

Volatile halogenated hydrocarbons over the western Pacific between 43° and 4°N

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Abstract. A spectrum of halogenated hydrocarbon compounds in marine air masses were surveyed over an area in the western Pacific between 43°N, 150°E and 4°N, 113°E in September 1994. The ship's track between northern Japan and Singapore traversed three climatic zones of the northern hemisphere. Recently polluted air, clean marine air derived from the central Pacific Ocean from different latitudes, and marine air from the Indonesian archipelago were collected. Tetrachloroethene and trichloroethene of anthropogenic origin, brominated halocarbons as tribromomethane, dibromochloromethane and bromodichloromethane of anthropogenic and natural sources, and other trace gases were measured in the air samples. Very sparse data on the distribution of these compounds exist for the western Pacific atmosphere. The distribution patterns of the compounds were related to synoptic-scale meteorology, spatial conditions, and origin of the air masses. Anthropogenic and natural sources for both chlorinated and brominated substances were identified. Tetrachloroethene and trichloroethene concentrations and their ratios identify anthropogenic sources. Their mixing ratios were quite low compared to previously published data. They are in agreement with expected low concentrations of photochemically active substances during autumn, with an overall decrease in concentrations toward lower latitudes, and with a decrease of emissions during recent years. Strong evidence for a natural source of trichloroethene was discovered in the tropical region. The concentrations of naturally released brominated species were high compared to other measurements over the Pacific. Gradients toward the coasts and elevated concentrations in air masses influenced by coastal emissions point to significant coastal sources of these compounds. The trace gas composition of anthropogenic and natural compounds clearly identified the air masses which were traversed during the cruise.

1. Introduction and Background

The atmosphere contains a variety of organic trace gases which originate from natural and anthropogenic sources. These gases influence the photochemical processes and oxidation chemistry in polluted and nonpolluted air masses. Especially in the marine environment, volatile halogenated hydrocarbons of anthropogenic and natural origin contribute significantly to the atmospheric chemistry and to the biogeochemical cycling of the trace elements chlorine, bromine, and iodine. The trace gases and their degradation products contribute to the destruction of ozone in the troposphere and stratosphere. Some halogenated compounds contribute to the greenhouse effect, and several substances are toxic, mutagenic, and carcinogenic to humans [Lovelock *et al.*, 1973; Lovelock, 1975; Wofsy *et al.*, 1975; Lahl *et al.*, 1981; Singh *et al.*, 1982; Whitehead, 1984; Sturges and Harrison, 1986; McElroy *et al.*, 1986; Barrie *et al.*, 1988; Ramanathan *et al.*, 1985; Prather and Watson, 1990; Kindler *et al.*, 1995].

The ocean and atmosphere play a complex role in the cycling of volatile halocarbons. Atmospheric chlorinated and brominated organic compounds have been measured over the

Arctic Ocean, the Antarctic Ocean and continent, the Atlantic Ocean, and the central and eastern Pacific Ocean, whereas only very few data exist for the western Pacific atmosphere [Murray and Riley, 1973; Singh *et al.*, 1983a, b; Berg *et al.*, 1984; Liss, 1986; Class and Ballschmiter, 1986a, b; Makide *et al.*, 1987; Atlas *et al.*, 1992, 1993; Sharp *et al.*, 1992; Reifenhäuser and Heumann, 1992; Koppmann *et al.*, 1993; Yokouchi *et al.*, 1994, 1997]. The processes which control the distribution of halogenated hydrocarbons in the atmosphere have been investigated in more detail in recent years. The composition of the volatiles in different air masses seems to be controlled mainly by their sources and their atmospheric life times, and the meteorological conditions such as wind speed and mixing height. Tetrachloroethene and trichloroethene are released mainly by urban and industrial activities. Total emission of the compounds has declined by 40% since 1982. Natural sources were discussed recently. The atmospheric sink for the compounds is mainly the oxidation by OH radicals. High concentrations of trichloroethene point to fresh anthropogenic emissions because of its short atmospheric lifetime of 7 days, based on the rate coefficients by Atkinson *et al.* [1989]. Tetrachloroethene, with a lifetime of about 5.4 months, is subject to long-range transport. Their concentrations can be used to document the anthropogenic influence on an air mass [Atkinson, 1985; Atkinson *et al.*, 1989; Atlas *et al.*, 1992, 1993; Abrahamson *et al.*, 1993; Quack, 1994; World Meteorological Organisation (WMO), 1995; Wang *et al.*, 1995; McCulloch and Midgley, 1996]. The concentration ratio between the longer-lived tetrachloroethene and the

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short-lived trichloroethene can be used to characterize the photochemical aging of contaminated air masses, because the ratio increases gradually with age. The concentration ratio of tetrachloroethene to trichloroethene ranges from 0.5 to 2 and sometimes up to 4 in freshly contaminated air masses, depending on local emittants. The ratio is consistent with estimates of industrial emissions for these compounds. In 1992, industrial release was 295×10^9 g/yr for tetrachloroethene and 197×10^9 g/yr for trichloroethene, yielding a ratio of 1.5. This ratio changes during transport to values as high as 100. This value was observed in Arctic air masses, which reach the North Sea (Otha *et al.*, 1976; Class and Ballschmiter, 1986a; Singh *et al.*, 1982, 1992; Quack, 1994). About 90% of the anthropogenic sources are concentrated in the latitudinal belt between 60° and 30° N, leading to a decreasing gradient of short-lived anthropogenic compounds toward the equator. This pattern corresponds to a latitudinal gradient of the OH radicals. Higher oxidation rates contribute to lower concentrations of the organic trace gases in tropical air masses [Spivakovsky *et al.*, 1990; Atlas *et al.*, 1993; Koppmann *et al.*, 1993; Wiedmann *et al.*, 1994].

Seasonal fluctuations of short-lived volatile halogenated organic compounds have been discovered in the northern hemisphere to be controlled by seasonal variations in photo-oxidant concentrations, speed of air mass transport, and solar UV radiance. A seasonal cycle of OH radicals in the atmosphere is most likely the cause of a seasonal cycle of tetrachloroethene with lower concentrations of the halogenated compounds during summer. The emissions of the compounds show no seasonality effect [Makide *et al.*, 1987; Cicerone *et al.*, 1988; Volz *et al.*, 1981; Koppmann *et al.*, 1993; Wang *et al.*, 1995; McCulloch and Midgley, 1996].

It could be determined that the oceans contain a variety of brominated and iodated compounds which are transported via air-sea exchange into the marine atmospheric boundary layer. Elevated concentrations of these compounds have been found in coastal regions. The sources are largely unknown, except for emissions by macroalgae, which are confined to the coastal zone and by a few species of phytoplankton. Other sources have been suggested as well: photochemical reactions, halogene substitution in seawater, and nonspecified biological sources in equatorial upwelling regions. Everything points to the fact that the ocean surface water is the main source of tribromomethane and dibromochloromethane for the troposphere [Lovell, 1975; Liss and Slater, 1974; Singh *et al.*, 1983b; Fogelqvist, 1985; Gschwend *et al.*, 1985; Class and Ballschmiter, 1988; Klick, 1992; Klick and Abrahamsson, 1992; Manley *et al.*, 1992; Atlas *et al.*, 1992, 1993; Moore and Tokarczyk, 1993; Krysell and Nightingale, 1994; Moore and Zafiriou, 1994; Tokarczyk and Moore, 1994]. Brominated halocarbons have anthropogenic sources as well. Anthropogenic tribromomethane, dibromochloromethane, and bromodichloromethane are produced during the chlorination of drinking and cooling waters. High concentrations of these compounds are found around seawater-cooled powerplants and can locally effect concentrations in the troposphere [Rook, 1974; Bellar *et al.*, 1974; Helz and Hsu, 1978; Fogelqvist and Krysell, 1991; Quack, 1994]. Photolysis seems to be the major atmospheric sink for the brominated and iodated compounds [Penkett *et al.*, 1985; Chameides and Davis, 1980].

These compounds and a variety of other trace gases, like iodated compounds and atmospheric-chemical-derived alkyl

nitrate, can be detected and quantified in a single sophisticated analytical method. High-resolution gas chromatography (HRGC) on capillary columns with electron capture detection (ECD) of previously adsorbed compounds was selected because of the mobility and ease of sampling, combined with a high-quality separation and detection.

The objective of the cruise was to survey the temporal and geographical distribution of the anthropogenic and natural organic trace gases and to learn more about the processes which control their distribution in the western Pacific atmosphere. The cruise 97/3 by R/V *SONNE* in September 1994 covered the area between 43° N, 150° E and 4° N, 113° E, traversing the western boundary current system of the North Pacific Ocean. The ship's track crossed three climatic regions where air masses of the temperate westwind zone, the subtropical Hadley circulation, and the intertropical circulation were sampled. The air masses reaching this western Pacific area during September are advected from different directions and cross different source regions. The area, close to the Asian continent, is affected by the emissions from a variety of neighboring states (e.g., Japan, North and South Korea, China, the Phillipines, Indonesia, Vietnam). Therefore it was possible to sample recently polluted air masses, clean marine air from different regions of the central Pacific Ocean, and marine air from the Indonesian Archipelago south of the Intertropical Convergence Zone (ITCZ).

In the following we present the concentrations of the five halocarbons, tetrachloroethene, trichloroethene, tribromomethane, dibromochloromethane, and bromodichloromethane, in these air masses. We relate their distribution pattern to synoptic meteorological conditions, interpret the differences of halocarbon concentrations, examine the possible sources for these compounds, and discuss relationships between the substances.

2. Materials and Methods

2.1. Collection of Air Samples

Air samples were collected on board R/V *SONNE* from an extendable platform on the bow of the ship to prevent any of the ship's influence while sampling approximately 15 m above the sea surface. Sampling was active only when the ship was underway and the wind direction was within $\pm 60^\circ$ of the bow. The airborne organic compounds were concentrated on adsorbents, sealed, cooled, and transported to the laboratory. After thermal desorption they were separated with HRGC and detected by ECD. The analytical procedure is shown in Figure 1.

Adsorbent glass tubes containing Tenax[®] GR were rinsed with methanol and pentane, heated to 300° C for 12 hours in a flow of high-purity nitrogen, flame-sealed, and kept in the dark until sampling. For collection of air samples, 4-20 L of air (an average of 10 L) were pumped with a diaphragm pump (SKC, model 224-PCXR 7) at a rate of 40-70 ml/min through two precleaned adsorption tubes which were connected in series in order to check for breakthrough of the collected substances. Airflow was measured by a mass flowmeter. For more details of the procedure and references, see Quack [1994]. During the ship's transit, 53 sampling intervals totaling 80 samples were taken, including duplicate and cumulative samples to examine the analytical precision. After sampling; the tubes were again flame-sealed, carried in dry ice to the shore-based laboratory, kept at -70° C, and analyzed within 2 months after collection.

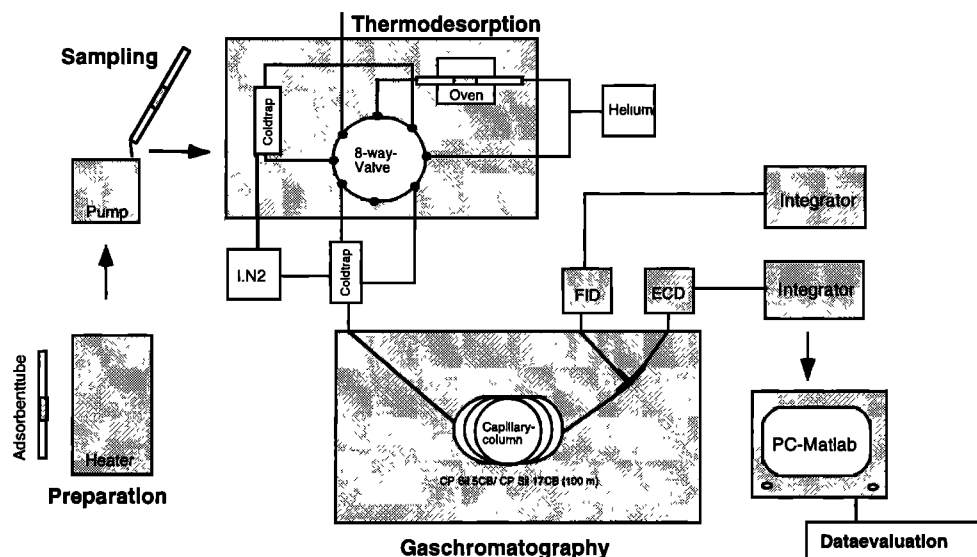


Figure 1. Analytical procedures for sampling, separation, detection, and quantification of volatile halocarbons and other organic trace gases in air [Quack, 1994].

2.2. Analysis of Halocarbons

The compounds were thermally desorbed from the adsorbent with high-purity helium at 40°-230°C under back-flush conditions onto a trap cooled with liquid nitrogen and then analyzed. High-resolution separation with temperature programming was performed on two coupled capillary columns of different polarity (50 m CP SIL® 5CB, 50 m CP SIL® 19CB; Chrompack). The electron-absorbing compounds were detected with an electron capture detector. Standard substances were injected to ascertain identity and retention times of the compounds. Under these conditions most bromocarbons, bromochlorocarbons and chlorocarbons in the air samples could be separated from other compounds. A typical chromatogram is shown in Figure 2. Quantification was achieved using calibration with external standard solutions (purity >99%; Supelco) of different concentrations in pentane.

Sampling and analytical precision were tested by replicate analysis of these standard solutions and by the analysis of duplicate samples. Standards were run every day between measurement of the samples to account for the drift in sensitivity of the detector. The detection limit was less than 0.1 parts per trillion by volume (pptv) (1-2 pg per compound of absolute mass) for most of the substances, and the precision was within 10-20% pptv for the halocarbons. The concentrations measured were between 0.02 and 140 pptv. Quantification was possible only for compounds with retention times larger than that of dibromomethane (Number 38 in Figure 2). Compounds with smaller retention times could not be quantified using this method because of considerable breakthrough. For compounds with retention times larger than that of 1-iodopentane (Number 83 in Figure 2), artifacts, contamination, and desorption caused some problems in quantification. This was shown with duplicate and cumulative samples. The target compounds quantified and reported here did not show significant artifacts or losses. With the analytical system used here, nonpolar organic compounds at the boiling point range of 90°-160°C were analyzed with the above precision.

3. Experiment

3.1. Sampling Area

During the cruise of R/V *SONNE 97/3* of September 1-16, 1994, air samples were taken between 43°N, 150°E and 4°N, 113°E, close to the Asian continent along the system of the western boundary currents of the North Pacific Ocean. Figure 3 shows the ship's track, the sampling intervals (midpoint) and the integrated wind direction and wind speed during the sampling periods. For some sampling intervals during very low wind speeds the integrated wind direction yields only a rough idea of the origin of the air mass (Figures 3 and 4).

3.2. Meteorological Conditions

A wide latitudinal range of climates was covered during the cruise. Air masses of the temperate westwind zone (43°-37°N), the subtropical Hadley circulation (37°-25°N), and the tropical zone (25°-4°N) were sampled [McDonald, 1938; Asnani, 1993]. Mean large-scale flow patterns are discussed along with transient synoptic scale features based on Asian Surface Analysis (ASAS) [1994] weather charts. Air mass transport during the cruise was influenced by moving depressions in the temperate zone, the end of the summer monsoon, the large clockwise circulation around the oceanic anticyclone at about 30° in the Pacific, frequent typhoons at this time of the year, and the ITCZ. The Intertropical Convergence Zone was traversed in the latter part of the cruise. Several characteristic water masses of the western Pacific boundary current system, the cold Oya-Shio current, and the warm Kuro-Shio current were also traversed during the cruise. Since the oceanic region sampled during the cruise is close to the source regions, the overriding meteorological factor is the recent air mass trajectory rather than the climatological conditions.

The development of meteorological and oceanic conditions along the ship's track as the cruise proceeded from 43° to 4°N is indicated by pressure, humidity, wind speed and wind

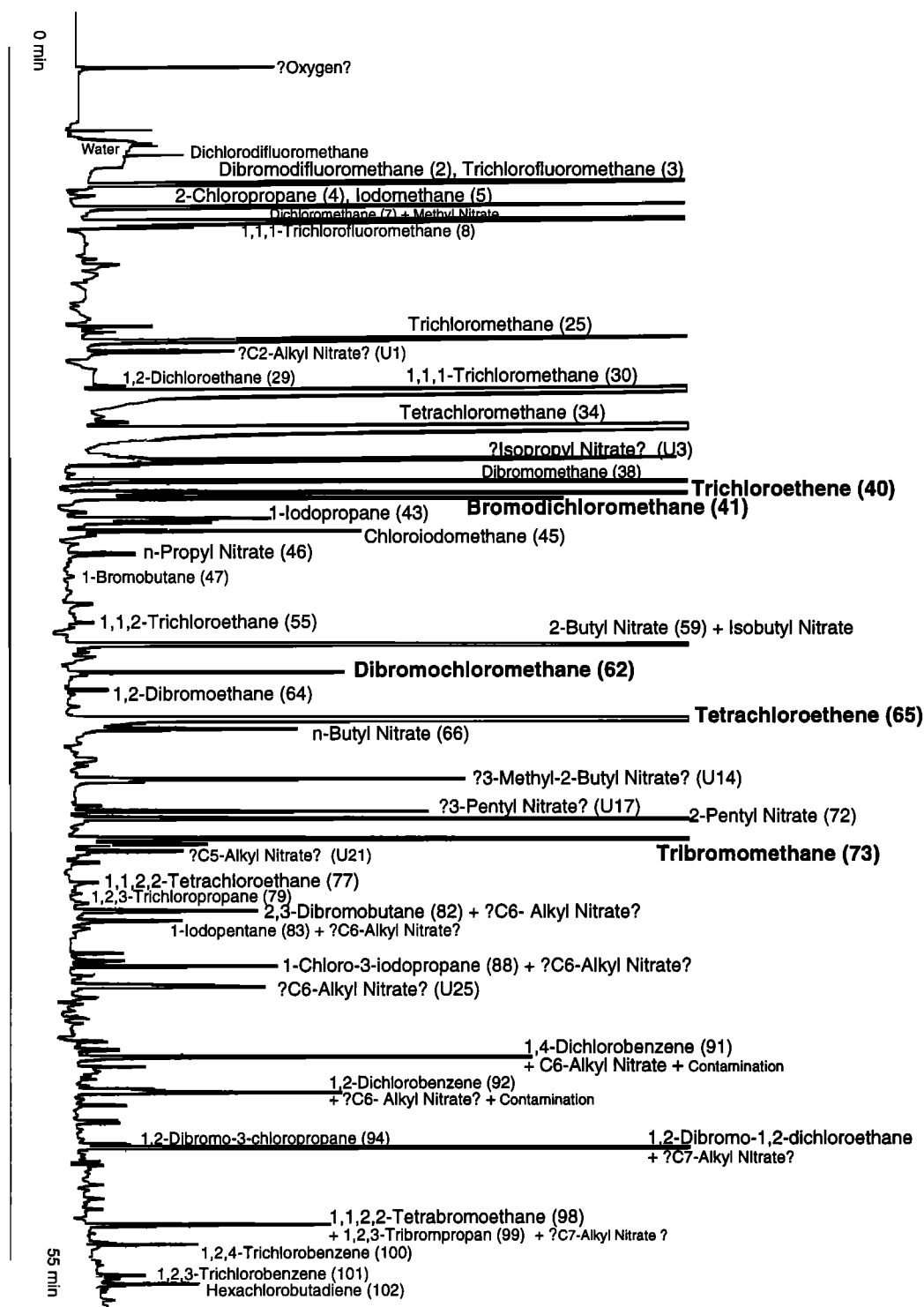


Figure 2. Electron capture detection chromatogram of an air sample (Number 5: 16 L, marine atmosphere off northern Japan). Peaks are labeled with compound names and numbers (in brackets, according to *Quack* [1994]). The most likely identification for each unknown compound (U1-U25) is indicated by compound name accompanied by question marks.

direction, air and water temperature, and their temperature differences (Figure 4).

The meteorological situation encountered was typical for the month of September. The atmospheric pressure (Figure 4a) developed from large deviations in the temperate zone at the beginning of the cruise to the typical 12 h oscillation in the

tropics [Asnani, 1993]. The air humidity was high (> 85%) during most of the time, showing peaks during rain events and increasing toward the equator (Figure 4b). The wind speeds were very low (1-6 m/s) during the entire cruise (Figure 4c), and often no winds at all were observed, leading to stationary air masses. The wind direction was influenced by the normal

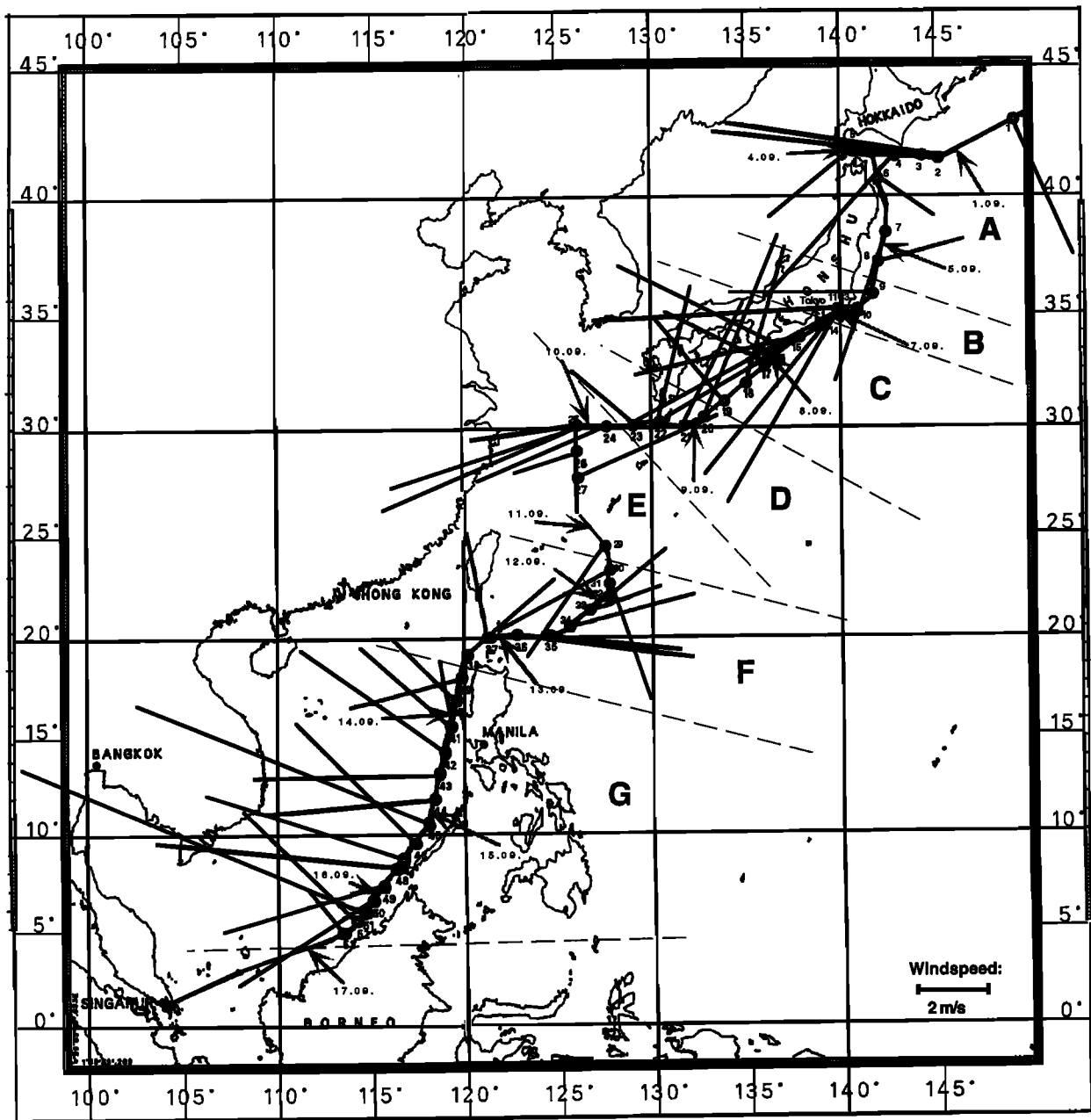


Figure 3. Dated cruise track of R/V SONNE, including sampling intervals (1-53), mean wind speed, and mean wind direction (origin of wind) during sampling intervals.

atmospheric circulation, the end of the summer monsoon, land and sea breeze circulation in the vicinity of land, and a passing typhoon on September 8-9, 1994 (Figure 4d). The air temperature (Figure 4e) rose from about 20°C at 40°N to about 28°C in the subtropical region and then fell again to 27°C in the tropical region. Rising humidity (Figure 4b) and falling air temperatures (Figure 4e) toward the equator, among other observations like clouds and no winds, indicated that a weak ITCZ was located at the Strait of Luzon, when the ship passed this area on the 13th of September. On this day a water mass of high sea-surface temperatures was passed (Figure 4f), which supports the presence of an ITCZ [Asnani, 1993]. The ship's track entered the cold Oya-Shio current, which is fed by polar waters, in the temperate zone between 43° and 38°N at the start of the cruise and left this water mass on the 5th of

September. The warm waters of the Kuro-Shio current were reached at about 33°N on the 8th of September and traversed several times, before the ship reached the north equatorial current on the 12th of September. After that the cruise proceeded through the South China Sea between 19° and 4°N, where warm equatorial waters enter the shelf to the north and the south of the Phillipine Islands and circulate in two gyres throughout the South China Sea [Dietrich *et al.*, 1975]. Unfortunately, there were no data available on the mixing heights of the marine boundary layer during the cruise. The water was generally warmer than the air (Figures 4e and 4f), especially while passing through the southern part of the area. The difference between air temperature and water temperature (Figure 4g) was negative, indicating that the atmospheric stratification was generally unstable.

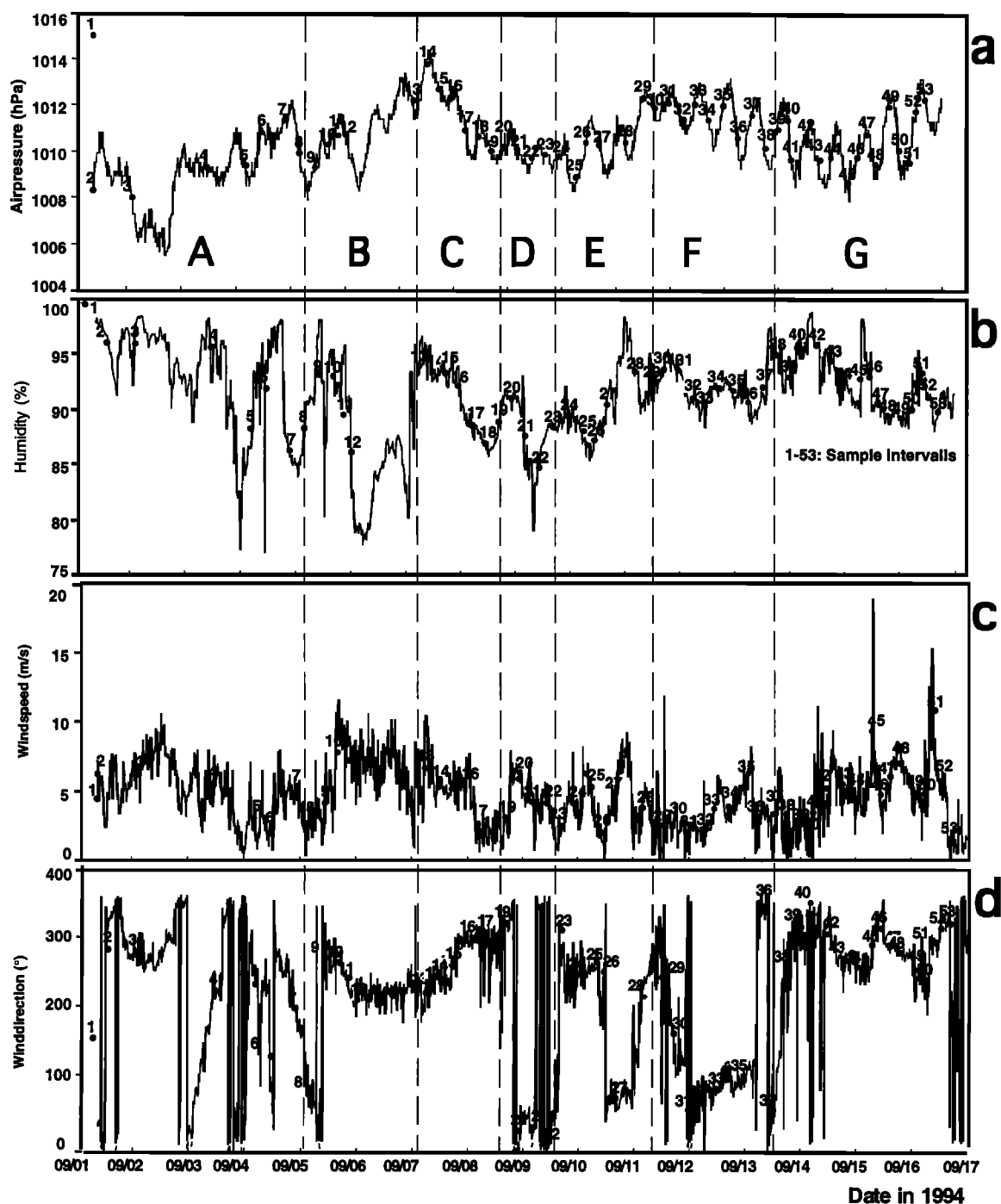


Figure 4. Meteorological parameters during cruise of *R/V SONNE* of September 1-17, 1994, in 10 min intervals (UTC). Sampling intervals (mean time and mean values) are marked with numbered points (1-53). Subdivided sample groups are marked A-G.

3.3. Grouping of Samples

It seemed expedient to subdivide the air samples into seven groups (Table 1), since the air masses reaching the western Pacific area during September proceed slowly from different directions and cross different source regions. For this purpose the meteorological and regional conditions (Figures 3 and 4) and air mass trajectories were considered. The information was obtained from 12 h weather charts available during the cruise and wind field charts [ASAS, 1994; *European Centre for*

Medium-Range Weatherforecasts, 1994; Jochen Püttger, Deutscher Wetterdienst, personal communication, 1995]. In most cases an inferred common wind direction and a common source region were the basis for subdividing the sample set into sample groups. These groups represent approximately the same air mass. In groups A, C, and E, different remote air masses of the same climatic zone were combined. The integrated sample groups A-G are further characterized in Table 1.

At the beginning of the cruise it was possible to sample air

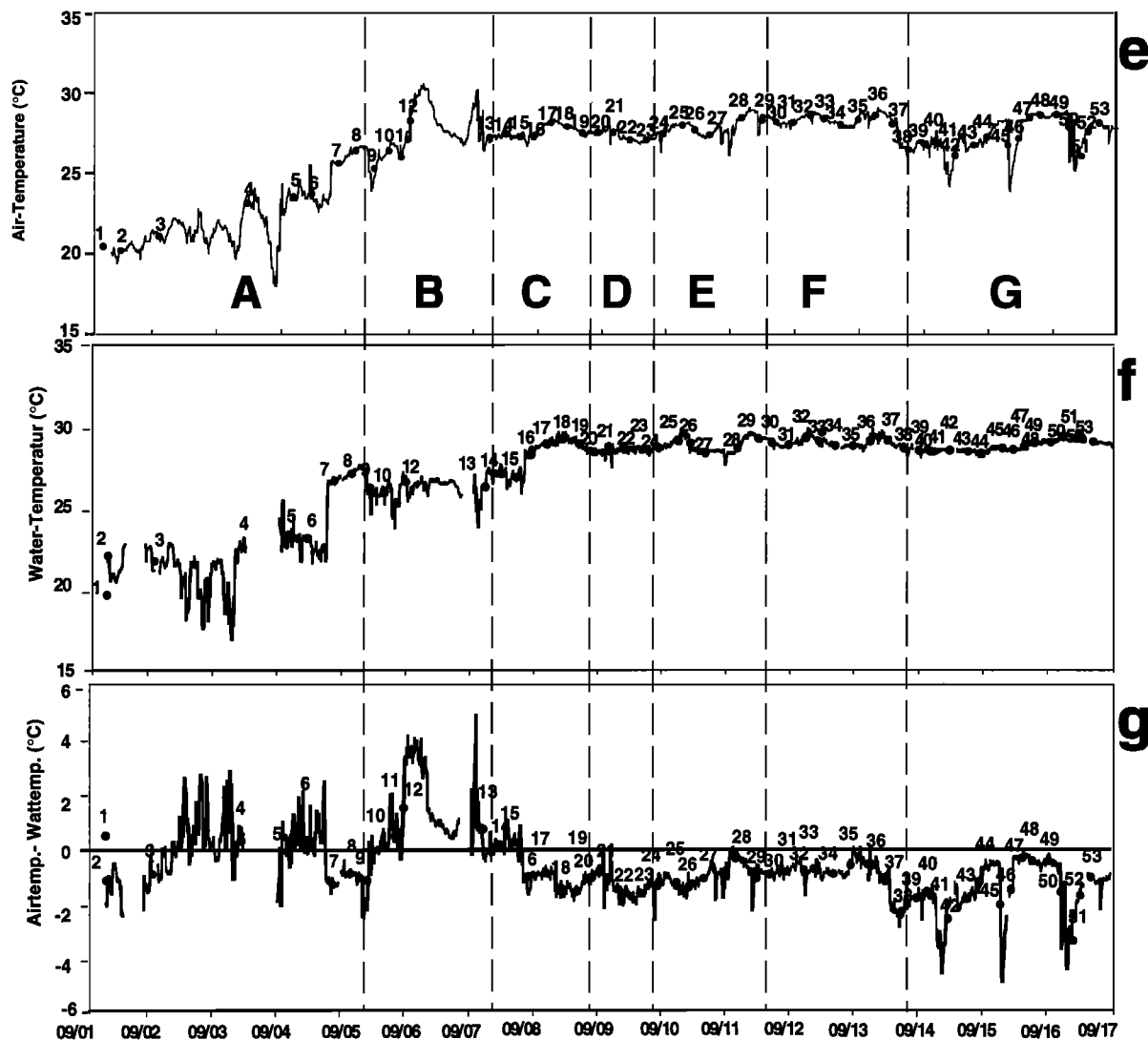


Figure 4. (continued)

of the temperate zone of westerly winds (group A: samples 1-8) that had passed over Hokkaido and then remained almost stationary. From the 5th to the 6th of September, anthropogenically contaminated air samples were taken in the region of Tokyo and in the Bay of Tokyo (group B: samples 9-13). During the following days, September 7 and 9, the ship passed through an area of clean southern marine air (group C: samples 14-16) that originated from the northern Pacific subtropical high pressure gyre and was deflected northward at the Nansei Islands. Because of a typhoon in the area from the 8th to the 9th of September, the Pacific air became stationary and finally was expelled by air passing over central Japan (group C: samples 17-19). The following day, air was sampled that had been transported 500 to 600 miles from the industrialized south of Japan (group D: samples 20-23). On the 10th of September the ship reached the East China Sea, where a stationary anticyclone with calm winds had been observed during the previous days. This caused descending marine air, which was sampled in this area initially. Later, branches of diluted anthropogenic contaminated air that had been transported for over 1000 miles from southern Japan reached the ship (group E: samples 24-29). The next two days, the 12th

and 13th of September, northeast trade winds reached the ship near the Nansei Islands, which brought air from the central and equatorial Pacific, mixed with air from the southeast trade winds of the eastern South Pacific (group F: samples 30-38). After passing the ITCZ, north of Luzon, the air which was sampled during the following days originated southeast of Indonesia from the southern hemisphere. This air mass was transported north and deflected to the right north of the equator, resulting in a southwesterly airflow into the South China Sea (group G: samples 39-53). The actual wind direction observed on the ship associated with this air mass was from northwest to west because of the land and sea breeze circulation caused by the island of Borneo, where a diurnal circulation of the wind direction was observed (Figure 4e).

4. Results and Discussion

Chlorinated, brominated, and iodated hydrocarbons as well as alkyl nitrates were identified in all samples of the western Pacific air. A typical ECD chromatogram of marine air influenced by anthropogenic emissions is shown in Figure 2. This air sample (Number 5, 16 L air, in Figures 3 and 5) was taken over

Table 1. Description of Grouped Air Samples (Groups A-G)

Sample Group	Samples (Total)	Climatic Zone	Latitude	Source Area of Contaminants	Influence of Source Region	Character of Sample Group
A-G	1-53 (53)	temperate zone through tropics	43-4	remote and anthropogenically contaminated air masses	anthropogenic and oceanic	
A	1-8 (8)	temperate zone (zone of westerly winds)	43-36	Hokkaido (0, 2: subpolar, 3, 4, 5: subtropical, 6, 7: continental air mass)	1-6: anthropogenic 7,8: aged anthropogenic	1-6: cold, humid 6,7: moderate warm (continental and maritime)
B	9-13 (5)	temperate zone (zone of westerly winds)	36-35	city and Tokyo Bay	strong anthropogenic	warm, dry (continental)
C	14-19 (6)	subtropics (Hadley circulation)	35-31	central Pacific, northern hemisphere (17-19: stationary air mass)	oceanic	moderate warm, humid (maritime)
D	20-23 (4)	subtropics (Hadley circulation)	31-30	south Japan (500-600 km distance from the industrialized area around Kobe and Hiroshima, chemical industries)	anthropogenic	moderate warm, dry (continental)
E	24-29 (6)	subtropics (Hadley circulation)	30-24	south Japan (1000 km distance from the industrialized area around Kobe and Hiroshima, chemical industries) and East China Sea, Taiwan	oceanic	warm, dry (continental)
F	30-38 (9)	tropics (Hadley circulation to ITCZ)	24-19	central Pacific, equatorial and southeast tradewind air masses (northeast tradewind)	oceanic	very warm, humid (maritime)
G	39-53 (15)	tropics (south of ITCZ)	19-4	southeast Asia, Indonesia, southern hemisphere (southwest monsoon)	anthropogenic and oceanic	warm, very humid (maritime)

the ocean off northern Japan. The same pattern of compounds, however, with changing abundances and ratios, was observed in each air sample collected during the cruise. Figure 5 shows the concentrations of tetrachloroethene, trichloroethene, tribromomethane, dibromochloromethane, and bromodichloromethane in marine air. The concentration ranges, the mean, and median values are summarized in Table 2. Figure 6 shows the average concentrations for individual groups.

4.1. Tetrachloroethene and Trichloroethene

The concentrations for tetrachloroethene in the atmosphere ranged from 0.83 to 128.7 pptv with a total average mixing ratio of 7.00 pptv and a median value of 3.10 pptv, excepting several contaminated samples. High concentrations were measured in air originating from industrialized areas; these samples showed mean mixing ratios of 36.64 (group B) and 10.02 pptv (group D). A gradual decrease toward the south was observed for tetrachloroethene (Figures 5 and 6). The mixing ratio of 7.76 pptv in the temperate zone (group A) decreased continuously toward the south in air masses from the remote atmosphere (group C: 3.47 pptv; group F: 2.22 pptv; group G: 1.29 pptv). The second chlorinated compound, trichloroethene, was abundant in the atmosphere with mixing ratios from 0.03 to 141.2 pptv with a total average of 3.52 pptv and a median of 0.32 pptv, excepting again the contaminated samples of group B. The highest concentrations were observed in the temperate zone (group A: 1.11 pptv), the area around Tokyo

(group B: 31.43 pptv) and the southern islands of Japan (Group D: 2.80 pptv). Concentrations in the remote atmosphere were very low, and a slight decrease of atmospheric concentrations to the south was noted (group E: 0.35 pptv; group F: 0.13; group G: 0.28 pptv). The concentration ratios between tetrachloroethene and trichloroethene were between 0.9 and 102.6 with an average of 12.6 (Table 2, Figure 7). The abundance of trichloroethene correlated well with tetrachloroethene (Figure 8).

The mixing ratios compare well with previous reported data from other remote air masses over the Atlantic and Pacific Ocean. Our measurements generally tend to be slightly lower than comparable results of previous seasonal and latitudinal similar observations (Tables 2 and 3, Figure 6). The data of the southernmost part of the *SONNE* transect (groups F and G) are among the lowest concentrations ever reported for remote regions [Yokouchi *et al.*, 1997; Wang *et al.*, 1995; Koppmann *et al.*, 1993].

The mixing ratio of 7.76 pptv for tetrachloroethene in group A at 40°N represents the high background of anthropogenic sources in the northern temperate zone. This value appears typical for this latitudinal belt for September, since halocarbons from anthropogenic emissions show concentration maxima between 30° and 45°N latitude in other remote areas. The tetrachloroethene concentrations during our observation were 25% lower than comparable seasonal and regional concentrations of about 10 pptv, which were obtained 10-15 years ago. This decrease certainly reflects the 40% decrease of

Figure 5. Concentrations of volatile halogenated hydrocarbons in air over the western Pacific Ocean from 43° to 5°N during cruise of R/V *Sonne* of September 1-16, 1994.

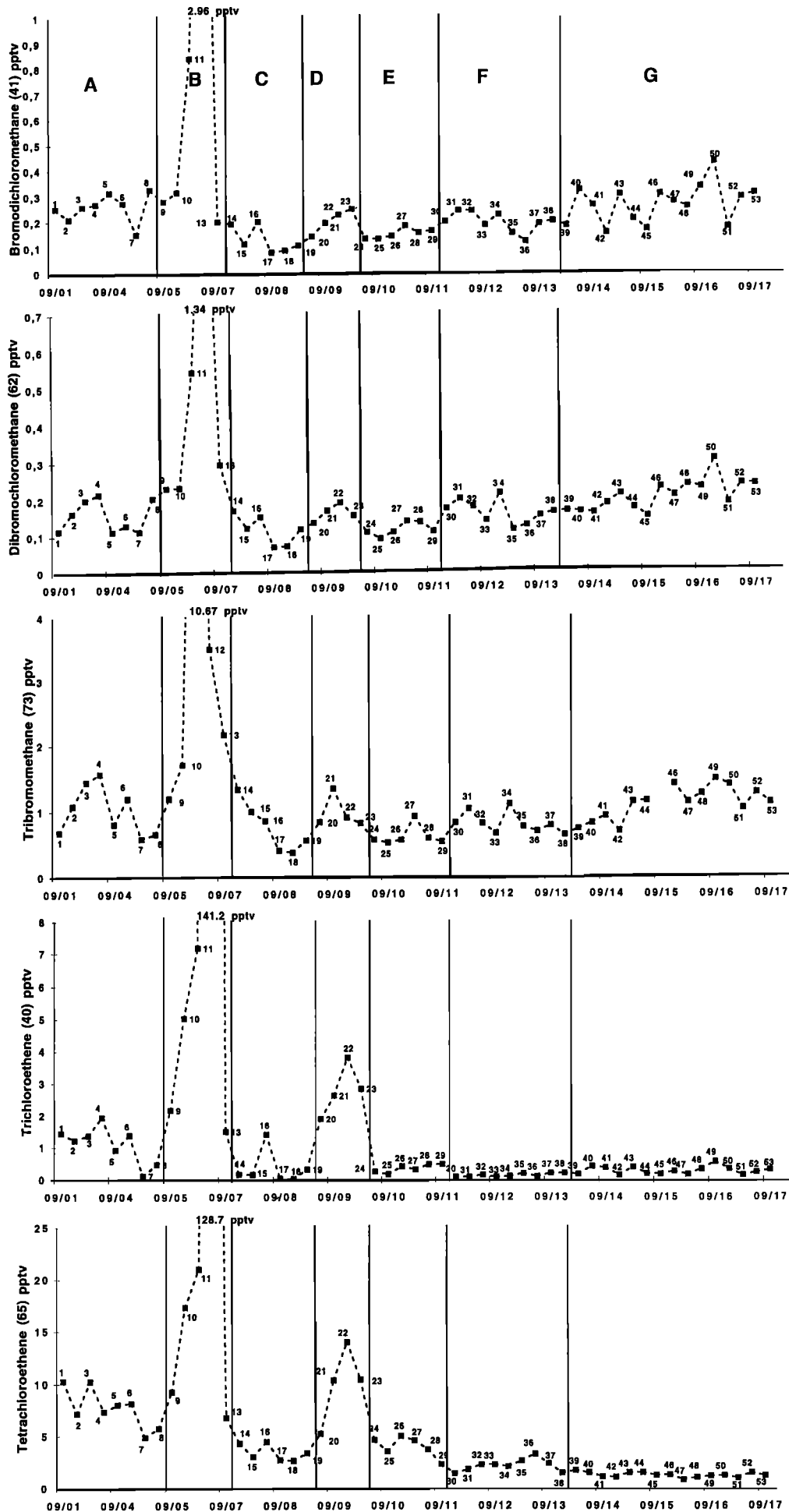


Table 2. Concentrations of Halocarbons over the Western Pacific (Groups A-G) and Standard Deviation σ of Mixing Ratios, September 1-16, 1994

Compound	Halocarbon Mixing Ratios, pptv			Standard Deviaton σ , %	
	Average	Range	Median	σ_a	σ_b
Bromodichloromethane CHBrCl ₂	0.28	(0.08-2.96)	0.21	139	35
Dibromochloromethane CHBr ₂ Cl	0.20	(0.07-1.34)	0.16	89	29
Tribromomethane CHBr ₃	1.20	(0.38-10.67)	0.92	117	33
Trichloroethene C ₂ HCl ₃	3.52	(0.03-141.2)	0.32	542	131
Tetrachloroethene C ₂ Cl ₄	7.00	(0.83-128.7)	3.10	249	81
Ratio C ₂ Cl ₄ / C ₂ HCl ₃	12.6	(0.9-102.6)	7.18		

Here σ_a is for all samples, and σ_b is for sample groups A and C-G, which excludes the highly contaminated sample group B; pptv, parts per trillion by volume.

anthropogenic emissions since 1982. It has been observed in other parts of the world as well in recent years. The mean mixing ratio of trichloroethene in group A samples was 1.11 pptv, which is only one third of the mixing ratio observed by Makide et al. [1987], and may also be due to the decrease of anthropogenic emissions, but combined with high oxidation rates in the late summer months. The low concentration of the chlorinated compounds and the high concentration ratio of 12 to 40 (Figure 7) between tetrachloroethene and trichloroethene clearly characterize the diluted and photochemically aged air mass and confirms their background character [Singh et al., 1983a; Makide et al., 1987; Atlas, 1990; Singh et al., 1992; Quack, 1994; Wang et al., 1995; WMO, 1995].

Air masses with the highest anthropogenic contamination were found in group B (Figure 5) where air of the urban area of Tokyo was sampled. The average mixing ratio for tetrachloroethene was 36.63 pptv and for trichloroethene was 31.43 pptv. The highest mixing ratios of all compounds during the entire cruise were found in Tokyo Bay (sample 12: tetrachloroethene: 128.7 pptv; trichloroethene: 141.25 pptv). This anomaly can readily be explained by local industrial sources [Otha et al., 1976]. Low concentration ratios of 0.9 to 4.5 (Figure 7) characterize the recent pollution.

Samples of group D represented air contaminated with trichloroethene and tetrachloroethene from the heavily industrialized region of southern Japan. This air mass was subsequently transported 500-600 km to the ship while being diluted. This leads to a slightly elevated concentration of the anthropogenically emitted compounds tetrachloroethene (10.02 pptv) and trichloroethene (2.80 pptv). Their concentration ratio was 3.6. Group E represented marine air off southern Japan as well and showed reduced influence of anthropogenic emissions. This air was apparently carried for 1000 km from the source region over the ocean toward the East China Sea and in the process was diluted by north central Pacific clean marine air. The concentrations of tetrachloroethene and trichloroethene decreased (tetrachloroethene: 4.00 pptv; trichloroethene: 0.35 pptv) and their ratio increased to 11 (Figure 7). The change in ratio showed the enhanced dilution and photochemical aging of the air mass as compared to air of group D from the same source region.

Remote air of the northern Pacific subtropical anticyclone was represented by group C during the ship's transit. Concentrations of 3.47 pptv for tetrachloroethene and 0.36 pptv for trichloroethene were observed. The concentration ratio between tetrachloroethene and trichloroethene was about 10. These values represent background concentrations and are similar to those in group E. Air of group F came from lower latitudes of the central Pacific Ocean. The concentrations of tetrachloroethene (2.22 pptv) and trichloroethene (0.13 pptv) were lower, and the concentration ratio of 17 was higher here than in group C samples. This is due to the mixing of air of the northern subtropical high pressure area with equatorial Pacific air, and with air carried by the southeast trade winds of the eastern South Pacific. The latter air mass has lower concentrations of anthropogenic halocarbons. A general concentration decrease of chlorinated anthropogenic compounds toward the south was expected from the general circulation conditions and could be documented during the SONNE cruise in 1994. Reasons for the north-south trend are a long residence time of the air in the Hadley cell with high concentrations of OH radicals. This leads to increased degradation of photochemically active compounds and an increased dilution of boundary layer air masses with subsiding air from higher altitudes, having low concentrations of halogenated compounds [Rasmussen and Khalil, 1981, 1982; Singh et al., 1983b; Atlas et al., 1992, 1993].

Atmospheric concentrations within 20° latitude of the equator are thought to be strongly correlated to the local conditions of the ITCZ [Atlas et al., 1993]. During the R/V SONNE cruise the ITCZ was most probably located at about 19°N. Group G samples therefore contained air originated in the southern hemisphere and hence showed the lowest concentrations of tetrachloroethene (1.29 pptv). This value is also among the lowest atmospheric concentrations of tetrachloroethene reported in the literature (Table 3). The trichloroethene concentrations of Group G samples were slightly higher (0.28 pptv) compared to the concentrations of the central equatorial Pacific samples (group F: 0.13 pptv), even when considering the highest analytical uncertainty of 20%. This is an unusual observation, because trichloroethene generally follows the trend of tetrachloroethene in the nor-

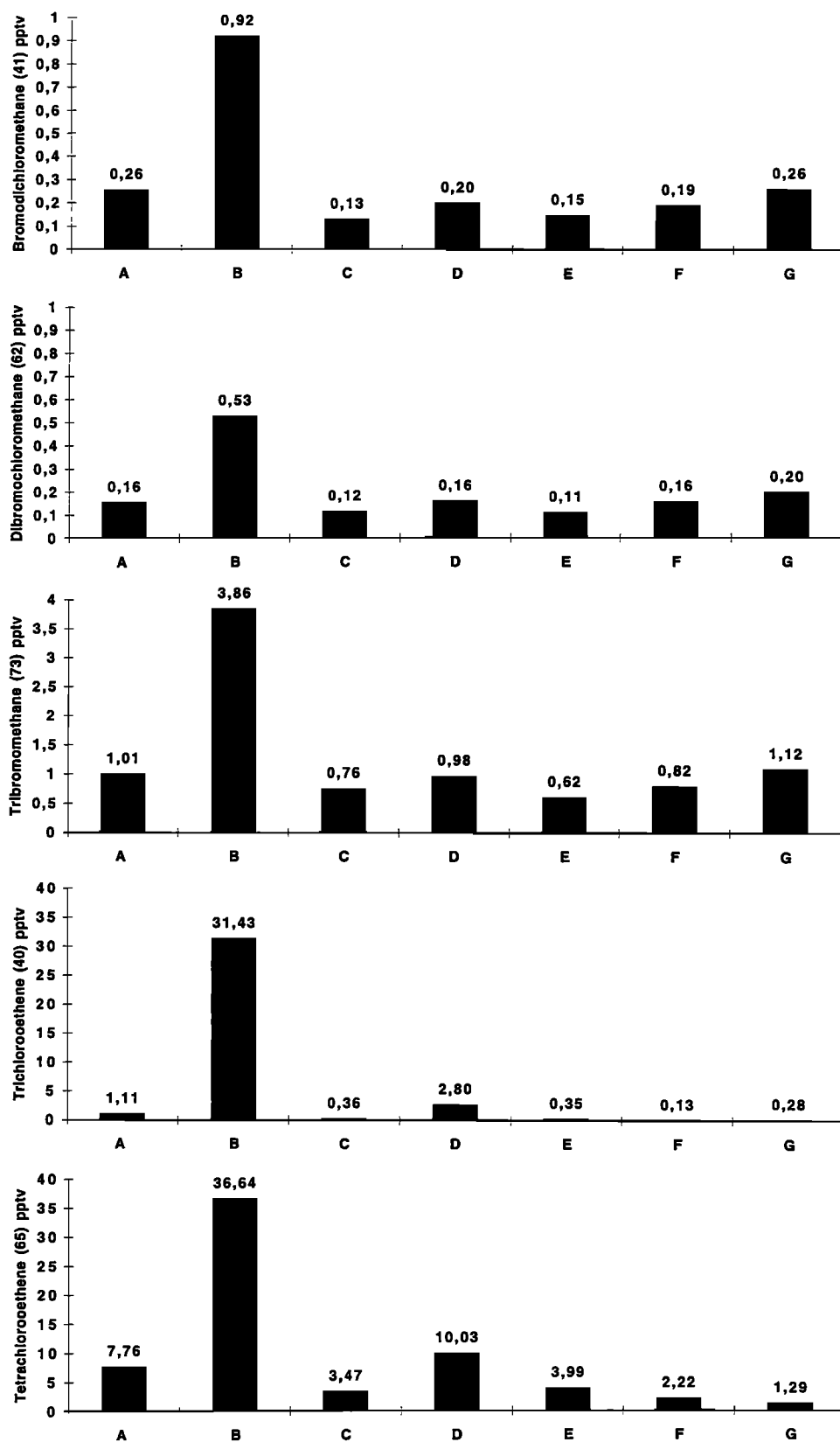


Figure 6. Average concentrations in the atmosphere of tetrachloroethene (65), trichloroethene (40), tribromomethane (73), dibromochloromethane (62), and bromodichloromethane (41) for sample groups A-G.

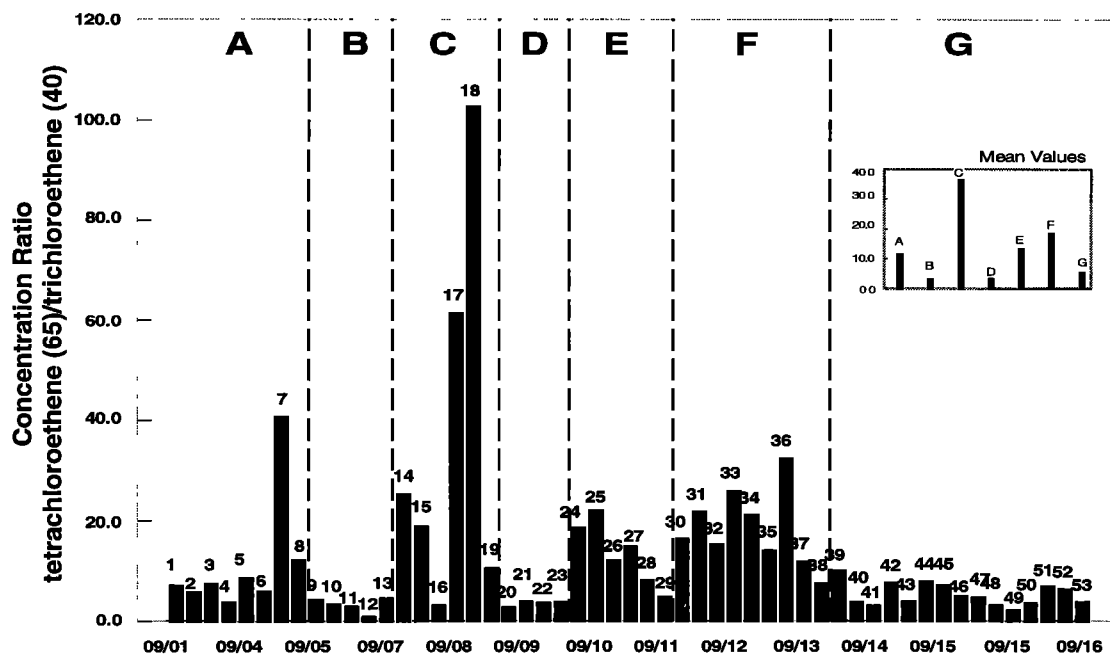


Figure 7. Concentration ratios of tetrachloroethene (65) and trichloroethene (41) of all air samples and average ratios of the sample groups A-G.

thern hemisphere and thus is expected to be lower in group G as well. Air of group G most probably originated from the Indonesian islands of Java and Sumatra and passed over Malaysia and Singapore. It is unlikely that there are large industrial sources only for trichloroethene and none for tetrachloroethene. The observations provide evidence for a natural source of this compound in the area of the Indonesian Archipelago. The mixing ratio of trichloroethene decreased, while wind speed increased (compare samples 42, 45, and 51 in Figures 3 and 5), which is an additional indication for local emittants. This may be part of the missing source for trichloro-

ethene to the atmosphere that was discovered recently and certainly needs further investigations [McCulloch and Midgley, 1996].

4.2. Tribromomethane, Dibromochloromethane, and Bromodichloromethane

The concentrations of the brominated compounds tribromomethane, dibromochloromethane, and bromodichloromethane are in reasonable agreement with earlier observations in Pacific areas (Table 3). Tribromomethane was always the most concentrated bromine compound in marine air with concentra-

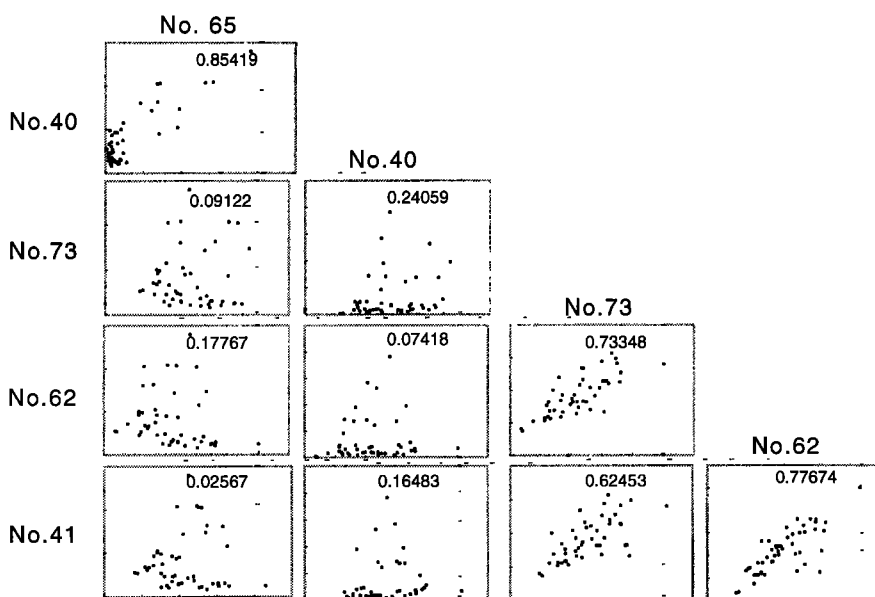


Figure 8. Correlation matrix and correlation coefficients (r^2) of tetrachloroethene (65), trichloroethene (40), tribromomethane (73), dibromochloromethane (62), and bromodichloromethane (41) for all air samples, excluding the highly contaminated air samples of sample group B (Tokyo Bay).

Table 3. Mixing Ratios of Volatile Halogenated Hydrocarbons in the Troposphere

Sampling Area and Date	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃	C ₂ HCl ₃	C ₂ Cl ₄	Reference
Western Pacific, Sept. 1994:						this work
Average (43-4°N)	0.28	0.20	1.20	3.52	7.00	
Range (43-4°N)	(0.08-2.96)	(0.07-1.34)	(0.38-10.67)	(0.03-141.2)	(0.83-128.7)	
Median (43-4°N)	0.21	0.16	0.92	0.32	3.10	
Eastern Pacific, 1982:						<i>Singh et al.</i> [1983a]
Northern hemisphere				12	29	
Southern hemisphere				< 3	5	
Atlantic, 1982:						<i>Penkett et al.</i> [1985]
Northern hemisphere			0.85 ± 0.44			
Southern hemisphere			0.58 ± 0.3			
Atlantic, 1985:						<i>Class and Ballschmiter</i> [1986a, b, 1988]
Northern hemisphere			1	5-10	15-30	
Southern hemisphere				< 2	5-10	
Japan, 1979-1986:						<i>Makide et al.</i> [1987]
Tokyo				> 1000	> 1000	
Hokkaido, winter				20	25	
Hokkaido, autumn				3	10	
Japan 1990:						<i>Sharp et al.</i> [1992]
Tsukuba town			0.70-1.71			
Seaside			0.91-2.18			
Pacific 1987:						<i>Atlas et al.</i> [1992]
Northern hemisphere		0.1	0.94		12	E. Atlas, unpublished data (1990)
Southern hemisphere			0.72		1.7	
Hawaii, May-June 1988		0.13 ± 0.06	0.2-0.25		4	<i>Atlas et al.</i> [1992]
Central Pacific, March 1990:						<i>Atlas et al.</i> [1993]
15°N		0.3-0.5	2.7		7.8	
Upper air mass		0.1-0.2	1.3		3.5	
10°S		0.1-0.2	1.3		2.6	
Atlantic, Aug.-Sept. 1989:						<i>Koppmann et al.</i> [1993]
Northern hemisphere (0-50°)				3 (0.3-15)	13 (1-30)	
Southern hemisphere				0.6	2.7	
Atlantic, 1982-1987:						<i>Wiedmann et al.</i> [1994]
Northern hemisphere (90-30°)					21 ± 5	
Northern hemisphere (0-30°)					7 ± 3	
Southern hemisphere					2.2 ± 0.5	
Arctic, April 1992:						<i>Yokouchi et al.</i> [1994]
After polar sunrise	0.26	0.2	1.6	2.4	6.8	
Pacific, Sept. 1989:						<i>Wang et al.</i> [1995]
Northern hemisphere					< 10	
Southern hemisphere					1-2	
Western Pacific, Sept.-Oct. 1992			0.13-2.9	0.1-13.5	0.4-40	<i>Yokouchi et al.</i> [1997]
Northsea, Sept. 1991	0.2-0.5	0.1-0.3	1.6-2.9	6-17	10-14	<i>Quack</i> [1994]
Arctic, Sept. 1991	0.3	0.2	1.7	6.7	2.2	<i>Quack</i> [1994]

Mixing ratios are in pptv.

tions more than 5 times higher than those of the corresponding bromochlorocompounds. Concentrations ranged from 0.38 to 10.67 pptv. Average concentrations for the sample groups ranged from 0.6 (group E) to 1.12 pptv (group G). High concentrations were measured in Tokyo Bay (group B: 3.86 pptv) and an overall average mixing ratio of 1.2 pptv and a median value of 0.92 pptv were observed. Tribromomethane as well as other brominated trace gases were more evenly distributed throughout the marine atmosphere of the western Pacific than were chlorinated anthropogenic compounds. The standard deviation of the substances given in Table 2 is a measure for this observation. The pattern reflects the wide distribution of their natural sources since they have comparatively short atmospheric residence times because of photolysis, for example about 2-4 weeks for tribromomethane [*Penkett et al.*, 1985].

Concentrations of dibromochloromethane ranged from 0.07 to 1.34 pptv with a mean mixing ratio of 0.20 pptv and a median value of 0.16 pptv. The highest concentration was

found in the Tokyo area (group B: 0.53 pptv). There was slightly more dichlorobromomethane in the atmosphere than dibromochloromethane. Its concentrations in the air ranged from 0.08 to 2.96 pptv with a mean mixing ratio of 0.28 pptv (Figure 6) and a median value of 0.21 pptv. The highest concentrations of dichlorobromomethane were found again in the Tokyo area with a mean value of 0.92 pptv.

The correlation coefficients between the three bromocarbon compounds were 0.62, 0.73, and 0.77 (Figure 8) suggesting similar emission and degradation scenarios. The bromocarbons were not correlated to the anthropogenic chlorinated compounds (Figure 7). However, they showed elevated concentrations in air masses with anthropogenic influence (Figure 5). The brominated compounds were also elevated in air samples that had recently been influenced by land and coastal areas (Figures 3 and 5).

In group A of the temperate zone (tribromomethane: 1.00 pptv; dibromochloromethane: 0.16 pptv; bromodichloromethane: 0.25 pptv) the brominated compounds showed an

increasing mixing ratio toward the coast (Figures 4 and 5). The cause could be elevated emissions of compounds from coastal waters compared to the open ocean water. Increased concentrations in coastal waters were observed earlier in the Arctic, in the North Sea, in the Baltic Sea, and in the North Atlantic Ocean. Release of brominated compounds from biological sources, possibly from brown and red algae, which are known to produce brominated hydrocarbons, could be the cause for higher concentrations in coastal seawater. An increased emission of brominated compounds to the atmosphere over oceanic waters of high concentrations is very probable. More efficient exchange processes at the coastal air-sea interface caused by breaking waves may add to the emission [Dyrssen and Fogelqvist, 1981; Singh *et al.*, 1983b; Berg *et al.*, 1984; Gschwend *et al.*, 1985; Cicerone *et al.*, 1988; Nightingale, 1991; Atlas *et al.*, 1992; Klick, 1992; Wallace and Wirick, 1992; Moore and Tokarczyk, 1993]. Increasing atmospheric concentrations toward the coast were also observed in group D samples, which represent air from the industrialized south of the Japanese Islands. The coastline, with its productivity of macroalgae and breaking waves, again may be a possible source; nevertheless, here are as well anthropogenic sources for these compounds. Power plants, often situated in industrialized coastal regions, can be additional sources [Fogelqvist and Krysell, 1991; Quack, 1994]. The two bromochlorocarbons correlated well with the anthropogenically chlorinated substances in group D. Natural sources could not be differentiated from anthropogenic sources, but certainly coastal emission from either one of these sources is the origin of these compounds to the atmosphere. The lowest concentrations of tribromomethane compounds were found in dry and warm air, mostly of continental origin (samples 7, 8, 17, and 18).

The highest concentrations of bromine compounds during the R/V SONNE cruise were found in Tokyo Bay (group B: tribromomethane: 3.86 pptv; dibromochloromethane: 0.53 pptv; bromodichloromethane: 0.92 pptv), which is another indication for anthropogenic sources. Yokouchi *et al.* [1997] found high tribromomethane concentrations in the harbors of Singapore and Punang in conjunction with high concentrations of chlorophyll *a*. These authors suggest the distribution of algae to be the reason for high concentrations in the atmosphere. However, there are more sources to be considered, especially in regions affected by industrialization. We believe that the high concentrations in Tokyo Bay are due to release of these substances from the cooling towers of power plants situated along the coast. These seem to be an important local source for the atmosphere in Tokyo.

The concentrations of brominated compounds tend to increase in air samples of lower latitudes (compare Figure 3 and Figures 5 and 6). The air masses that reached the ship in the latter part of the cruise came from highly productive oceanic areas and coastal regions (groups E, F, and G; Table 1). Air of the central and equatorial Pacific showed high concentrations of tribromomethane (group F: 0.82 pptv) and bromochlorocarbons (> 0.2 pptv), which implicates the ocean as a source for these compounds. Previously, it was discovered that air over the equatorial Pacific was enriched with organic bromine compounds, tribromomethane, and dibromochloromethane, probably related to the high productivity of equatorial waters and ocean upwelling [Atlas *et al.*, 1993].

High concentrations of the brominated compounds tribromomethane (1.12 pptv), dibromochloromethane (0.2 pptv), and

bromodichloromethane (0.26 pptv) were found in group G samples from southern marine air masses. These had previously passed over the Indonesian Archipelago and over the South China Sea. The concentrations of the brominated species were higher at low wind speeds (e.g., samples 31-34, 38-40, 46, and 50; compare Figure 3, Figure 5) than at high wind speeds (e.g., samples 36, 45, and 51). Low wind speeds can lead to an accumulation of ocean-derived and coastal-emitted substances in the atmosphere, as observed previously over the North Sea. High wind speeds promote the air-sea exchange of marine trace gases but dilute the atmospheric concentrations when the source area is spatially restricted. This supports the idea that the shallow ocean margins and the long coast line of the Indonesian Archipelago could be the source for elevated brominated compounds to the atmosphere since those areas are known to be rich in red algae [Lüning, 1985; Berg *et al.*, 1984; Watson *et al.*, 1991; Quack, 1994].

All observations made during the R/V SONNE cruise provide evidence for a general enrichment of marine air with short-lived brominated compounds. Coastal natural emissions and productive oceanic regions may cause the atmospheric concentrations to increase even more. Anthropogenic sources are locally important for the atmospheric concentrations of tribromomethane, dibromochloromethane, and bromodichloromethane.

5. Conclusion and Outlook

The distribution of anthropogenic and natural organic trace gases in the atmosphere over the western Pacific Ocean is seen in terms of sources, sinks, trajectories, and photochemical reactivities. A close relationship between the composition and the origin and history of an air mass could be established, indicating that transport is the main factor controlling the concentrations and distribution of these trace gases. Concentrations and relative abundances of the anthropogenic and naturally occurring halocarbons as well as the observed meteorological conditions enabled us to characterize air masses and identify sources of the compounds. Tetrachloroethene and trichloroethene can serve as tracers for the anthropogenic influence on an air mass. Their concentrations and concentration ratio change during transport of a polluted air mass because of the different lifetimes of these compounds. Remote air masses showed low concentrations and high ratios (5-102) between tetrachloroethene and trichloroethene, while recently contaminated air masses showed high concentrations and low ratios (0.5-4). It became evident that the atmospheric concentrations of the anthropogenically chlorinated compounds have declined over recent years, most likely in response to decreased production, use, and anthropogenic emission. Strong evidence for a natural source of trichloroethene in the tropical region was found.

Marine air masses were generally enriched with the short-lived brominated compounds. Coastal natural emissions and productive oceanic regions were found to add to the atmospheric load. Industrial sources, such as power plants, were locally important for the concentrations of tribromomethane, dibromochloromethane, and bromodichloromethane in the atmosphere over the western Pacific Ocean. The chlorinated and brominated compounds can be used as tracers for transport pathways and dilution of anthropogenic and marine air masses. The natural sources of these compounds and the processes which influence their distribution in the atmosphere need

further investigation. The main driving forces of air-sea exchange of halogenated compounds from natural oceanic and coastal sources in the western Pacific should be explored on a seasonal basis.

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