (41°S, 145°E) Nov-Dec 1995 (ACE-1)	in situ PALMS	Cl	Sect. 4	Murphy et al. (1997)
CGR9698	Cape Grim, Australia (41°S, 145°E) Jan 1996 - Jul 1998	bulk IC	Na	Figs. 2, 10	Ayers et al. (1999) and Ayers (unpublished)
CRE97	Finokalia, Crete, (35°N, 26°E) Feb - Oct 1997	CI IC	Mg	Fig. 3	Mihalopoulos et al. (1997) <sup>4</sup> and Kouvarakis and Mihalopoulos (unpublished)
CRE99	Nopigia, Crete (36°N, 24°E) May 1999	CI IC	Mg	Fig. 3	Kouvarakis et al. (2002)
CRO9698	Crozet (46°S, 52°E) Jul 1996-Mar 1999	bulk IC	Na	Fig. 2	Baboukas (2000) and Baboukas (unpublished)

**Table 2.** (continued)

data set	Location Date (Campaign <sup>1</sup> )	Sampling <sup>2</sup> Analysis <sup>3</sup>	<i>EF</i> vs.	Result	Reference
ENE79	Enewetak, Pacific (11°N, 162°E) Apr-May 1979 (dry season) and Jul-Aug 1979 (wet season) (SEAREX)	CI + bulk NAA	Na	Fig. 3	Duce et al. (1983)
HAR83	Isle of Harris, Great Britain (58°N, 7°W) Apr-May 1983	bulk XRF <sup>7</sup>	Na	Fig. 2	Sturges (1990)
HAW62	Hawaii (20°N, 155°W) May 1962	silver rods NAA	Cl	Fig. 2	Duce et al. (1963)
HAW63	Hawaii (20°N, 155°W) Summer 1963	CI NAA	Cl	Fig. 3	Duce et al. (1965)
HAW66	Hawaii (20°N, 155°W) Summer 1966	CI NAA	Cl	Fig. 3	Duce et al. (1967)
HAW67	Oahu, Hawaii (22°N, 158°W) Fall 1967	CI NAA	Cl	Fig. 3	Duce and Woodcock (1971)
HAW69	Oahu, Hawaii (22°N, 158°W) Jul/Aug 1969	CI NAA	Cl	Figs. 2, 3	Moyers and Duce (1972)
HAW99	Oahu, Hawaii (22°N, 158°W) Aug-Oct 1999	CI + bulk IC <sup>5</sup>	Mg	Figs. 2, 3, 5	Pszenny et al. (2003)
HAW99b	Oahu, Hawaii (22°N, 158°W) Sep 1999	bulk IC	Na	Fig. 9	Phillips et al. (2000) and Huebert et al. (unpublished)
INDXX	Mahabaleshwar, India (18°N, 74°E) during summer monsoon (year=?)	CI NAA	Na	Fig. 3	Sadasivan (1980)
IND73	Indian Ocean cruise May-Jun 1973	CI NAA	Na	Fig. 3	Sadasivan (1978), Sadasivan (1980)
IND99	Indian Ocean flights Feb-Mar 1999 (INDOEX)	SFU IC	Na	Fig. 2	Gabriel et al. (2002) and Gabriel (pers. comm., 2001)
JAB9596	Jabiru, Australia (13°S, 133°E) May 1995-Dec 1996	SFU NAA	Na	Figs. 2, 5	Maenhaut et al. (2000) <sup>4</sup> and Maenhaut et al. (unpublished)
MHD8994	Mace Head, Ireland (53°N, 10°W) Aug 1989-Aug 1994 (AEROCE)	bulk NAA	Na	Figs. 2, 11	Arimoto et al. (1995) <sup>4</sup> and Arimoto et al. (unpublished)
MHD93	Mace Head, Ireland (53°N, 10°W) Jun-Aug 1993 (AEROCE)	CI NAA	Na	Fig. 3	Arimoto et al. (unpublished)
MOR81	Morecambe Bay, Great Britain (54°N, 3°W) Oct-Dec 1981	bulk XRF <sup>7</sup>	Na	see note <sup>6</sup>	Sturges and Harrison (1986a)
MOR8283	Morecambe Bay, Great Britain (54°N, 3°W) Dec 1982-Jan 1983 and Sep-Oct 1983	bulk XRF <sup>7</sup>	Na	see note <sup>6</sup>	Sturges and Harrison (1986b)
MQI9597	Macquarie Island (55°S, 159°E) Dec 1995-Apr 1997	SFU IC	Na	Fig. 2	Ayers et al. (1999)
NOS91	North Sea cruise Sep 1991 (NOSE)	SFU NAA	Na	Figs. 2, 5	François et al. (1993) <sup>4</sup> and Maenhaut et al. (unpublished)
NOS92	North Sea research platform (55°N, 7°E) Sep 1992 (ASE)	SFU NAA	Na	Figs. 2, 5, 7	François and Maenhaut (1994) <sup>4</sup> and Maenhaut et al. (unpublished)
NZ83	New Zealand (35°S, 173°E) Jun-Aug 1983 (SEAREX)	CI + bulk NAA	Na	Figs. 3, 5	Arimoto et al. (1990) and Pszenny (1987) <sup>4</sup>
PAC79	Pacific cruise Apr-Jun 1979 (polyester sailboat)	CI PIXE	K	Fig. 3	Maenhaut et al. (1983)

**Table 2.** (continued)

data set	Location Date (Campaign <sup>1</sup> )	Sampling <sup>2</sup> Analysis <sup>3</sup>	<i>EF</i> vs.	Result	Reference
PAC82	Pacific cruise Jun-Aug 1982 (R/V Conrad)	CI + bulk PIXE	Na, K	Figs. 2, 3	Raemdonck et al. (1986)
PAC8586	Pacific cruise Dec 1985 - Feb 1986 (R/V Xi- angyanghong)	CI + bulk NAA	Na	Fig. 3	Zhou et al. (1990)
PD86	Drake Passage cruise Mar-Apr 1986 (R/V Polar Duke)	CI IC <sup>5</sup>	Na	Figs. 3, 5	Pszenny et al. (1989) <sup>4</sup>
PSI91	North East Pacific cruise May 1991 (PSI-3)	CI IC	Na	Fig. 3	Howell et al. (1998) <sup>4</sup>
PUR71	Puerto Rico (18°N, 66°W) Nov 1971	CI NAA	Na	Fig. 3	Martens (1973)
RITS90	Equatorial Pacific cruise Jan-Feb 1990 (RITS)	CI IC <sup>5</sup>	Mg	Fig. 3	Pszenny (1992) <sup>4</sup>
RITS91	Atlantic cruise Jul-Sep 1991 (RITS)	CI IC	Na	Figs. 3, 5	Pszenny et al. (1993) <sup>4</sup>
SAM76	Samoa (14°S, 171°W) Jul-Sep 1976	CI PIXE	Cl	Fig. 3	Maenhaut et al. (1981a)
SAM81	Samoa (14°S, 171°W) Jan-Feb 1981 (wet season) and Jul-Aug 1981 (dry season) (SEAREX)	CI + bulk NAA + IC <sup>5</sup>	Na	Fig. 3	Arimoto et al. (1987) and Pszenny (1987) <sup>4</sup>
SWE8586	Utlängen (56°N, 16°E), Landsort (59°N, 18°E), and Svenska Högarna (59.5°N, 19.5°E), Sweden Mar 1985-Dec 1986	SAM PIXE	Na	see note <sup>6</sup>	Swietlicki (1989)
TEN8997	Izaña, Tenerife (29°N, 17°W) May 1989-Dec 1997 (AEROCE)	bulk NAA	Na	Sect. 4.2	Arimoto et al. (1995) <sup>4</sup> and Arimoto et al. (unpublished)
TEN94	Punta del Hidalgo, Tenerife (29°N, 17°W) Jul 1994 (AEROCE)	CI NAA	Na	Fig. 3	Arimoto et al. (unpublished)
TEX91	Texel, The Netherlands (53°N, 5°E) Sep 1991 (NOSE)	SFU NAA	Na	Figs. 2, 5	François and Maenhaut (1994) <sup>4</sup> , François et al. (1993) <sup>4</sup> and Maen- haut et al. (unpublished)

All data sets listed as unpublished are based on measurement methods presented in Sect. 2.1.

<sup>1</sup> The acronyms of the field campaigns are: ACE-1 = First Aerosol Characterization Experiment; AEROCE = Atmosphere/Ocean Chemistry Experiment; ASE = EUROTRAC subproject Air-Sea Exchange; EUROTRAC = European Experiment on Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe; INDOEX = Indian Ocean Experiment; NOSE = North Sea Experiment; PSI-3 = Third Pacific Sulfur/Stratus Investigation; RITS = Radiatively Important Trace Species; SEAREX = Sea/Air Exchange; SOAPEX = Southern Ocean Atmospheric Photochemistry EXperiment. For ship cruises, the name of the ship is given.

<sup>2</sup> The sampling devices are: bulk = aerosol sampled in bulk on filters; CI = cascade impactor; HVDVI = high-volume dichotomous virtual impactor; SAM = stationary aerosol monitor as described by Hansson and Nyman (1985); SFU = 2-stage stacked filter unit.

<sup>3</sup> The analytical methods are: IC = ion chromatography; NAA = neutron activation analysis; PIXE = particle (or 'proton') induced X-ray emission; PALMS = particle analysis by laser mass spectrometry; XRF = X-ray fluorescence.

<sup>4</sup> This reference contains general information about the field campaign. However, it does not contain the aerosol bromine data that we present here.

<sup>5</sup> The reference element was analyzed using atomic absorption spectroscopy (AAS).

<sup>6</sup> CGR94: Tab. 4 in Ayers et al. (1999) lists a mean value of  $EF = 0.51$ ; MOR81: A good correlation between Br and Pb was found with only a small sea-salt contribution; MOR8283:  $EF \approx 0$  after correction for Br from vehicles; SWE8586:  $EF > 1$  for submicrometer particles.

<sup>7</sup> The reference element was analyzed using flame photometry.

chlorine deficits are large (e.g. Keene et al., 1990; Sander and Crutzen, 1996), significant bias is associated with this approach.

For the ease of data evaluation, we define a dimensionless enrichment factor  $EF(\text{Br})$  for bromine, using Na as a reference element, as follows:

$$EF(\text{Br}) = \frac{([\text{Br}]/[\text{Na}]_{\text{meas}})}{([\text{Br}]/[\text{Na}]_{\text{seawater}}} \quad (1)$$

where square brackets denote concentrations and ‘meas’ stands for ‘measured’. Analogous definitions can be made for other sea-water elements. In this paper we abbreviate  $EF(\text{Br})$  as  $EF$ . When the enrichment factor of another element (e.g. Cl) is mentioned, it will be denoted explicitly as  $EF(\text{Cl})$ .

Some authors report relative bromine *depletions* rather than enrichment factors. The simple relationship between them is:

$$\text{depletion} = 1 - EF \quad (2)$$

We prefer  $EF$  here because it avoids the complication of ‘negative depletion’ in the case when the aerosol is enriched in bromine, i.e. when  $EF > 1$ .

Available evidence suggests that fresh sea-salt aerosol has an inorganic composition indistinguishable from that of surface seawater, i.e.,  $EF = 1$  even though the aerosol is substantially enriched in organic constituents (Duce and Woodcock, 1971; Duce and Hoffman, 1976; Turekian et al., 2003).

While the dimensionless quantities  $EF$  and ‘depletion’ describe the *relative* composition, we will use the terms ‘excess’ and ‘deficit’ to refer to *absolute* quantities (e.g. expressed as mass per volume of air). We define ‘excess Br’ as the concentration of aerosol bromine above that which originated from sea salt:

$$\text{excess Br} = [\text{Br}]_{\text{meas}} - \left[ [\text{Na}]_{\text{meas}} \times \left( \frac{[\text{Br}]}{[\text{Na}]} \right)_{\text{seawater}} \right] \quad (3)$$

The simple definition of the deficit is:

$$\text{Br deficit} = -\text{excess Br} \quad (4)$$

Absolute quantities are especially useful when analyzing size-segregated data as shown in Sect. 4.1. Values for different size bins can simply be added up. If the total value of ‘excess Br’ is negative, it yields a rough estimate of what to expect in the gas phase, assuming that bromine originates from sea salt and is just cycled between the phases. However, this estimate needs to be treated with caution because organobromine species also originate from seawater and cycling between phases does not preclude differential atmospheric lifetimes against deposition.

### 2.3 Measurements of inorganic gas-phase species

As discussed in more detail below, chemical characterization of marine aerosol often reveals substantial enrichments

in submicrometer Br and large deficits in supermicrometer Br relative to sea salt. These observations indicate that Br actively cycles between phases. The most likely forms of inorganic gas-phase bromine involved in such transformations include  $\text{Br}_2$ ,  $\text{BrCl}$ ,  $\text{IBr}$ ,  $\text{Br}$ ,  $\text{BrO}$ ,  $\text{HOBr}$ ,  $\text{BrNO}_2$ ,  $\text{BrNO}_3$ ,  $\text{HBr}$ , and possibly other species (e.g. Behnke et al., 1994; Sander and Crutzen, 1996; Vogt et al., 1996, 1999; Sander et al., 1999). Several techniques have been developed to quantify gas-phase Br.

The most widely used approach employs an alkaline-impregnated filter positioned downstream of a filter that removes particulate Br from the air stream. Available evidence suggests that such filter-pack devices efficiently sample reactive inorganic Br while effectively discriminating against organic Br gases (Rahn et al., 1976; Li et al., 1994). As for gas-phase Cl (Berg and Winchester, 1978), activated charcoal sampling media (Moyers and Duce, 1972) probably efficiently collect both inorganic and organic forms of gas-phase Br. Several potential artifacts are associated with the use of filter-pack samplers. Reactions on the upstream bulk filter between constituents of chemically distinct aerosols or between particulate-phase species and gases in the sample air stream could lead to positive or negative bias in volatile Br sampled downstream. In addition, the specificity of such samplers for most Br compounds has not been confirmed via testing with calibration gases.

Tandem mass spectrometry (Spicer et al., 1998) and long path differential optical absorption spectroscopy (LP-DOAS) (Hebestreit et al., 1999; Martinez et al., 1999) have been used to measure  $\text{Br}_2$  and  $\text{BrO}$ , respectively, in Arctic marine air. Detection limits for the current generation of these instruments are near the upper limits of model-calculated mixing ratios over the open ocean. Consequently, most deployments to date do not have adequate resolution to reliably discern signal from noise in the mbl at lower latitudes. However, the development of Multi-Axis DOAS (MAX-DOAS) (Hönninger, 2002; Hönninger and Platt, 2002; Leser et al., 2003) allows very sensitive measurements of  $\text{BrO}$  in the planetary boundary layer. Recently,  $\text{BrO}$  was quantified in the mbl of the North Atlantic using this new approach (Leser et al., 2003).

Techniques have been developed to measure mixing ratios of Br-atom precursors (primarily  $\text{Br}_2$  and  $\text{HOBr}$ ) (Impney et al., 1997) and to infer Br-atom concentrations based on relative concentration changes in hydrocarbons (Jobson et al., 1994) under conditions of enhanced Br chemistry during sunrise in the Arctic. However, such approaches have so far lacked adequate sensitivity to reliably characterize these species in marine regions at lower latitudes.

### 2.4 The detection limit

Differences in methods used to address measured concentrations below the analytical detection limit (DL) are an important and often overlooked factor influencing the compa-

rability of reported data sets. Since particulate bromine in marine air is typically present at low concentrations relative to the resolution of current analytical techniques or the blank level of the filter material, most data sets include a significant fraction of observations below the DL. Some laboratories report only detectable concentrations. Others convert measured concentrations below zero (which occasionally result from random analytical variability around low ambient concentrations) to zero. A third approach sets all values less than the DL to the DL. All of these approaches cause positive bias in resulting population statistics. Some laboratories employ an alternative approach of setting all measured concentrations less than the DL (both positive and negative) to zero, which results in negative bias in population statistics. To minimize bias of this nature, values below the DL are sometimes set to 0.5 times the DL. However, the lower limits on distributions established by this approach reflect laboratory-specific analytical resolution rather than ambient concentrations. Finally, some laboratories report concentrations as measured, including both positive and negative values less than the DL. This approach retains analytical uncertainties in the lower end of concentration distributions, which results in apparently 'noisier' data. Assuming that the measurements are unbiased, however, this latter approach yields the most representative population statistics. If the method for handling concentrations below the DL is not specified, it is impossible to explicitly evaluate the potential importance for the comparability of all data reviewed herein. Undoubtedly, however, some of the observed differences at the lower end of concentration distributions result from such effects.

### 3 Compilation of measurements

Since the early 1960s, particulate bromine has been measured in most regions of the mbl (see Fig. 1). Available data sets, many previously unpublished (but from laboratories with methodologies published in the literature cited here), are summarized in Table 2. The abbreviations shown in the first column are used throughout the text to refer to individual data sets. Readers are referred to the original publications for detailed information concerning previously reported results. Unpublished data sets are briefly described in this section.

Between 1988 and 1998, the composition of marine aerosol sampled in bulk was measured as part of the Atmosphere-Ocean Chemistry Experiment (AEROCE). Amongst other elements, the particles were analyzed for Br, Cl, and Na. North Atlantic data sets are available from three mbl tower sites at Barbados (BAB8897), Bermuda (BEM8897), and Mace Head, Ireland (MHD8994), and also from one high-elevation (2360 m above sea level) site at Izaña, Tenerife (TEN8997). AEROCE-related investigations also characterized the chemical composition of size-segregated aerosols in the mbl as part of intensive field exper-

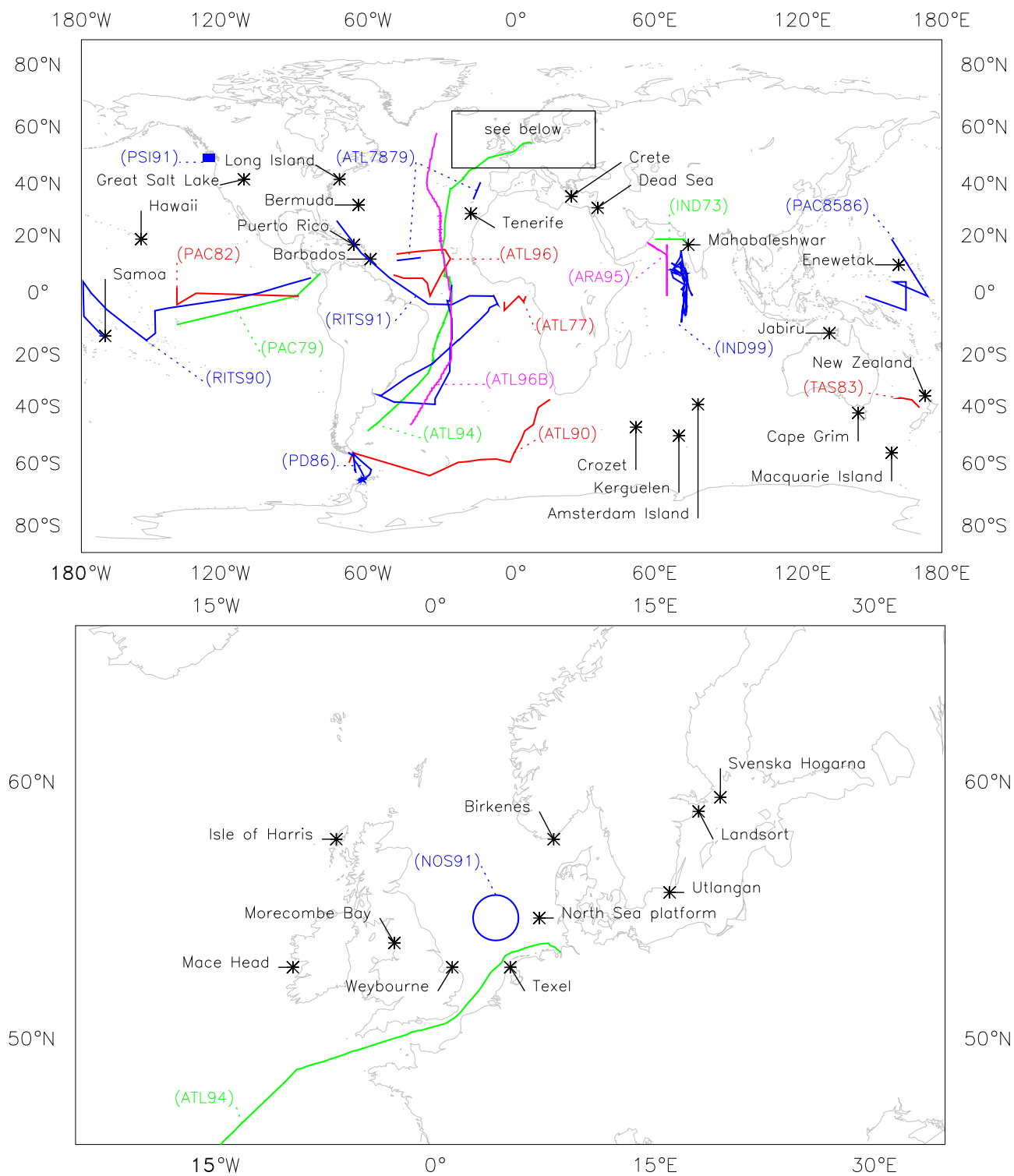
iments at Barbados (BAB94), Bermuda (BEM93, BEM96, BEM97, BEM98), Mace Head (MHD93), and Punta del Hidalgo, Tenerife (TEN94). An additional, size-segregated data set was generated at the joint Texas A&M University – University of Hawaii tower on the windward coast of Oahu, Hawaii, in autumn 1999 (HAW99). All of these sampling campaigns employed Graseby-Andersen hi-vol cascade impactors deployed on towers and operated under similar conditions. For data sets BAB94, BEM93, BEM96, and MHD93, the impactors were configured with an upper '0' stage, Whatman 41 substrates, and backup filters as described by Keene and Savoie (1998). For BEM97 and HAW99, the impactors were also configured with an upper '0' stage but aerosols were sampled on frosted polycarbonate (Lexan) impaction substrates and quartz fiber (Pallflex 2500 QAT-UP) backup filters (Keene et al., 2002; Pszenny et al., 2003). For BEM98, the upper '0' stage was not used and the standard impactors were configured with precombusted glass fiber substrates and backup filters (Turekian et al., 2001, 2003). Data sets BAB94, BEM93, BEM98, and MHD93 correspond to 24-hour or longer sampling intervals whereas those for BEM96, BEM97, and HAW99 were discrete daytime or nighttime sampling intervals.

The experiments at Enewetak (ENE79), Samoa (SAM81), and New Zealand (NZ83) were conducted as part of the SEAREX (Sea/Air Exchange) program. The overall strategy for SEAREX was to sample the four major wind regimes, that is, the tradewinds and westerlies in both the Northern and Southern hemispheres, over the Pacific Ocean.

Maenhaut et al. (unpublished) analyzed bromine in aerosols at several locations (ATL90, BIR9196, JAB9596, NOS91, NOS92, TEX91). Most of the samples were collected either from ships (ATL90, NOS91), a platform (NOS92) or from stations near the coast (BIR9196, TEX91). Only Jabiru (JAB9596) is at 60 km away from the coast. However, it is only slightly above sea level, and sea salt is quite important there. The NOS91 data was obtained from the two ships Alkor (NOS91a) and Belgica (NOS91b) which were located on a circle of 200 km in diameter in the North Sea with Belgica always downwind of Alkor (see Fig. 1). The NOS92 data was obtained at two heights: On deck (NOS92-DECK) and from the mast of the platform (NOS92-MAST). All samples, (except for ATL90) were collected with the Gent PM10 stacked filter unit (SFU) sampler equipped with a PM10 inlet which separates the aerosol into two size fractions: Coarse (2 to 10  $\mu\text{m}$  aerodynamic diameter (AD)) and fine ( $< 2 \mu\text{m}$  AD). The collection surfaces were for the coarse fraction an 8  $\mu\text{m}$  pore size Apiezon®-coated Nuclepore® polycarbonate filter and for the fine fraction a 0.4  $\mu\text{m}$  pore size Nuclepore® polycarbonate filter. The ATL90 samples were also collected with a SFU, but without the PM10 inlet. Here, the coarse filter was a 5  $\mu\text{m}$  pore size Nuclepore® polycarbonate filter.

Van Dingenen et al. (unpublished) collected aerosols during Polarstern cruise ANT XII/1 from Bremerhaven to Chile





**Fig. 1.** Locations where atmospheric inorganic bromine has been measured in the mbl. Stationary sites are marked with asterisks. Cruise and flight tracks (colored) are labeled in parentheses using the data set names from Table 2. Some are approximate and show only the part where samples were taken. More details may be found in the original publications.

(ATL94). Sample collection was identical to the method of Maenhaut et al. as described above but without PM10 inlet. Several elements were measured, including Br, Cl, Ca, K, Zn, and Fe. Na was not measured, so the enrichment factors are calculated using Ca as the sea-salt reference element. A second Atlantic cruise on the Polarstern which followed almost the same course was conducted in 1996 (ATL96b). Size-segregated aerosols were collected in six different size ranges with a Sierra-Andersen hi-vol cascade impactor and analyzed by IC.

During 20 days of the HAW99 experiment (described above), Huebert et al. (unpublished) sampled particulate bromine in bulk aerosol on PTFE filters (HAW99b). Starting each day at midnight, aerosols were sequentially sampled over approximately 3-hour intervals (total  $n = 152$ ). Samples were analyzed by IC.

In the Southern Indian Ocean long-term aerosol measurements were performed at two remote islands. At Amsterdam Island (AMS9298), size-segregated aerosols were collected on Whatman 41 substrates and backup filters by means of a six-stage Sierra-Andersen hi-vol cascade impactor. The sampling was sectorized based on wind direction to minimize the potential for contributions from local terrestrial sources. The sampling intervals were 24-hours or longer. At Crozet (CRO9698), aerosols were collected on PTFE filters with a sampling interval ranging between 24 and 48 hours. All samples were analyzed for major anions and cations by IC.

Available nonspecific measurements of gas-phase inorganic Br are summarized in Table 3 and measurements of BrO using the DOAS technique are summarized in Table 4. The abbreviations used to define the gas-phase data sets end with ‘-G’.

Bromine concentrations measured in rain are summarized in Table 5. Abbreviations for these data end with ‘-R’.

## 4 Results and discussion

Results of the aerosol bromine measurements mentioned above are presented in several figures. Most data sets used to produce the figures are also available in the electronic supplement ([www.atmos-chem-phys.org/acp/3/1301/acp-3-1301\\_supp.zip](http://www.atmos-chem-phys.org/acp/3/1301/acp-3-1301_supp.zip)) to this paper. Figure 2 shows that bromine is depleted from most bulk samples (except for the North Sea samples). Data sets for size-segregated measurements are shown individually in Fig. 3 and in a combined plot in Fig. 4. Absolute bromine concentrations and excess bromine relative to sea water are shown in Fig. 5 separately for submicrometer (radius  $r < 1\mu\text{m}$ ) and supermicrometer aerosol. The size-resolved plots show that for almost all supermicrometer particles  $EF < 1$ . Submicrometer aerosol usually shows a Br/Na ratio higher than that of sea water. However, sea-salt concentrations in these size fractions are relatively low. In addition, the long atmospheric lifetimes for these submicrometer size fractions (5 to 10 days) increases

the potential for crustal contributions from remote continental sources and thus, sea-salt reference species may not be conservative. Consequently, these enrichment factors are associated with substantially greater uncertainty and must be interpreted with caution. We return to this point in Sect. 4.1.

A few data sets were unusual in that bromine was enriched rather than depleted in samples of supermicrometer or bulk aerosol.

- Samples from the polluted North Sea (see Fig. 2) show a bulk  $EF > 1$ . This is due to a high bromine content in the submicrometer particles (see Sect. 4.1). Supermicrometer sea salt particles show the usual bromine depletion (see Fig. 5).
- The only other outlier of the bulk data sets is HAR83. It is possible that the aerosol was influenced by Arctic air which at that time of year (spring) shows increased bromine concentrations (e.g. Berg et al., 1983).
- Two data sets corresponding to samples collected at elevated locations inland from the coast indicate significant bromine enrichments. Duce et al. (1965) (HAW63-HILL) found that bromine was enriched relative to chlorine (their sea-salt reference species) in inland (approximately 16 km, 2000 m elevation) relative to coastal samples. Sadasivan (1980) sampled aerosol near the west coast of India at an altitude of 1380 m and at a distance of about 65 km from the coast (INDXX). However, no such bromine enrichment was observed at Jabiru (JAB9596), which is 60 km away from the coast but only slightly above sea level. A potential explanation for these observations is fast release of bromine to the gas phase close to the coast, followed by particle loss and readsorption of gas-phase bromine onto the remaining particles. Such an effect has also been seen in a model study by Moldanová and Ljungström (2001).
- Murphy et al. (1997) report that their measurements (CGR95) are consistent ‘with a slight enrichment of bromine’. However, this conclusion was based on less than 4% of their PALMS spectra. When all spectra are used (including those with a signal to noise ratio  $< 1000$ ) they find that bromine is below the DL in about 85% of the particles.
- For the bromine enrichment of CGR79 we do not have a satisfactory explanation, especially since other campaigns performed at Cape Grim (CGR94, CGR9698) show bromine depletion.

### 4.1 Size dependence

Duce et al. (1967) were the first to observe that  $EF$  varies as a function of particle size. Since then, many other studies have confirmed this size dependence. Figure 3 shows several data sets obtained at marine sites throughout the world. The

**Table 3.** Measurements of inorganic gas-phase bromine species (other than BrO)

data set	Location Date (Campaign)	Sampling Analysis <sup>1</sup>	Result	Reference
ATL77-G	Atlantic (0°N, 0°W) Jun 1977	filter + LiOH NAA	3.4 pmol/mol	Kritz and Rancher (1980)
ATL80-G	North and South Atlantic (20°N to 30°S) Oct-Nov 1980	see note <sup>2</sup> see note <sup>2</sup>	2.6±1.1 pmol/mol during day 3.2±1.4 pmol/mol at night	Berg et al. (1982)
BEM74-G	Bermuda (32°N, 64°W) Jun-Oct 1974	filter + LiOH NAA	6.7 pmol/mol	Rahn et al. (1976)
HAR83-G	Isle of Harris, Great Britain (58°N, 7°W) Apr-May 1983	filter + KOH XRF	7.9 pmol/mol	Sturges (1990)
HAW63-G	Hawaii (20°N, 155°W) summer 1963	K <sub>2</sub> CO <sub>3</sub> impinger NAA	2 to 12 pmol/mol	Duce et al. (1965)
HAW69-G	Hawaii (20°N, 155°W) Jul/Aug 1969	activated charcoal NAA	13 to 20 pmol/mol (prob- ably includes organic bromine as well)	Moyers and Duce (1972)
HAW99-G	Hawaii (20°N, 155°W) Sep 1999	filter + K <sub>2</sub> CO <sub>3</sub> IC	4.9 pmol/mol daytime average 2.8 pmol/mol nighttime aver- age (Fig. 8)	Perner et al. (2000) and Pszenny et al. (2003)
MOR8283-G	Morecambe Bay, Great Britain (54°N, 3°W) Dec 1982-Jan 1983 and Sep- Oct 1983	filter + KOH XRF	2.8±1.7 pmol/mol	Sturges and Harrison (1986b)
NY96-G	Long Island, New York, USA (41°N, 72°W) Jun 1996	APCIMS	small Br <sub>2</sub> signal detected (but did not exceed detection limit of 6 pmol/mol)	Spicer et al. (1998) and Fos- ter et al. (2001)

<sup>1</sup> APCIMS = atmospheric-pressure chemical ionization mass spectrometry; IC = ion chromatography; NAA = neutron activation analysis; XRF = X-ray fluorescence.

<sup>2</sup> The sampling and analysis methods were not specified by Berg et al. (1982).

medians of these data sets are shown in a composite plot in Fig. 4. Most of the size distributions exhibit asymmetric U shapes with three distinct regions:

1. For very large particles, the composition approaches that of sea water ( $EF \approx 1$ ).
2. Particles in the medium size range of a few  $\mu\text{m}$  diameter are depleted in bromine ( $EF < 1$ ).
3. Very small particles often show high bromine enrichment ( $EF \gg 1$ ).

These three regions are discussed in detail below.

1. Compared to smaller aerosols, the largest sea-salt particles are associated with both shorter atmospheric lifetimes against deposition and smaller surface/volume ratios. Consequently, rates of chemical processing (e.g. alkalinity titration) are slower and their average age is smaller (Erickson et al., 1999). For these reasons, they deviate less from the sea-water composition than the smaller particles. However,

since the largest sea-salt aerosols turn over at much faster rates (several hours versus a mass-weighted average of 1.5 to 2 days for all sea salt (Erickson et al., 1999), even relatively small bromine depletions in these size fractions reflect disproportionately greater percentages of the total Br flux to the gas phase. For example, applying the average dry-deposition velocities for each size fraction of the BEM98 data set (Turekian et al., 2003) to the corresponding average Br deficits clearly indicates that the largest aerosols often dominate this flux.

2. Medium-sized sea-salt particles between one and a few  $\mu\text{m}$  are usually depleted in bromine. A mechanism for the loss of bromine from marine aerosol to the gas phase has been presented by Vogt et al. (1996). They proposed a reaction cycle that releases Br<sub>2</sub> and BrCl from slightly acidified sea-salt particles, as discussed in detail in Sect. 6.

3. Submicrometer aerosol often shows very high values of  $EF$ . It is still an open question how the high bromine concentrations can be sustained in these particles. At first

**Table 4.** DOAS Measurements of BrO in the mbl and over inland saline water bodies.

data set	Location Date (Campaign <sup>1</sup> )	Result	Reference
ATL00-G	Atlantic (54°N to 34°S) Oct 2000 (Polarstern)	two days (around 35°N) with BrO average of 0.7 pmol/mol and a maximum of 2.4 pmol/mol, below DL elsewhere	Leser et al. (2003)
CRT00-G	Finokalia, Crete (35°N, 26°E) Jul - Aug 2000	BrO below detection limit of 0.7 to 1.5 pmol/mol	Hönninger (2002)
GOME95-G	global Jul-Dec 1995 (GOME)	first evidence for tropospheric BrO in the GOME data set	Hegels et al. (1998)
GOME96-G	southern hemisphere (40°S to 77°S) Sep 1996 (GOME)	tropospheric BrO detected (mainly in the Antarctic)	Wagner and Platt (1998)
GOME97a-G	northern hemisphere (40°N to 90°N) Feb-Jul 1997 (GOME)	tropospheric BrO detected (mainly in the Arctic)	Richter et al. (1998)
GOME97b-G	global Apr-Oct 1997 (GOME)	tropospheric BrO detected (mainly in the Arctic)	Chance (1998)
GOME97c-G	global 1997 (GOME)	tropospheric BrO detected over Caspian Sea and over ocean bays where sea ice exists	Wagner et al. (2001)
GSL00-G	Great Salt Lake, USA (41°N, 112°E) Oct 2000	up to 6 pmol/mol BrO	Stutz et al. (2002)
HAW99b-G	Hawaii (20°N, 155°W) Sep 1999	BrO below detection limit of 2 pmol/mol	Pszenny et al. (2003)
ISR97-G	Dead Sea, Israel (31°N, 36°E) May-Jun 1997	up to 176 pmol/mol BrO	Hebestreit et al. (1999) and Matveev et al. (2001)
MHD96-G	Mace Head, Ireland (53°N, 10°W) Jul - Aug 1996 (EASE96)	BrO close to detection limit (estimate of 0.3 to 1.8 pmol/mol)	Allan (1998) and James et al. (2000)
MHD97a-G	Mace Head, Ireland (53°N, 10°W) Apr - May 1997 (EASE97)	BrO close to detection limit (estimate of 1.1 to 2.5 pmol/mol)	Allan (1998) and James et al. (2000)
MHD97b-G	Mace Head, Ireland (53°N, 10°W) Apr - Jun 1997 (EASE97)	BrO below detection limit of 1.69 pmol/mol	Alicke (1997)
MHD98-G	Mace Head, Ireland (53°N, 10°W) Sep - Oct 1998 (PARFORCE)	BrO below detection limit of about 1 pmol/mol	Hönninger (1999)
SAOZ9798-G	global 1997 and 1998 (GOME, SAOZ)	comparing GOME with SAOZ implies 1 to 2 pmol/mol tropospheric BrO if it is distributed homogeneously	Pundt et al. (2000)
TEN97-G	Tenerife (29°N, 17°W) Jun - Jul 1997 (ACE 2)	average of 3 pmol/mol BrO but detection uncertain due to high scatter	Allan (1998)
WEY96a-G	Weybourne, Great Britain (53°N, 1°E) Oct 1996	BrO below detection limit of 2 pmol/mol	Allan (1998)
WEY96b-G	Weybourne, Great Britain (53°N, 1°E) Oct 1996	BrO below detection limit of 2.59 pmol/mol	Alicke (1997)

<sup>1</sup> ACE 2 = Aerosol Characterisation Experiment 2; EASE = East Atlantic Summer Experiment; GOME = Global Ozone Monitoring Experiment; PARFORCE = Particle Formation and Fate in the Coastal Environment; Polarstern = Polarstern cruise leg ANT XVIII/1; SAOZ = Systeme d'Analyse par Observation Zenitale.

glance, it seems logical that bromine that was previously released from sea-salt aerosol subsequently condensed onto these small particles which have a high surface/volume ratio. However, if there is a mechanism that transfers sea-salt

bromine into the gas phase, why doesn't it work for sub-micrometer particles? The inorganic components of sub-micrometer marine aerosols are typically dominated by deliquesced, highly acidic sulfate compounds (Keene et al.,

**Table 5.** Bromine measured in marine rain samples

data set	Location Date (Campaign <sup>1</sup> )	Analysis <sup>2</sup>	EF vs.	Result	Reference
AMS9099-R	Amsterdam Island (38°S, 78°E) Jan 1991-Mar 1999	IC	Na	mean EF = 0.939	Baboukas (2000) and Baboukas (unpublished)
CGR9697-R	Cape Grim, Australia (41°S, 145°E) Jun 1996-Jan 1997	IC	Na	EF=0.613±0.022 (similar to aerosol EF)	Ayers et al. (1999)
CRO9199-R	Crozet (46°S, 52°E) Nov 1991-Mar 1999	IC	Na	mean EF = 0.963	Baboukas (2000) and Baboukas (unpublished)
HAW62-R	Hawaii (20°N, 155°W) May 1962	NAA	Cl	EF = 2	Duce et al. (1963)
HAW63-R	Hawaii (20°N, 155°W) summer 1963	NAA	Cl	EF = 0.7 to 5	Duce et al. (1965), Seto et al. (1969)
NZ83-R	New Zealand (35°S, 173°E) Jun-Aug 1983 (SEAREX)	IC	Na <sup>3</sup>	mean EF = 1.08	Pszenny (1987) <sup>4</sup>
IND7175-R	Mahabaleshwar and vicinity, India (18°N, 74°E) 1971-1975	NAA	Na	EF = 0.9 to 3.6	Sadasivan and Anand (1979)
IND99-R	Indian Ocean cruise Feb-Mar 1999 (INDOEX)	IC	Na	EF ≈ 1	Granat et al. (2002)
INDXX-R	Mahabaleshwar, India (18°N, 74°E) during summer monsoon (year=?)	NAA	Na	EF = 3.6±1.6	Sadasivan (1980)
KER9398-R	Kerguelen (49°S, 70°E) Jan 1993-Nov 1998	IC	Na	mean EF = 0.958	Baboukas (2000) and Baboukas (unpublished)
PUR71-R	Puerto Rico (18°N, 66°W) Nov 1971	NAA	Na	EF 30% higher than for aerosol	Martens and Harriss (1973)
SAM81-R	Samoa (14°S, 171°W) Jan-Feb 1981 (wet season) and Jul-Aug 1981 (dry season) (SEAREX)	IC	Na	mean EF = 0.99 (wet season) mean EF = 1.34 (dry season)	Pszenny et al. (1982) <sup>4</sup>
TAS83-R	Tasman Sea cruise Sep 1983 (SEAREX)	IC	Na <sup>3</sup>	mean EF = 0.82	Pszenny (1987) <sup>4</sup>

<sup>1</sup> Campaign names are described in footnote of Table 2.

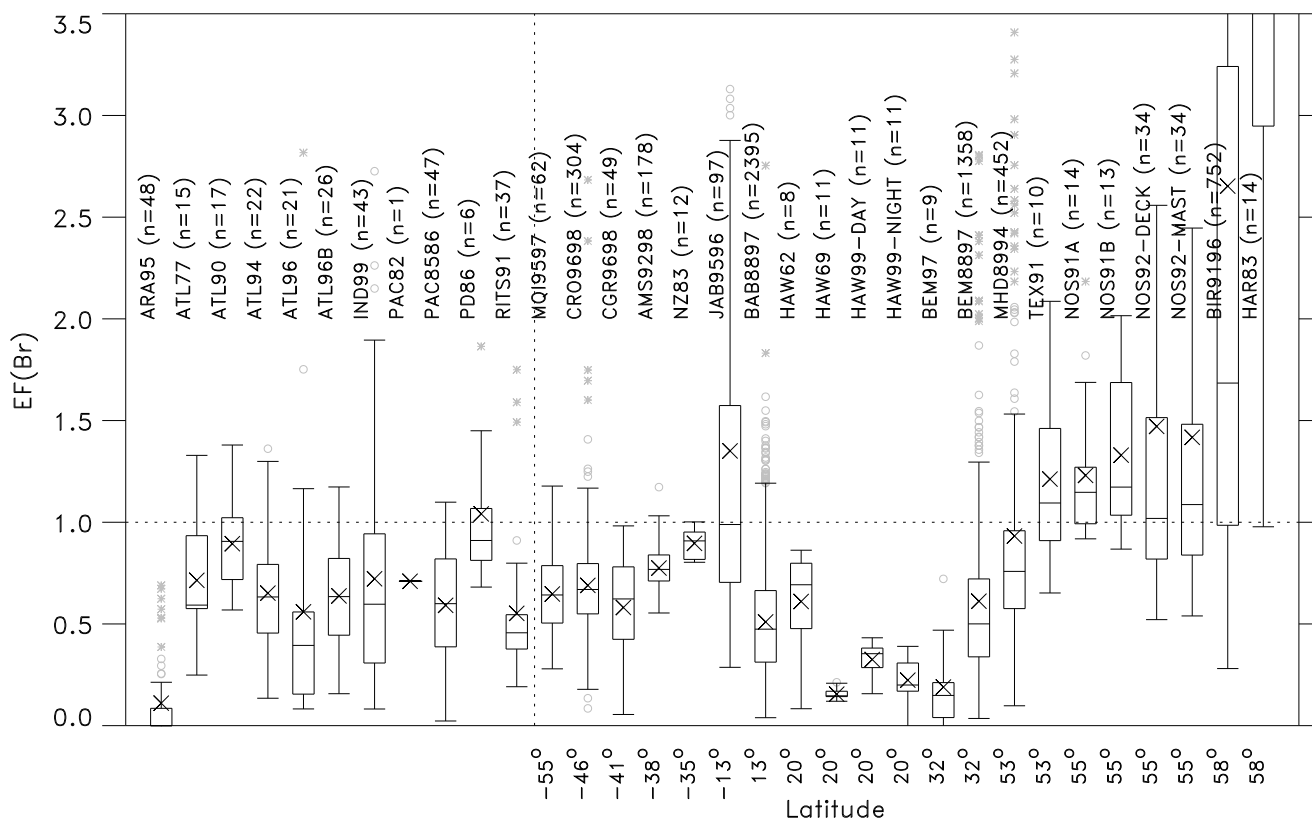
<sup>2</sup> Analytical methods are described in footnote of Table 2.

<sup>3</sup> The reference element was analyzed using atomic emission spectrophotometry (AES).

<sup>4</sup> This reference contains general information about the field campaign. However, it does not contain the rainwater bromine data that we present here.

2002), which should facilitate Br activation. Indeed, Vogt et al. (1996) suggested that recycling through sulfate aerosol should enhance production of Br<sub>2</sub> and BrCl relative to that expected based only on reactions in sea-salt solutions. There is one situation where bromide enrichment in submicrometer particles can be explained with current models: When ozone drops to almost zero during a polar ozone depletion event, the bromine activation chain (see Sect. 6) is interrupted, and bromide can accumulate in the submicrometer particles. However, there are no such extreme ozone depletion events at mid-latitudes, and therefore we must look at other potential explanations for this discrepancy.

First, it could be that submicrometer bromine exists in a form other than Br<sup>-</sup>. This bromine would have to be in a chemically inert form that cannot be converted to volatile species like Br<sub>2</sub> and BrCl. It would then be possible for this form of bromine to accumulate in submicrometer aerosol. A way to investigate this is to compare measurements of total bromine made by NAA (or PIXE) with specific measurements of the bromide anion made with IC. We are not aware of a campaign outside of the Arctic in which the same samples were analysed by both methods. However, Barrie et al. (1994) analyzed bromine in splits of bulk aerosol sampled on PTFE filters in the Arctic. These paired data indicated that



**Fig. 2.** Box-and-whisker plots of  $EF(\text{Br})$  for bulk aerosol samples. For size-segregated measurements, the sum of all sizes was used. IND99 is an exception, here only the coarse mode is available. Cruises are shown in the left part. Stationary locations (right part) are sorted by latitude. The data set names are defined in Table 2. The number of samples  $n$  is given in parentheses. The plots were made following the recommendations by Frigge et al. (1989) (using their definition 6 for the quartiles): 25% of the data are below the box and 25% are above. Thus the box presents the middle 50% (interquartile range). The horizontal line within the box is the median. A cross denotes the mean value. A ‘step’ is defined as 1.5 times the height of the box. The whiskers extend to the minimum and the maximum of the data set if these are within one step of the box. The maximum length of the whiskers is one step. Outliers more than one step away from the box are marked individually: A circle is used for those less than 2 steps away and an asterisk otherwise.

most particulate bromine during that experiment was in the form of soluble bromide. In addition, results from different campaigns using different analytical techniques reveal similar enrichments in submicrometer aerosols (red, green, and black lines in Fig. 4). Comparisons of the data sets from Bermuda are especially useful in this regard. For BEM93 and BEM96 bromine was analyzed by NAA. The analysis method changed to IC for BEM97 and BEM98. Although substantial interannual variability is evident, mean values for all submicrometer size fractions indicate  $EF > 1$ . This implies that the bromide ion  $\text{Br}^-$  is the main chemical form of bromine in these particles.

Alternatively, some submicrometer  $\text{Br}^-$  could be externally mixed with chemically distinct particles such as mineral aerosol, soot carbon, or organic carbon, which lack sufficient water and/or acidity to sustain Br recycling. However, available evidence based on model calculations and chem-

ical analysis of single particles (e.g. Dentener et al., 1996; Anderson et al., 1996) suggests that most mineral aerosol and soot in the mbl are often coated with hygroscopic reactive surface layers, which should sustain aqueous chemical pathways. In addition, high concentrations of dust and soot in the mbl are typically limited to regions downwind of arid continents and/or extensive fossil fuel and/or biomass burning, respectively. We observe no obvious evidence for similar spatial patterns in  $EF$ . In contrast to dust and soot, submicrometer organic carbon is produced primarily by gas-to-particle conversion. Most of it is internally mixed with inorganic constituents rather than externally mixed as isolated organic aerosols (Middlebrook et al., 1998). Consequently, it seems unlikely that external mixing with chemically distinct aerosol types could sustain substantial particulate bromine in marine air.

Finally, it is possible that some other as yet unidentified

pathway(s) lead to the accumulation of  $\text{Br}^-$  in submicrometer aerosol. Resolution of this issue remains an open question.

It should be noted, though, that  $EF$  must be treated with caution here. Since sea salt occurs mainly in the supermicrometer range, there is only little Na and Mg in submicrometer aerosol. Calculating  $EF$  involves dividing by the concentration of the reference element and is therefore strongly dependent on the accuracy of the measurement of that species.

#### 4.2 Altitudinal variation

It is important to note that the exact location of the sampling site plays a role. Aerosol and rain samples (HAW63 and HAW63-R) collected in Hawaii by Duce et al. (1965) showed a systematic increase of  $EF$  with distance from the shore and height above the sea. In general, the farther the sampling location is from the sea surface, the more the aerosol composition deviates from sea water. Duce and Woodcock (1971) compared particles taken at the top (24 m above sea level) and the bottom (4 m a.s.l.) of a sampling tower (see HAW67-BOTTOM and HAW67-TOP in Fig. 3). Bromine depletion was observed only in the samples collected at the top of the tower. At the bottom  $EF$  was close to unity. This can be explained by large but short-lived sea-salt particles close to the surface that have a composition very similar to sea water.

In another study, François and Maenhaut (1994) collected samples on the deck (NOS92-DECK, 27 m a.s.l.) and from a mast (NOS92-MAST, 45 m a.s.l.) of a platform in the North Sea. Data from both altitudes are compared in Fig. 7. Coarse mode Na decreases with altitude simply because of the vertical gradient in sea-salt aerosol mass. Coarse mode Br shows a similar decrease and thus, a significant difference of  $EF$  between these heights cannot be seen. There is almost no vertical gradient of sea-salt aerosol mass in the fine mode and a linear regression of  $\text{Na}_{\text{mast}}$  vs.  $\text{Na}_{\text{deck}}$  (Fig. 7e) yields a slope of 1.05 and a correlation coefficient of  $r^2 = 0.993$  (after excluding one outlier). Bromine concentrations at both heights are also similar (Fig. 7f). However, due to a higher analytical standard deviation the correlation is not as good as for Na.

Even though these data show no dependence of  $EF$  on height up to 45 m a.s.l., it should be noted that model calculations by von Glasow et al. (2002a) predict that acid-catalyzed bromine activation is more efficient in higher layers of the mbl.

Sampling at even higher altitudes can change the results drastically. The station at Izaña, Tenerife is at 2360 m a.s.l. and often encounters free tropospheric air. The aerosol data set obtained here (TEN8997) shows little similarity with sea salt aerosol even though the site is on a small island in the Atlantic. Values of  $EF$  are distributed between 0 and 40. The high variability is expected because sources of Na and Br other than sea salt are significant, e.g. crustal Na.

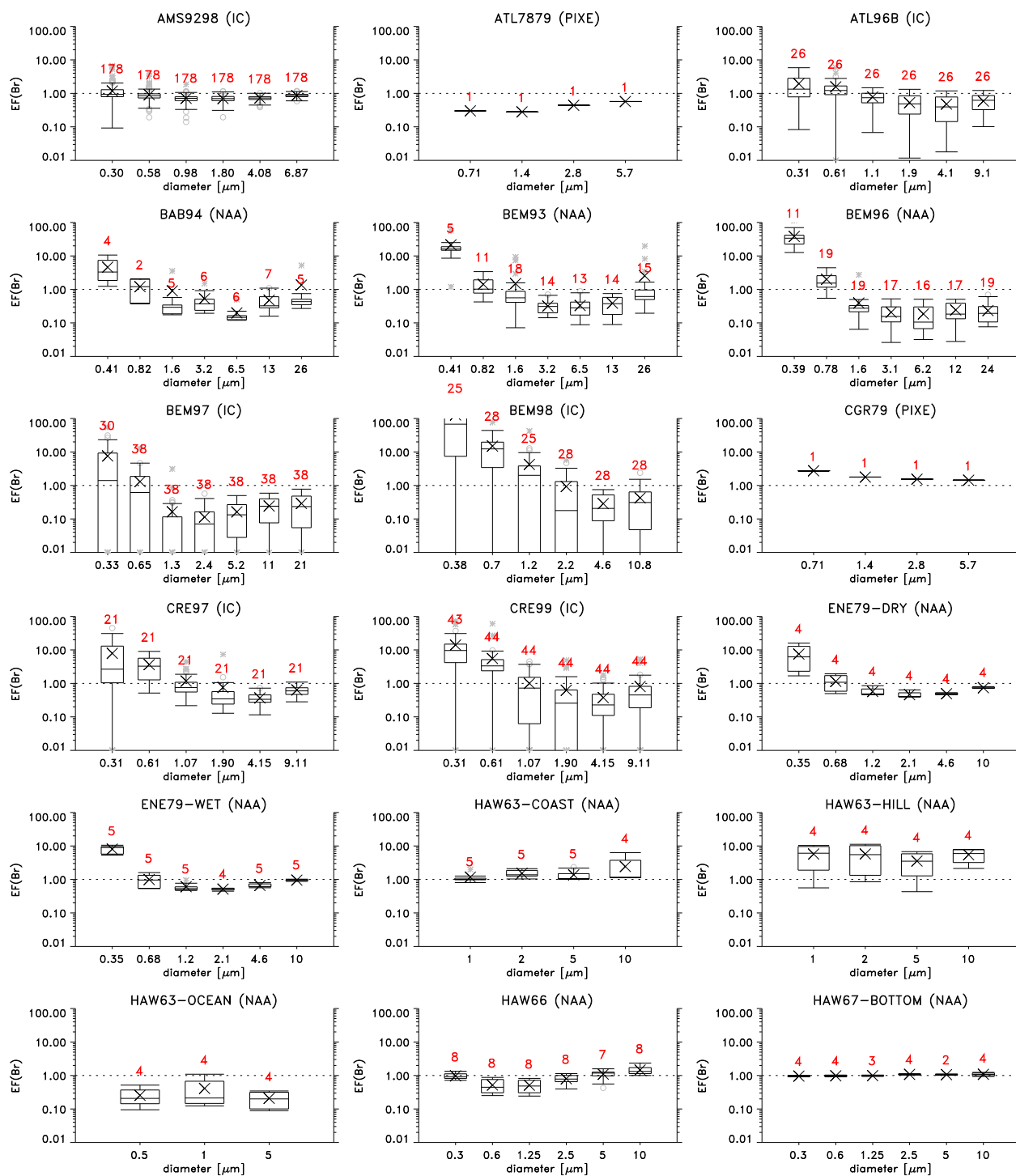
#### 4.3 Latitudinal variation

High concentrations of bromine are observed every spring in the Arctic (e.g. Berg et al., 1983; Sturges et al., 1993; Barrie et al., 1994; Martinez et al., 1999; Michalowski et al., 2000). A similar situation probably exists in the Antarctic (Wagner and Platt, 1998). Outside of the polar regions, there is no clear evidence for a dependence of  $EF$  on latitude, except for the high bromine contents of the North Sea aerosol, which are probably due to anthropogenic influence, as discussed in Sect. 4.8. The bromine measurements plotted in Fig. 2 show no systematic variation with latitude. Data from two Atlantic cruises (ATL94 and ATL96b) are shown in Fig. 6. No clear correlation between latitude and  $EF$  can be seen. If a dependence exists, it is masked by other factors. Anthropogenic pollution, aerosol acidity, biomass burning plumes, and mineral dust can all affect  $EF$ . However, there seems to be one indication for a latitudinal trend. As discussed below (see Sect. 4.5), the seasonal cycle of  $EF$  is very pronounced in the southern hemisphere, whereas it is more difficult to see in most data sets from the northern hemisphere.

#### 4.4 Diurnal variation

Very few studies have investigated the diurnal variation in gas-phase and particulate bromine. The results are inconsistent. Moyers and Duce (1972) found that the gaseous bromine concentrations did not differ in samples collected during sunlight hours versus those collected at night (HAW69). Systematic diurnal variation in particulate bromine was also examined but the limited number of samples precluded a statistically meaningful evaluation. Size-segregated data from a more recent study at Bermuda during spring (BEM96) also reveal no discernable evidence for significant diurnal variation (Keene et al., unpublished). However, the resolution of that data set is limited by the relatively small number of samples coupled with dynamic meteorological conditions.

In contrast to the above, Rancher and Kritz (1980) measured large diurnal variabilities in both gas-phase and particulate bromine during stable meteorological conditions over the tropical South Atlantic Ocean (ATL77). Gas-phase inorganic bromine was approximately two times greater during the day relative to night. Particulate bromine varied by similar magnitudes but was anticorrelated with highest concentrations at night. Recent measurements in coastal air at Hawaii during late summer also reveal persistent, large diurnal variabilities in both gas-phase (HAW99-G, see Fig. 8) and particulate (HAW99b, see Fig. 9) bromine. Maxima in daily  $EF$  values ranged from 0.22 to 1.2 and minima from <DL to 0.33. Day-night patterns and absolute differences in concentrations were similar to those reported by Rancher and Kritz (1980). The consistency between results from these latter studies in different areas suggests that diurnal variation in gas-phase and particulate inorganic bromine is a characteris-



**Fig. 3.** Size-resolved measurements of  $EF(\text{Br})$ . The box-and-whisker plots are defined as explained in Fig. 2. The number of samples is shown in red above each box. The x-axes differ between plots. The characteristic aerosol diameter at ambient relative humidity for each impactor stage was estimated as the geometric mean diameter (GMD) of the 50% cutoff diameters for that stage and for the preceding stage. For the top stage corresponding to the largest size fraction, we assume a GMD  $\sqrt{2}$  times larger than the cutoff diameter of that stage. For the backup filter corresponding to the smallest size fraction, we assume a GMD  $\sqrt{2}$  times smaller than the cutoff diameter of the preceding impactor stage. For INDXX, the sizes of the stages are not known.



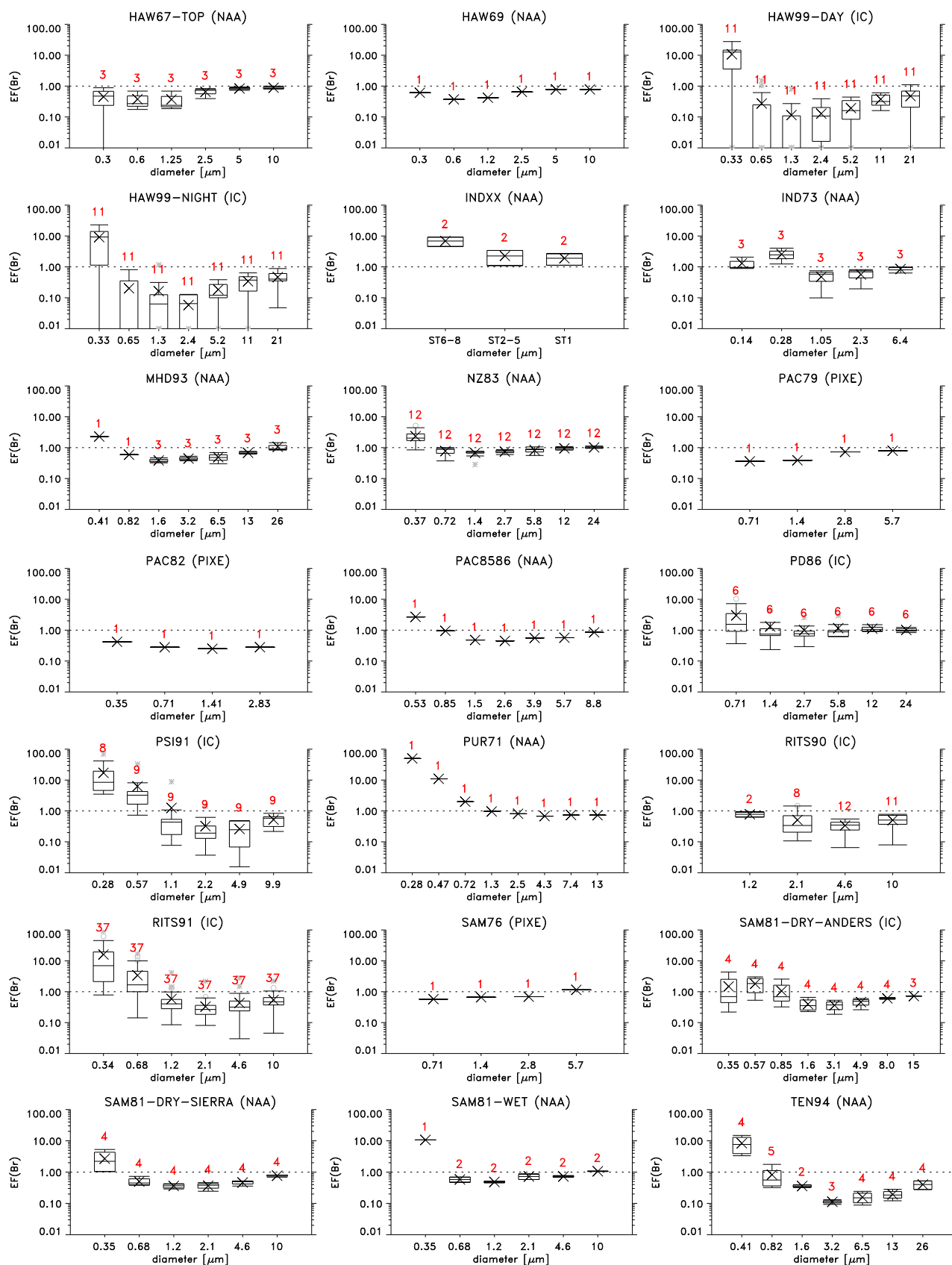
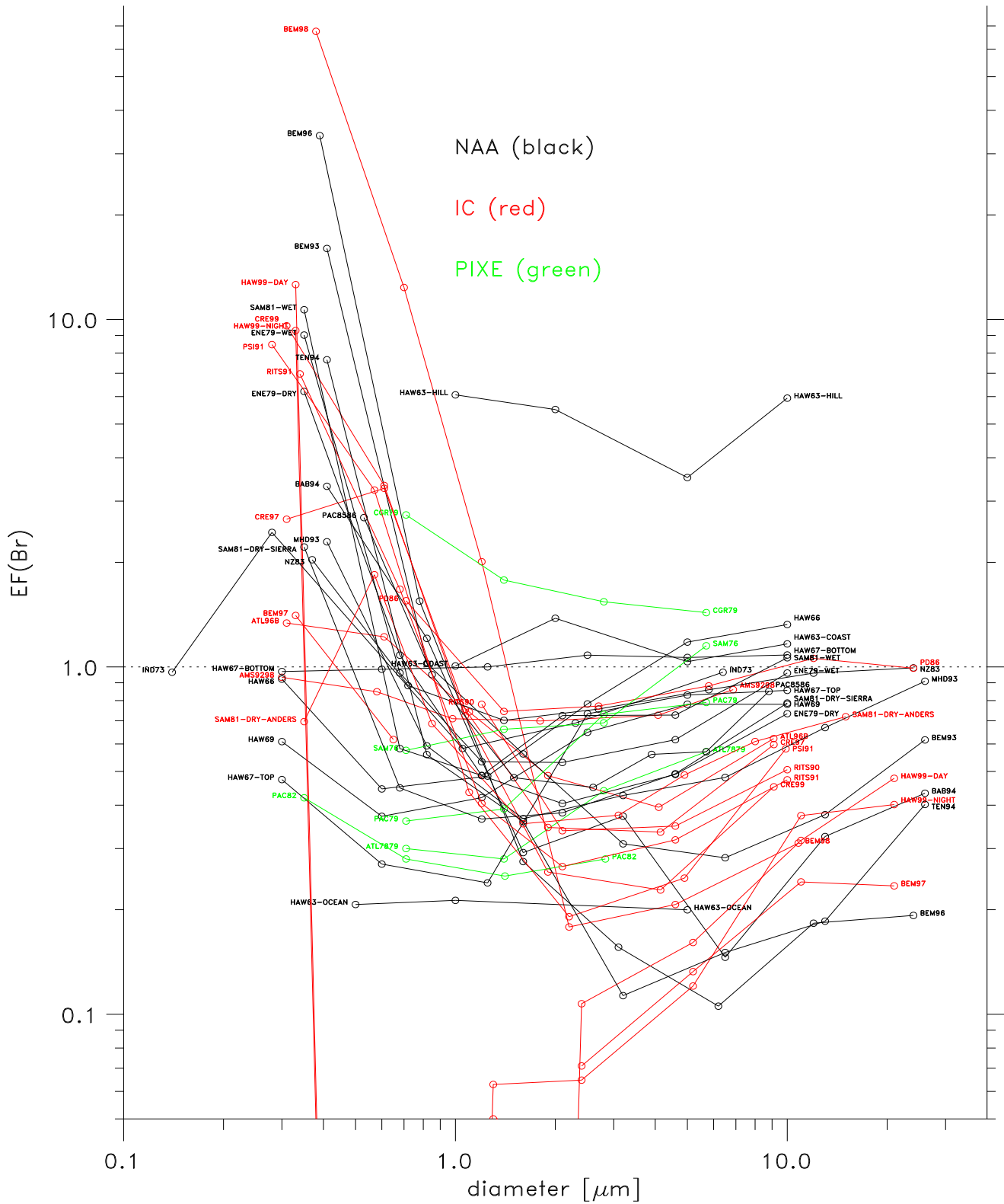
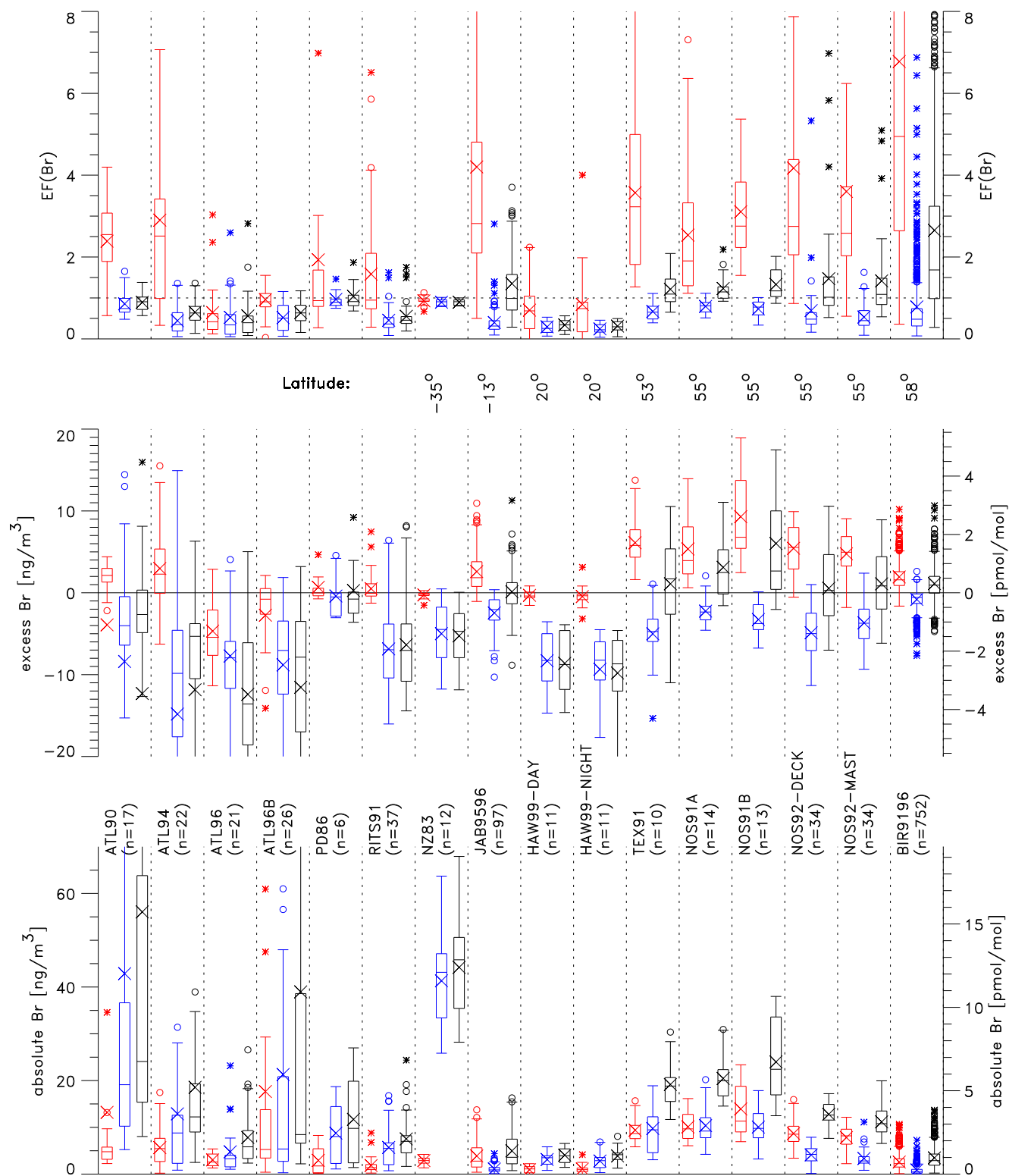


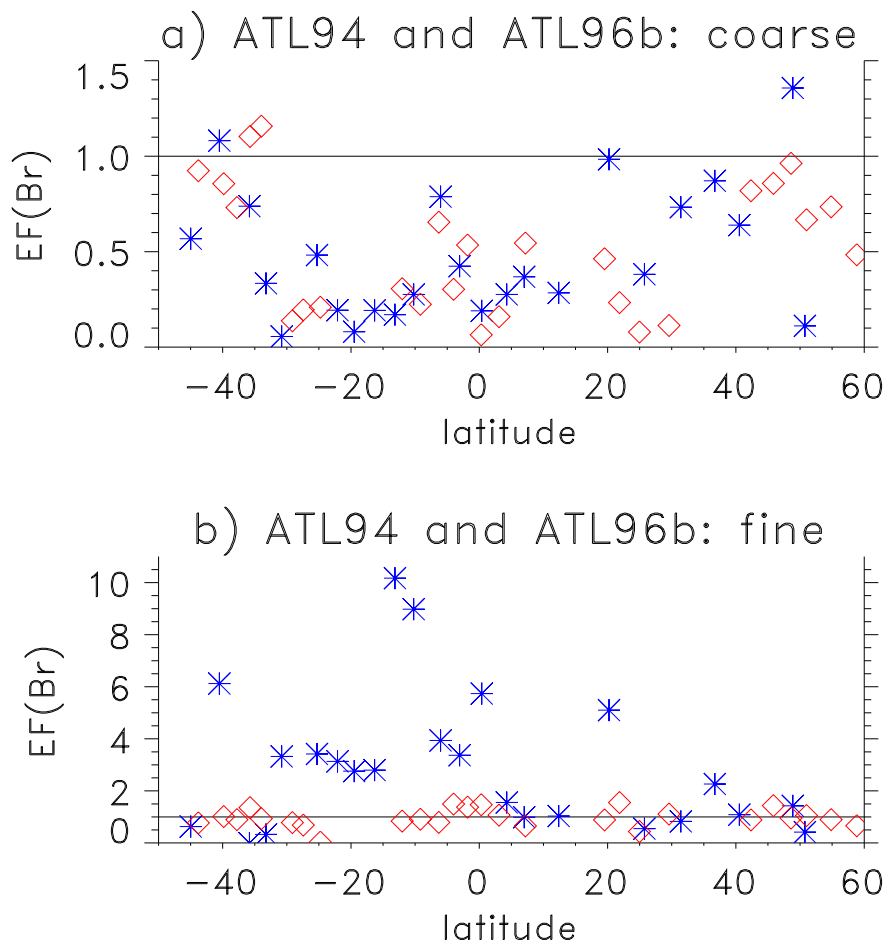
Fig. 3. (continued)



**Fig. 4.** Composite plot of the medians in Fig. 3. Different analytical methods are shown in different colors.



**Fig. 5.** *EF* (top), excess Br calculated using Eq. (3) (middle), and absolute bromine concentrations (bottom). The data set names are defined in Table 2. The number of samples  $n$  is given in parentheses. The plots show the SFU data sets as well as those CI data sets that include all stages for all samples. The box-and-whisker plots (as defined in Fig. 2) are shown for submicrometer (red), supermicrometer (blue) and total aerosol (black). The mixing ratio plotted at the right axis was calculated at  $T = 273.15$  K and  $p = 101325$  Pa.



**Fig. 6.** Bromine enrichment factors as a function of latitude for ATL94 (blue asterisks) and ATL96b (red diamonds).

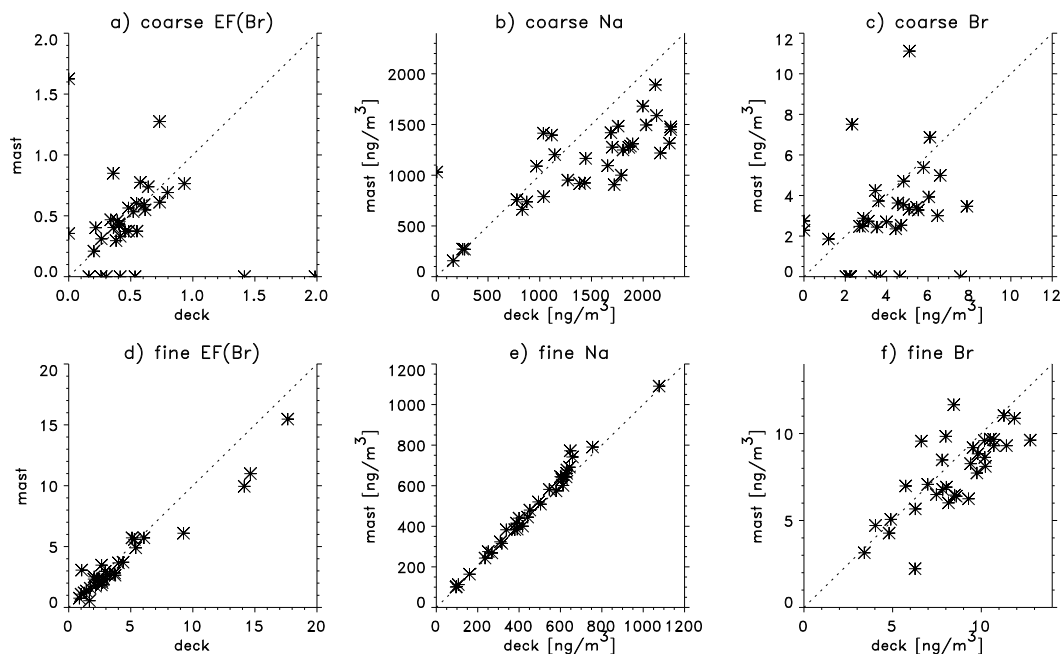
tic feature of the mbl in at least some tropical and subtropical regions. By considering the effect of stratiform clouds, von Glasow et al. (2002b) were able to reproduce this diurnal cycle with the one-dimensional column model MISTRA.

#### 4.5 Seasonal and long-term variation

The seasonal variation in aerosol bromine has been investigated by Ayers et al. (1999). Bromine in particles of  $< 10 \mu\text{m}$  diameter was measured at Cape Grim from January 1996 until May 1997. They found the highest depletions in the (austral) summer. The reason for the seasonal cycle is probably changing aerosol acidity (see Sect. 4.6). More recent data from June 1997 until July 1998 (Ayers, unpublished) show that the seasonal variation continues as predicted. The complete data set (CGR9698) is shown in Fig. 10a. Very similar seasonalities were observed at Crozet (CRO9698, Fig. 10b), Amsterdam Island (AMS9298, Baboukas (2000)), and at Macquarie Island (MQI9597) in the Southern Ocean (as shown by Ayers et al. (1999) in their Fig. 12).

The long-term measurements made as part of AEROCE are also very useful for revealing seasonal trends. Figures 11a–c show the development of  $EF$  over time for Barbados (BAB8897), Bermuda (BEM8897), and Mace Head (MHD8994). Since there were several extreme outliers in the data sets we decided to use medians and not means for our analysis. There is evidence for a seasonal variation at Barbados for the whole time and for Bermuda from 1988 to 1993. Again,  $EF$  reaches a maximum in the winter and a minimum in summer. For Bermuda since 1994 and for Mace Head, the seasonal variation (if any) is much less pronounced. A long-term study in Norway (BIR9196) does not show a consistent seasonal variation (Fig. 12), either. In summary, seasonal trends are most obvious in unpolluted regions of the southern hemisphere.

In addition to seasonal trends, it is also interesting to analyze the data for long-term variations. However, we cannot see any significant difference between the data from the beginning of AEROCE in 1988 and ten years later in 1998. Similarly, the measurements at Birkenes (BIR9196) do not



**Fig. 7.** Correlation between aerosol samples collected on deck (NOS92-DECK) and from the mast (NOS92-MAST) of a platform (values below the detection limit are set to zero). Data points with equal values at both heights lie on the dotted diagonal.

show a long-term trend, either (see Fig. 12).

#### 4.6 Correlation to acids

Laboratory studies show that bromine release is acid-catalyzed (see Sect. 7). Thus a correlation of bromine depletions with aerosol acidity is to be expected. Three data sets can be used to directly address this topic. Murphy et al. (1997) analyzed aerosols in clean marine air at Cape Grim (CGR95). They observed an anticorrelation of bromine with sulfate. Assuming that sulfate is a tracer for aerosol acidity, this indicates enhanced loss of bromine from the aerosol when the particles are acidified. The long-term studies by Ayers et al. (1999), which was also performed at Cape Grim (CGR9698), and by Baboukas (2000) at Crozet (CRO9698) confirm this result. The monthly mean bromine depletions show a strong correlation with methane sulfonic acid (MSA), which is shown in Fig. 10. Still, the acidification is not strong enough for significant loss of chloride via acid displacement, and  $EF(\text{Cl})$  thus remains close to unity (also shown in Fig. 10).

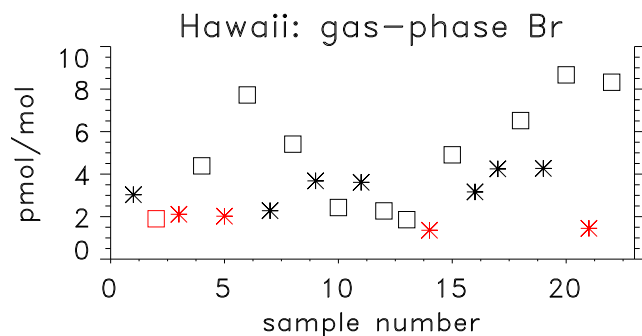
Most acids in the mbl over the high-latitude southern ocean are of natural origin (Ayers et al., 1999) and consequently, loss of bromine to the gas phase reported in the above studies is a naturally occurring phenomenon that is not driven by anthropogenic pollutants. As noted by Ayers et al. (1999), however, during colder months at Cape Grim, when sea-salt concentrations are higher and ambient acids lower, bromine enrichment factors are closer to one. There-

fore, it is reasonable to speculate that the enhanced fluxes of acids from anthropogenic activities to the global mbl have increased both the spatial and temporal extent of bromine depletion and related chemical processes over the world's oceans.

#### 4.7 Correlation to sea-salt concentration

Another observation made by Ayers et al. (1999) was that low  $EF$  values correlated well with low total concentrations of Na. A likely explanation involves acidity again. Since the pH of sea water is about 8, the production of sea-salt particles is a source of atmospheric alkalinity. Higher aerosol acidities are expected when the concentrations of sea salt particles and thus Na are low relative to acids.

The correlation to Na can also be seen at Crozet (CRO9698, Fig. 10b) and in the AEROCE data sets (BAB8897, BEM8897, MHD8994), as shown in Figs. 11d–f. If  $[\text{Na}] > 10 \mu\text{g}/\text{m}^3$ , then in almost all cases  $EF(\text{Br}) > 0.3$ . It is interesting to compare  $EF(\text{Br})$  to  $EF(\text{Cl})$  in Figs. 11j–l. Since dechlorination is mainly driven by acid displacement, chlorine deficits indicate acidified particles. Bermuda is often heavily impacted by anthropogenic acids transported from North America and the associated acidification of sea-salt aerosol results in lower  $EF(\text{Cl})$  values compared to Barbados and Mace Head. The lowest  $EF(\text{Cl})$  are at low concentrations of Na.  $EF(\text{Cl})$  is never below 0.5 when the concentration of Na is above  $5 \mu\text{g}/\text{m}^3$ . For Mace Head and Barbados,  $EF(\text{Cl})$  is close to 1.  $EF(\text{Br})$  is in a similar range for



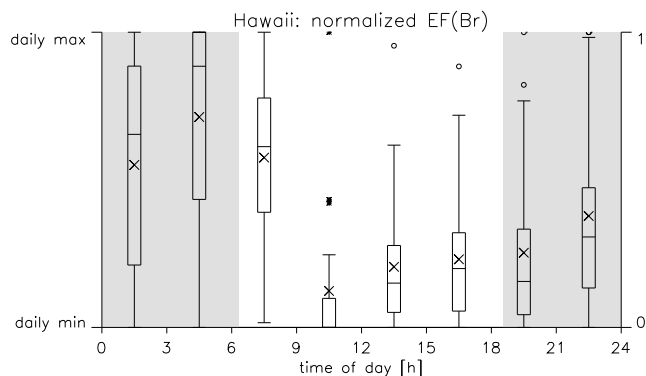
**Fig. 8.** Night (asterisks) and day (squares) mixing ratios of reactive gas-phase bromine compounds measured during September 1999 at Hawaii (HAW99-G). Values below DL are shown in red.

all three sites suggesting that the lack of strong aerosol acidification events at Barbados and Mace Head does not prevent debromination. This is consistent with models results (Keene et al., 1998) which show that strong acidification is necessary for chlorine release while bromine can escape from only slightly acidic solutions around  $\text{pH}=5.5$ . It indicates that whenever substantial debromination occurs, atmospheric acidity is present at levels sufficient to titrate sea-salt alkalinity. We note in this regard that mixing chemically distinct aerosols (e.g. supermicrometer sea salt and submicrometer sulfate on bulk filters) can cause artifact acid displacement of HCl (e.g. Keene et al., 1990). Thus caution is warranted in interpreting chlorine deficits associated with bulk aerosol.

Wind speed directly influences these processes in several important respects. Sea-salt production increases as a power function of wind speed (Gong et al., 1997; Gong and Barrie, 2003). Increased wind velocities lead to increased production fluxes of sea-salt aerosols and associated alkalinity, higher concentrations of atmospheric sea salt, increased mean sea-salt sizes and total aerosol surface areas (but decreased mean surface/volume ratio), decreased sea-salt lifetimes, decreased rates of gaseous uptake and loss from individual particles, and increased overall scavenging and deposition of acids (e.g. Woodcock, 1953; Erickson et al., 1999). It is evident from the above discussion that all of these effects will influence the rate and degree of aerosol acidification and associated debromination.

#### 4.8 Correlation to anthropogenic influence

It was shown in Sect. 4.1 that submicrometer aerosol often shows very high values of  $EF$ . Samples that do not show such an enrichment are mostly taken from remote regions (see AMS9298, PAC79, PAC82, and SAM76 in Fig. 3). A comparison of the Atlantic cruises ATL94 and ATL96b (Fig. 6b) shows high  $EF$  for many submicrometer particles during 1994 but  $EF \approx 1$  in 1996. This may be related



**Fig. 9.** Diurnal cycle of normalized  $EF(\text{Br})$  at Hawaii (HAW99b). To eliminate the influence of day-to-day variability, the data for each day were normalized individually, where 0 represents the daily minimum and 1 the daily maximum. The box-and-whisker-plot conventions are explained in Fig. 2. The time from sunset to sunrise is shaded in grey.

to biomass-burning plumes encountered during ATL94 (see Sect. 5.3) while low levels of CO measured in 1996 indicate clean air masses. In addition to analyzing the relative enrichment factor  $EF$ , it is thus also important to look at absolute concentrations of bromine and ‘excess Br’, as defined in Eq. (3) and plotted in Fig. 5. Since most data sets shown here are from SFU sampling, they are divided into only two size bins: submicrometer and supermicrometer aerosol. As expected, the submicrometer particles show positive excess bromine (red in Fig. 5) and the supermicrometer particles negative values (blue). For many data sets, the bromine concentration in submicrometer particles is too small to compensate for the bromine deficit in supermicrometer particles and the total excess bromine (black in Fig. 5) is thus negative. However, all data sets from the polluted North Sea (TEX91, NOS91, NOS92, BIR9196) show median excess bromine greater than zero. This suggests contributions from a non-sea-salt (possibly anthropogenic) source to submicrometer bromine in this region. Potential sources are discussed in Sect. 5. Alternatively, these enhanced enrichments may be related to physical (e.g. submicrometer volume) or other chemical (e.g. solution acidity) differences in the aerosol populations associated with relatively greater concentrations of pollutants.

Another indication for anthropogenic influence may be the fact that a seasonal cycle of  $EF$  can only be seen in the remote, pristine southern hemisphere (see Sect. 4.5). If the reason is indeed changing aerosol acidity, one cannot expect such a cycle in regions where anthropogenic pollution acidifies the aerosol throughout the year.

#### 4.9 Inorganic gas-phase bromine species

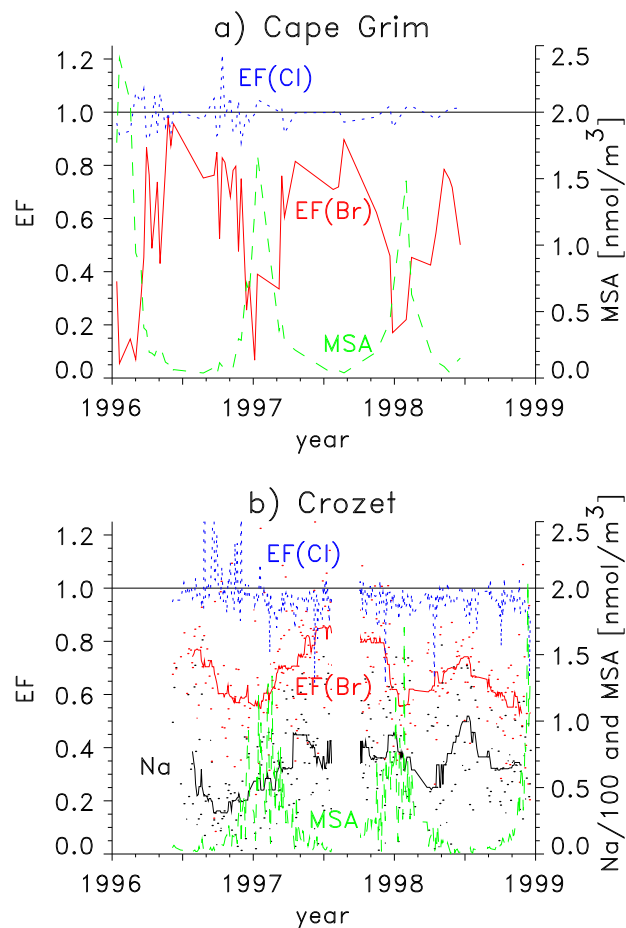
Several measurements of unspecified gas-phase inorganic bromine have been made in the mbl since the 1960s (see Table 3). They typically show mixing ratios between 2 and 10 pmol/mol. This is slightly larger than the bromine missing from the aerosol as shown in Fig. 5.

In addition to the direct measurements, there is also indirect support for the existence of inorganic gas-phase bromine compounds. Enrichment factors in rain (Table 5) range from about 0.6 to 5. Most values are above one. In all cases the *EF* for rain is larger than those for aerosol particles collected during the same campaign. A likely explanation is that clouds and falling rain drops scavenge not only particulate bromine, but also soluble gas-phase bromine (e.g. HBr).

Ozone measurements have also been used to indirectly infer the presence of inorganic gas-phase bromine. Dickerson et al. (1999) analyzed diurnal variations of O<sub>3</sub> in the Indian Ocean and partly attributed the changes to bromine chemistry. Nagao et al. (1999) analyzed a long-term ozone record from Ogasawara Island in the subtropical Pacific. Their data showed pronounced ozone destruction at sunrise, especially in the winter when ozone concentrations are high. Bromine chemistry was given as a potential explanation. Galbally et al. (2000) also suggested a bromine (and iodine) based mechanism to explain their observation of sunrise ozone destruction at Cape Grim. Nowak et al. (2001) speculate on the reaction of gas-phase BrO with dimethyl sulfide (DMS) to explain observed levels of dimethyl sulfoxide (DMSO). However, they conclude that this reaction cannot explain production of DMSO at night. Sciare et al. (2000) find that 2 to 3 pmol/mol of BrO can reproduce the observed daytime cycle of their DMS measurements.

Encouraged by these indications that reactive bromine exists in the mbl, there were several attempts to detect individual bromine species, especially BrO (see Table 4). Hebestreit et al. (1999) and Matveev et al. (2001) were able to detect very high mixing ratios of up to 176 pmol/mol BrO over the Dead Sea, Israel (ISR97-G) with LP-DOAS. Compared to the open ocean, however, the Dead Sea has a much higher bromide content and is also acidic with a pH < 7 (Nishri and Stiller, 1997), which favors heterogeneous reactions releasing bromine (see also Sects. 6 and 7). Recently, Stutz et al. (2002) reported BrO mixing ratios up to 6 pmol/mol at the Great Salt Lake, USA (GSL00-G) even though it has bromide content lower than sea water. However, major differences between these salt lakes, which are usually surrounded by salt pans, and the open ocean are the large salt surface areas available for heterogeneous reactions on salt pans and the different ionic composition including pH of most salt lakes compared to standard ocean water. Therefore, these results are not representative for the mbl over the open ocean.

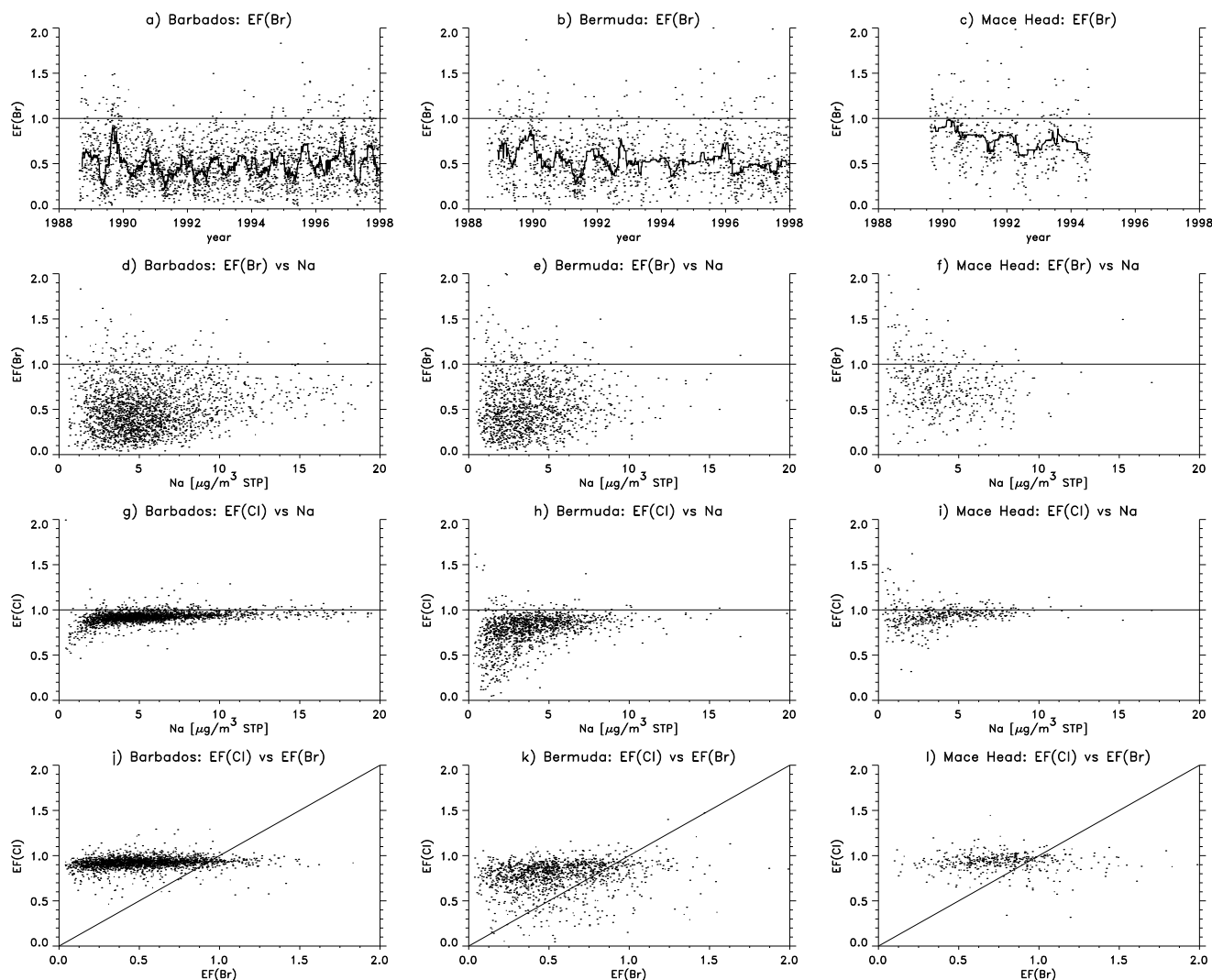
GOME (Global Ozone Monitoring Experiment) satellite observations of column-integrated BrO have been reported by several authors (Richter et al., 1998; Chance, 1998;



**Fig. 10.** Bulk *EF*(Br) (red, solid), *EF*(Cl) (blue, dotted), and MSA concentrations (green, dashed) at (a) Cape Grim (CGR9698) and (b) Crozet (CRO9698). For CRO9698, Na is also shown (black, solid). Since there is a lot of scatter in the *EF*(Br) and Na data for Crozet, the individual data points are shown as dots and the solid line represents the 20-point running median.

Hegels et al., 1998; Wagner and Platt, 1998; Wagner et al., 2001). In both polar regions, enhanced BrO vertical column densities indicate boundary layer BrO regularly during the spring months. Except for the polar regions during spring-time, however, the total BrO column is governed by BrO in the stratosphere. The relative contributions from the troposphere or even the mbl cannot be reliably separated from the total BrO column.

However, comparison with total column measurements from the ground (e.g. Friess et al., 1999) or with measurements of the stratospheric BrO column from balloon-borne instruments (e.g. Pundt et al., 2000; Harder et al., 2000) allow derivation of the tropospheric BrO fraction. If uniformly distributed over the complete altitude range of the troposphere the inferred tropospheric BrO column can be converted to a mixing ratio of 1 to 2 pmol/mol BrO (SAOZ9798-



**Fig. 11.** Bulk AEROCE data for Barbados (BAB8897), Bermuda (BEM8897), and Mace Head (MHD8994). (a–c) Bromine enrichment vs. time. The thick solid line is a 40-point running median. Labels for the years mark 1 January. (d–i) Enrichment factors plotted against Na concentrations (STP refers to  $T = 273.15$  K and  $p = 101325$  Pa). (j–l) A comparison between  $EF(Cl)$  and  $EF(Br)$ . The diagonal lines divide the regions where  $EF(Br) < EF(Cl)$  (upper left) and  $EF(Br) > EF(Cl)$  (lower right).

G). Several attempts have been made to measure BrO in the mbl outside the polar regions, both at a clean remote site (HAW99b-G) and also at sites that are more polluted to varying degrees (MHD96-G, MHD97a-G, MHD97b-G, MHD98-G, TEN97-G, WEY96a-G, WEY96b-G, CRT00-G). The results from these LP-DOAS measurements indicate ambient concentrations around or below the DL of the respective instruments (about 1 to 3 pmol/mol) (Alicke, 1997; Allan, 1998; Hönninger, 1999; Hönninger, 2002).

Recently Leser et al. (2003) performed shipborne MAX-DOAS measurements during an Atlantic transect from 54°N to 34°S (ATL00-G). Between 37° and 30° N BrO was observed in the mbl with an average of  $0.7 \pm 0.2$  pmol/mol and

maximum values reaching up to  $2.4 \pm 2.1$  pmol/mol. For the rest of the transect BrO ranged below the DL of 1 to 3.6 pmol/mol for individual measurements. In contrast to the LP-DOAS measurements mentioned above, which are only sensitive to the respective absorption path, MAX-DOAS provides some extent of vertical resolution with the maximum sensitivity over the lowest kilometer of the atmosphere.

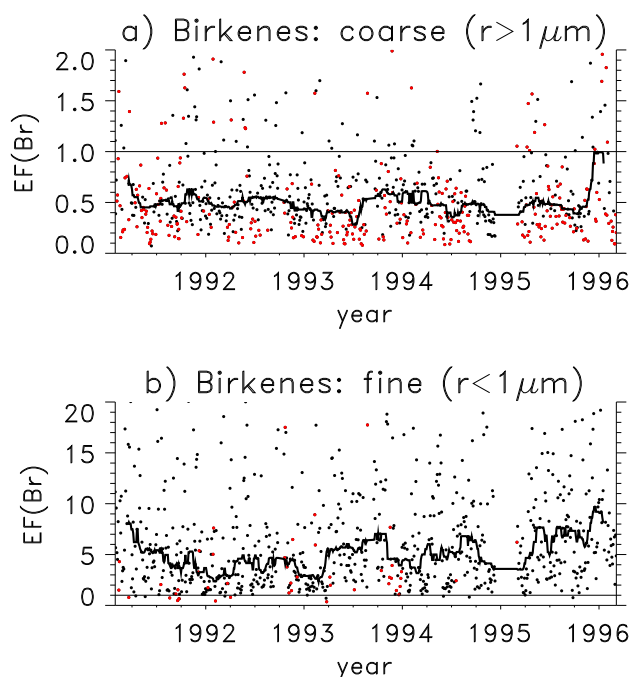
In summary, except for a few data points, individual gas-phase inorganic Br compounds have not been reliably characterized in the mbl at lower latitudes. Total gas-phase inorganic Br has been measured at several locations and typically appears to be around a few pmol/mol.



**Table 6.** Elemental Br/Na mass ratios in different materials

Material	$m(\text{Br})/m(\text{Na})$	Reference
continental crust	0.0000623	Wedepohl (1995)
	0.000088	Mason and Moore (1982)
sea water	0.00625	Wilson (1975)
biomass-burning		
- aerosol (South Africa)	0.015 to 0.059	Maenhaut et al. (1996b)
- savanna fires (South Africa)	0.0176	Andreae et al. (1998)
- herbaceous and wood fuels (wind tunnel)	0.022 to 1.29	Turn et al. (1997)
biofuels		
- wood, foliage, bark, soil, ...	see note <sup>1</sup>	McKenzie et al. (1996)
- wood	0.007 to 0.01	Slocum et al. (1978)
- charcoal	0.014 to 0.025	Slocum et al. (1978)
- rice straw	0.028 to 0.45	Saito et al. (1994)
leaded petrol	(very large)	

<sup>1</sup> McKenzie et al. (1996) measured Cl but not Na. They report  $m(\text{Br})/m(\text{Cl})$  between  $<0.0013$  and  $>8.2$ .



**Fig. 12.** Bromine enrichment measured at Birkenes (BIR9196) vs. time. The thick solid line is a 40-point running median. Labels for the years mark 1 January. In cases where measured bromine was below DL (shown in red), values were set to 50% of the DL.

## 5 Primary sources of inorganic bromine

Although most inorganic bromine in the marine troposphere is produced from the ocean surface in association with sea-salt aerosol, other sources must also be considered. This is especially relevant for the high enrichment factors observed

in submicrometer particles. The Br/Na mass ratios of different materials are listed in Table 6.

### 5.1 Sea-salt production

The emission flux of particulate Br from the surface ocean to the atmosphere can be estimated from reported production fluxes of sea-salt aerosol and the measured composition of surface sea water. Based on the production flux of sea-salt chloride of 1785 Tg/a (Erickson et al., 1999) and the Br/Cl mass ratio of 0.00348 kg/kg (Table 1), we estimate a direct bromine production flux of 6.2 Tg/a from the surface ocean. This pathway is the principal global source for atmospheric Br.

### 5.2 Mineral aerosol

Strong winds during dry seasons sporadically inject large amounts of soil dust from semi-arid regions (primarily from northern Africa and central Asia) into the middle troposphere where it can be transported long distances over oceans by prevailing winds before removal via wet and dry deposition (Swap et al., 1992; Prospero et al., 1996). A well-known example is Saharan dust which can often be seen in marine aerosol samples. The element Al can be used as a conservative tracer for dust. In principle, it is possible to obtain the dust-derived contribution  $[\text{Br}]_{\text{dust}}$  to the total bromine content:

$$[\text{Br}]_{\text{dust}} = [\text{Al}]_{\text{meas}} \times \left( \frac{[\text{Br}]}{[\text{Al}]} \right)_{\text{dust}} \quad (5)$$

where  $[\text{Al}]_{\text{meas}}$  = measured Al concentration and  $([\text{Br}]/[\text{Al}])_{\text{dust}}$  = elemental ratio typical for mineral aerosol. However, it is difficult to derive a value for the ratio Br/Al in dust because the composition of mineral aerosol is distinct

from that of Earth's crust (Schütz and Rahn, 1982) and also varies spatially. The bromine content of the continental crust is very low with  $m(\text{Br})/m(\text{Al}) = 2.07 \times 10^{-5}$  kg/kg (Wedepohl, 1995). This value does not apply to airborne particles. Bromine concentrations in atmospheric dust near source regions are substantially greater than those in crustal rock. Since most dust originates from deflation of seasonally wetted soils (Prospero et al., 1996), this relative enrichment can be attributed in part to the dissolution, upward migration, and subsequent evaporative concentration of soluble salts near the soil surface over wet/dry cycles. Adepetu et al. (1988) analyzed dust in Nigeria that originated in the Sahara. Their 6 samples collected between 1981 and 1984 showed bromine enrichments from 10 to 300 relative to crustal rock and a mean value of  $m(\text{Br})/m(\text{Al}) = 3.19 \times 10^{-3}$  kg/kg. They state that this enrichment could be due to bromine-containing pesticide residues and automobile exhaust in the local environment. Consequently, the data by Adepetu et al. (1988) probably represent upper limits for the bromine content of Saharan dust.

Approximately 73 Tg/a of mineral Al is deposited from the atmosphere to the world's oceans (Duce et al., 1991). Adopting the Br/Al mass ratio from Adepetu et al. (1988) as an upper limit and assuming similar atmospheric lifetimes for crustal Br and Al, we estimate that an upper limit of about 0.23 Tg/a of crustal Br is deposited to the world's oceans. Although this flux of crustal bromine is small (about 4%) compared to the global flux of sea-salt bromine, most crustal bromine is deposited over the equatorial Atlantic and North Pacific Oceans, which lie downwind of the major dust source regions in North Africa and central Asia, respectively. Thus, the relative contributions of crustal to total bromine in these regions are considerably greater than the global average.

The chemical evolution of mineral aerosol is poorly understood (e.g. Dentener et al., 1996) and that of crustal bromine virtually unexplored. Assuming that water and acids accumulate on aging atmospheric dust (probably as aqueous surface films) (e.g. Dentener et al., 1996; Li-Jones et al., 1998), bromine activation reactions analogous to those in sea salt aerosol should proceed. Such reactions could have important implications for the chemical evolution of dust plumes.

### 5.3 Biomass burning

Biomass contains significant Br which is emitted to the atmosphere during combustion (e.g. Andreae et al., 1996; McKenzie et al., 1996). Based on the few available compound specific measurements,  $\text{CH}_3\text{Br}$  comprises relatively minor fractions (5%) of the emitted Br (e.g. Andreae et al., 1996). As for Cl (e.g. Keene et al., 1999), it appears that most Br is emitted from burns in the form of volatile inorganic and particulate compounds. Particulate Br is enriched in biomass burning plumes, particularly from savanna fires (e.g. Echalar et al., 1995; Maenhaut et al., 1996b; Andreae et al., 1998; Kleeman et al., 1999). The relative importance of primary

emissions versus secondary production cannot be reliably differentiated from such measurements. This raises the possibility that transformations involving Br radicals, analogous to those in marine air, may influence the chemical evolution of biomass-burning plumes. The advection of burning emissions over the ocean contributes combustion-derived Br to the multiphase mbl system. Particulate Br/Na and Br/Ca ratios in aged biomass burning plumes are greater than those in sea water (see Table 6) which complicates the interpretation of Br enrichment factors in marine air. Data from the experiments ATL94 and BEM98 provide context for assessing relative contributions of combustion-derived Br in marine regions significantly impacted by biomass-burning products.

During the ATL94 cruise between  $10^\circ\text{S}$  and  $30^\circ\text{S}$  in the Atlantic,  $EF$  relative to sea-salt Ca for fine-fraction aerosols ranged from 3 to 10 while the coarse fractions were depleted (Fig. 6). Ratios of particulate Zn/Ca and K/Ca (e.g. Maenhaut et al., 1996b) indicate the presence of significant biomass-burning emissions in this region suggesting that burning-derived Br may have contributed to the apparent fine-fraction enrichments relative to sea salt. However, the Br/Zn ratio characteristic of burning over southern Africa (Maenhaut et al., 1996b) suggests that 30% to 80% of the observed fine-fraction Br originated from sources other than biomass burning.

During BEM98, the western North Atlantic mbl was significantly impacted by emissions from extensive wildfires in Latin America and Florida that were associated with a particularly strong El Niño (Turekian, 2000). The corresponding biomass burning emissions of Br probably explain why  $EF$  in the finer aerosol size fractions was higher than during other years at Bermuda (BEM93, BEM96, BEM97), as shown in Fig. 4.

### 5.4 Fossil-fuel combustion

Duce et al. (1965) suggested that bromine from automobile exhaust may also contribute to the atmospheric burden. This is especially true for a polluted atmosphere (Moyers et al., 1972). However, it can also apply to the marine environment. Martens (1973) concluded that 'leaded aerosols appear to be a major source of bromine in small particles' for marine aerosols collected in Puerto Rico. Leaded petrol contains tetraethyl lead ( $\text{Pb}(\text{C}_2\text{H}_5)_4$ ) which is a good tracer for automobile pollution for regions where leaded petrol is still used. Leaded petrol also contains the additives 1,2-dibromoethane ( $\text{BrCH}_2\text{CH}_2\text{Br}$ ) and 1,2-dichloroethane ( $\text{ClCH}_2\text{CH}_2\text{Cl}$ ) (Hamilton, 1996). During the combustion process the lead and halogen compounds react and predominantly produce  $\text{PbBrCl}$  which is emitted into the atmosphere (Habibi, 1973). Thus a ratio  $n(\text{Br})/n(\text{Pb}) = 1$  mol/mol is expected for freshly emitted particles. This is equivalent to a mass ratio of  $m(\text{Br})/m(\text{Pb}) = 0.386$  kg/kg (Lininger et al., 1966; Harrison and Sturges, 1983). A study in urban Honolulu, Hawaii, by Jernigan et al. (1971) showed a strong cor-

relation between Pb and Br in the particles. The portion of bromine resulting from sea salt was small even though the city is in the middle of the Pacific Ocean. A similar result was obtained by Sturges and Harrison (1986b): Aerosol collected at a coastal site in northwest England (MOR8283) also showed a strong correlation between Pb and Br. The ratio Br/Pb was close to that expected for petrol. To obtain the petrol-derived contribution to the bromine contents  $[\text{Br}]_{\text{petrol}}$ , a formula similar to Eq. (5) can be applied:

$$[\text{Br}]_{\text{petrol}} = [\text{Pb}]_{\text{meas}} \times \left( \frac{[\text{Br}]}{[\text{Pb}]} \right)_{\text{petrol}} \quad (6)$$

where  $[\text{Pb}]_{\text{meas}}$  = measured Pb concentration and  $([\text{Br}]/[\text{Pb}])_{\text{petrol}}$  is the elemental ratio typical for petrol. A very different result was obtained by Sturges (1990) at a site in Scotland (HAR83). In this case contamination from petrol could not explain the high bromine content.

The decline in the world-wide use of leaded petrol (Thomas et al., 1997) is reflected in the atmosphere. For example, at Bermuda, aerosol lead concentrations have decreased by an order of magnitude from the 1970s to the mid-1990s (Huang et al., 1996). Since unleaded petrol does not contain the additive 1,2-dibromoethane, aerosol bromine from petrol has also decreased (Thomas et al., 1997). In India, leaded petrol has only recently been phased out. During the INDOEX measurements in the Indian Ocean (IND99), a steep gradient with increasing aerosol bromide concentrations towards the Indian coast was observed (Gabriel et al., 2002).

### 5.5 Other sources

Degradation of short-lived organobromine compounds like  $\text{CH}_3\text{Br}$  (e.g. Khalil et al., 1993; Yokouchi et al., 2000) and  $\text{CHBr}_3$  (Quack and Wallace, 2003) via photolysis and reaction with OH also represents a source of inorganic bromine in the mbl. WMO (1998) lists global fluxes of 0.043 to 0.244 Tg/a of  $\text{CH}_3\text{Br}$  and 0.1965 Tg/a of  $\text{CHBr}_3$ . However, these numbers are upper limits for the contribution to inorganic reactive bromine because only a part of these molecules reacts in the mbl.

Degradation of longer-lived organobromine compounds in the stratosphere and subsequent downward transport is also a potential source. Accurate data are not available but nevertheless it is possible to get a rough estimate. Schauffler et al. (1998) measured a total organic bromine content near the tropopause of about 17.4 pmol/mol, i.e. a mass mixing ratio of  $4.8 \times 10^{-11}$  kg/kg. Multiplying this with an estimated downward mass exchange through the troposphere of  $7.2 \times 10^{16}$  kg/month (Grewe and Dameris, 1996) yields a source strength on the order of 0.04 Tg/a.

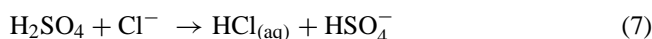
Other sources of bromine that have been proposed in the literature are coal burning (Duce et al., 1983) and volcanic emissions (Harrison and Sturges, 1983, and references therein). Bobrowski et al. (2003) recently detected BrO in a

volcanic plume. Swietlicki (1989) applied a principal component analysis to bromine data from 600 submicrometer aerosol samples collected at 3 Swedish sites in the Baltic Sea (SWE8586). He concluded that 'bromine is found at elevated relative amounts following transport, implying a gas-to-particle conversion for this element during transportation'.

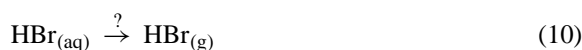
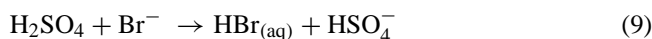
## 6 Modeling the mechanism of bromine chemistry in the MBL

From the previous sections it is clear that a substantial fraction of the bromine in sea-salt particles is transferred into the gas phase. The question is which chemical mechanism causes this.

One may think that acid displacement plays a role. Acid displacement is an important mechanism by which sea-salt particles lose chloride in polluted air, e.g.:



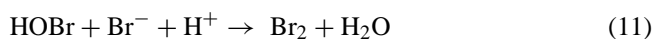
An analogous reaction for bromine would be:



However, this pathway can be ruled out because HBr is about 600 times more soluble than HCl (Sander, 1999). Therefore most of the chloride would have escaped from acidified particles before evaporation of HBr starts. This is in contrast with measurements which show that chlorine depletions are almost always smaller than bromine depletions (see Figs. 10 and 11j–l). Thus a different mechanism must be responsible for debromination.

Under polluted conditions, the nitrogen oxides  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$  can react with  $\text{Br}^-$  on the surface of sea-salt particles (Finlayson-Pitts and Johnson, 1988; Finlayson-Pitts et al., 1990; Behnke et al., 1994). This forms the gas-phase species  $\text{BrNO}$  and  $\text{BrNO}_2$ . However, in clean marine air, the concentrations of nitrogen oxides are low and thus these reactions cannot explain the large bromine deficits measured in unpolluted regions of the mbl.

The first mechanism for low- $\text{NO}_x$  conditions was proposed by Fan and Jacob (1992), though for a different environment: The reaction of HOBr with  $\text{Br}^-$  in Arctic sulfate aerosol particles:



Mozurkewich (1995) noticed that this reaction would also be possible in acidified Arctic sea-salt particles. Using the box model MOCCA, Sander and Crutzen (1996) applied the mechanism to polluted marine air at mid-latitudes. Vogt et al. (1996) found a synergism between bromine and chlorine chemistry which makes the release of bromine possible even under clean air conditions. They proposed the reaction

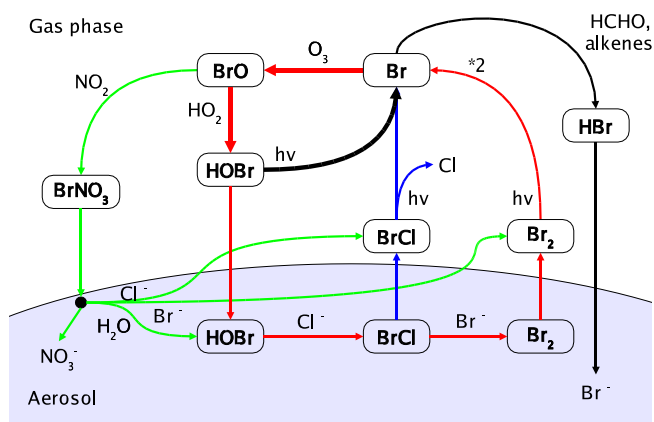
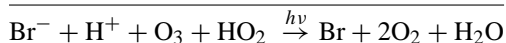
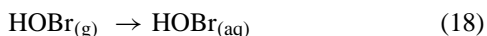
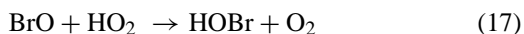
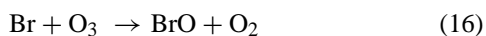
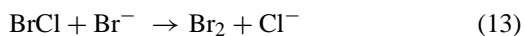
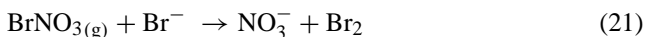
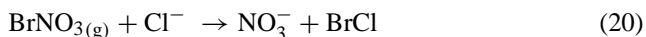
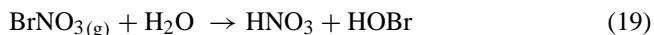


Fig. 13. Simplified reaction scheme of marine bromine chemistry.

of HOBr with  $\text{Cl}^-$  as the key reaction of an autocatalytic cycle that converts relatively inert sea-salt bromide into reactive inorganic gas-phase bromine species. The complete cycle is:

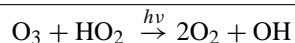
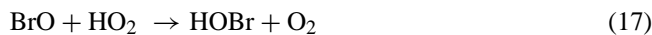
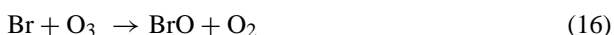


This cycle is shown with red lines in Fig. 13. There are several alternative pathways that may contribute as well. For example, the direct reaction of HOBr with  $\text{Br}^-$  in Eq. (11) is equivalent to the sequence of reactions (12) and (13). If there is not enough bromide in the aerosol for reaction (13) to proceed, BrCl can volatilize. The photolysis of BrCl is a source of reactive chlorine in the gas phase (see blue lines in Fig. 13). The additional effect of  $\text{BrNO}_3$  chemistry was analyzed by Sander et al. (1999).  $\text{BrNO}_3$  can hydrolyze or react with chloride or bromide:



This is represented by the green lines in Fig. 13. Note that reactions (20) and (21) can produce BrCl and  $\text{Br}_2$  without the need of aerosol acidity.

In addition to their effect on aerosol bromide, these reaction cycles also influence ozone (thick lines in Fig. 13):



It should be noted here that the self-reaction of BrO, which is important in the Arctic tropospheric ozone depletion events during spring (e.g. Tuckermann et al., 1997), only plays a minor role in the mbl at mid-latitudes due to the lower concentration of BrO.

Several initialization reactions can start the autocatalytic bromine activation:

- $\text{Br}^- + \text{O}_3$  (Oum et al., 1998; Rudich et al., 1998; Hirokawa et al., 1998; Anastasio and Mozurkewich, 2002)
- $\text{Br}^- + \text{OH}$  (Mamou et al., 1977)
- $\text{Br}^- + \text{NO}_3$  (Sander and Crutzen, 1996; Rudich et al., 1998)
- $\text{Br}^- + \text{N}_2\text{O}_5$  (Finlayson-Pitts et al., 1990; Behnke et al., 1994)
- $\text{Br}^- + \text{HSO}_5^-$  (Mozurkewich, 1995)
- photolysis of organic bromine species (Moortgat et al., 1993)
- photolysis of organic iodine species and subsequent interaction with the bromine chemistry (Vogt et al., 1999)

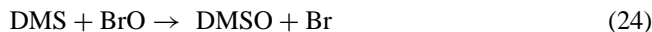
Once a small amount of a reactive bromine species has been produced via one of these reactions, a steady state of modeled bromine release is reached quickly.

Bromine species can also affect sulfur chemistry. The rate of scavenging of  $\text{SO}_2$  into aerosols is mainly determined by the rate at which it is oxidized in the aqueous phase. HOBr serves as another oxidant in addition to  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ :



Only the rate constant for reaction (23a) has been measured (Troy and Margerum, 1991). Assuming that reaction (23b) proceeds at the same rate, Vogt et al. (1996) found that it can contribute about 20% to S(IV) oxidation. It will thus increase scavenging of  $\text{SO}_2$  into the particles considerably.

Another link between bromine and sulfur chemistry exists in the gas phase, as pointed out by Toumi (1994):



This reaction will reduce the overall yield of  $\text{SO}_2$  resulting from DMS oxidation by the OH radical. Boucher et al. (2003) conclude that even BrO below 1 pmol/mol would be significant for DMS. Note that both reactions (23) and (24) reduce gas-phase  $\text{SO}_2$ . This leads to less  $\text{H}_2\text{SO}_4$  in the gas

phase with possible consequences for cloud microphysics and climate (Andreae and Crutzen, 1997).

Although models are able to explain the loss of bromine from sea-salt aerosol qualitatively, model-calculated  $EF$  are typically lower than those obtained from measurements. In Sect. 8, we list several ideas to improve the current models. However, in addition to model deficiencies, this discrepancy may also be caused by artificially truncated  $EF$  distributions for observations where samples with bromine below DL were deleted from the data set, as explained in Sect. 2.4. In this regard, we note that some of the data sets reporting lowest median  $EF$ s for sea-salt size fractions (e.g. BEM97, HAW99, Figs. 2 and 4) correspond to those for which data below detection limits were retained without manipulation.

## 7 Laboratory Studies

Release of gas-phase bromine from aerosol is supported by several laboratory studies. Hirokawa et al. (1998) exposed ground NaBr salt in a reaction chamber to ozone and humidity. Using mass spectrometry they observed a release of bromine. Control experiments confirmed that both ozone and gaseous  $H_2O$  are necessary for the formation of  $Br_2$ . The presence or absence of irradiation (Xe arc lamp) made no difference in their study. They propose the reaction



as the first step in the formation of  $Br_2$ . According to Mochida et al. (2000), bromide in sea-salt is much more reactive to ozone than pure bromide. Anastasio and Mozurkewich (2002) found evidence for a glass-surface mediated bromide oxidation in the presence of ozone.

Disselkamp et al. (1999) let ozone flow through a solution containing NaBr and followed the acidity (ion-sensitive electrode) and the concentration of  $Br^-$  (ion chromatography). They found that  $H^+$  and  $Br^-$  disappear at the same rate, which is consistent with reaction (25) followed by reaction (11). An enhanced bromide oxidation rate was observed when chloride was added to the solution. In that case  $Br^-$  and  $Cl^-$  disappeared at equal rates which is consistent with the formation of  $BrCl$  via reaction (12).

Behnke et al. (1999) generated sea-salt aerosol in a smog chamber and exposed it to ozone and light. They conclude that  $Br_2$  and  $BrCl$  are produced. However, in contrast to Hirokawa et al. (1998), they observed a dependence on light intensity and claim that reaction (25) cannot be the (only) initiating step.

Abbatt and Waschewsky (1998) investigated the uptake of HOBr on NaCl solution in an aerosol kinetics flow tube. They obtained an uptake coefficient of  $\gamma > 0.2$  for solutions of  $pH \leq 7.2$ . For alkaline solution, the uptake was much slower. This is consistent with an acid-catalyzed reaction proceeding via Eq. (12). Using a wetted-wall flow tube,

Fickert et al. (1999) confirmed that a  $pH$  of 7 or less is necessary for uptake of HOBr on NaCl or NaBr solutions. Varying the composition of the solution they found, even with a molar  $[Br^-]/[Cl^-]$  ratio below  $1 \times 10^{-3}$ , preferential formation of  $Br_2$  relative to  $BrCl$ . Thus in the mbl, fresh aerosol particles with the sea water composition of  $[Br^-]/[Cl^-] \approx 1.5 \times 10^{-3}$  mol/mol should lose  $Br^-$  preferentially over  $Cl^-$  via this pathway. Wachsmuth et al. (2002) investigated uptake of HOBr on NaBr aerosol particles and found a mass accommodation coefficient of  $\alpha = 0.6$ . Uptake of HOI on bromide has also been studied (Mössinger and Cox, 2001; Holmes et al., 2001).

## 8 Future projections

Based on current understanding of Br cycling through marine air, the projected increases in atmospheric acidification perhaps coupled with climatological alteration in global wind fields may lead to significant future changes in rates of Br activation and associated environmental impacts. Future increases in world population and per-capita energy use will almost certainly be associated with substantially increased emissions of  $SO_2$ ,  $NO_x$ , and other acid precursors from fossil-fuel and biomass combustion and other activities (e.g. Galloway, 1996). The transport of increasing concentrations of these compounds and their reaction products over the oceans will in turn increase the rates and spatial extent of sea-salt aerosol acidification. Since ships emit substantial amounts of unregulated exhaust directly into the mbl (e.g. Capaldo et al., 1999), increasing ship traffic will likely contribute disproportionately to aerosol acidification of more remote regions of the mbl. Substantial bromine activation is limited to acidic aerosol solutions and, consequently, increased acidification of marine air will lead to increased rates of Br cycling. Since Br activation is relatively insensitive to  $pH$  variability in acidic aerosol, small to negligible influences are expected in polluted regions (such as the western North Atlantic Ocean) where most sea-salt aerosols are currently acidified within seconds to minutes anyway (e.g. Erickson et al., 1999). However, in more remote regions such as the high latitude southern oceans where Br activation may be limited by available acidity (e.g. Ayers et al., 1999), modest increases in acidification could lead to substantial increases in the rates, spatial extent, and seasonal duration of Br activation and cycling.

Potential modification in global wind fields associated with changes in Earth's climate would influence the distributions of atmospheric acidity via controls on long-distance transport as well as rates of air-sea exchange of both acid precursors (e.g. DMS) and bases (sea-salt alkalinity and  $NH_3$ ). Changes in wind velocity would also alter the production fluxes, atmospheric concentrations, size distributions, and associated rates of multiphase transformations involving sea-salt Br. Since sea-salt production is a power function of wind

**Table 7.** Acronyms used in the text

AA	atomic absorption
AAS	atomic absorption spectroscopy
AD	aerodynamic diameter
AES	atomic emission spectrophotometry
AMS	aerosol mass spectrometry
APCIMS	atmospheric-pressure chemical ionization mass spectrometry
ATOFMS	aerosol time-of-flight mass spectrometry
CI	cascade impactor
DL	detection limit
DOAS	differential optical absorption spectroscopy
EF	enrichment factor
GMD	geometric mean diameter
IC	ion chromatography
LP-DOAS	long path DOAS
MAX-DOAS	Multi-Axis DOAS
MBL	marine boundary layer
NAA	neutron activation analysis
PALMS	particle analysis by laser mass spectrometry
PIXE	particle-induced X-ray emission
PTFE	poly tetra fluoro ethylene
SFU	stacked filter unit
XRF	X-ray fluorescence

velocity, relatively small changes in wind speed would have disproportionately large influences on sea-salt fluxes. Despite the dynamic and highly non-linear nature of the underlying processes, available evidence suggests that the temporal and spatial extent of active Br cycling will probably increase, particularly in more remote regions.

We thus see the need for additional field experiments, model studies, and laboratory investigations in the future. Simultaneous measurements of inorganic bromine in both phases, using all available techniques in one campaign (as well as obtaining auxiliary data like aerosol pH) would enhance our understanding a great deal. In particular, paired analyses of splits from size-segregated aerosol samples for total bromine (NAA or PIXE) and bromide (IC) would help elucidate the nature of bromine enrichments in submicrometer particles. A higher time resolution of the aerosol measurements is needed for a better analysis of the diurnal cycles. Developing improved techniques to lower the DL for BrO would be particularly useful because the current DL is close to model-predicted concentrations. More measurements of bromine in mineral dust will help to better quantify its relevance as a source of bromine.

Future computer simulations should move from current box and one-dimensional (1D) to three-dimensional (3D) models. However, computing limitations do not allow the direct inclusion of full scale chemical mechanisms from the box models into global models. Therefore, a robust parameterisation of the halogen chemistry must be developed. An-

other aspect of future models will be explicit treatment of chemistry in size-resolved aerosols. In addition to sulfate and sea-salt aerosol, it will be necessary to consider the effect of other aerosol types like dust and soot on halogen chemistry.

Future laboratory studies are needed for the reaction of BrNO<sub>3</sub> with aerosol particles under conditions relevant to the mbl. Also, the conditions under which the slow aqueous-phase reaction of O<sub>3</sub> + Br<sup>-</sup> is accelerated in/on sea-salt aerosol (surface effects, light, catalysts, ...) should be investigated further.

## 9 Conclusions

Based upon a large number of observations, we come to the following conclusions:

- The main source of bromine in the mbl is sea salt. Other sources may contribute locally in some regions.
- Relative to seawater, supermicrometer sea-salt aerosol is substantially depleted in bromine (often exceeding 50%).
- Bromine depletions occur naturally in clean marine air as well as in anthropogenically influenced air.
- Acidity promotes aerosol debromination. However, the degree of debromination appears to be relatively insensitive to variability in the pH of acidic aerosol solutions.
- Marine submicrometer aerosol is often enriched in bromine, especially in polluted regions.
- Bromine from automobile petrol or biomass burning contributes in some regions to enrichment in submicrometer particles.
- A diurnal variation (with increased gas-phase concentrations and aerosol depletion during the day) has been observed at some, but not at all sites.
- Seasonal variation of *EF* is most pronounced in the cleaner southern hemisphere.
- Inorganic bromine species exist in the gas phase at several pmol/mol but the speciation has not been reliably measured.
- *EF* in rain is higher than in aerosol particles, possibly because clouds and rain drops scavenge bromine species from the gas phase.
- Laboratory results show that aerosol bromide can be transformed into volatile, reactive forms of bromine.

Several questions remain:

- Which species comprise ‘volatile inorganic bromine’?

- Why do some sites show a diurnal or seasonal variation of  $EF$  whereas others don't?
- Is there a vertical gradient of  $EF$  in the mbl?
- How can bromine accumulate in submicrometer particles instead of being recycled back into the gas phase?

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