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Concentration Variability of Anthropogenic Halocarbons and Applications as Internal Reference in Volatile Organic Compound Measurements

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This work investigated concentration variability of anthropogenic halocarbons by performing four separate sample collections in urban, industrial, and background atmospheric environments. Large concentration variability was found for CFC-12, CH_3CCl_3 , $\text{CCl}_2=\text{CCl}_2$, and $\text{CCl}_2=\text{CCl}_2$ in nonbackground environments. In comparison, the variability of CFC-113 and CCl_4 was small regardless of the environments and was also close to the precision of the analytical system, implying that CFC-113 and CCl_4 have relatively little emissions in Taiwan. The uniform property associated with atmospheric CCl_4 is suggested as an "intrinsic" internal reference for quality control of VOC analysis.

Introduction

The ubiquitous presence of chlorofluorocarbons (CFCs) and some other anthropogenic halocarbons, such as methylchloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4), in the atmosphere is attributed to their long-term emissions compounded by long atmospheric lifetimes. The combined anthropogenic chlorine loading has more than doubled over the last 2 decades (1), clearly reflecting the worsening trend of ozone depletion (2). After implementation of the 1987 Montreal Protocol (3, 4), and subsequent amendments (5), production of these ozone depleting substances was largely phased out. Hence, the growth of several major halocarbons, e.g., CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $\text{CCl}_2\text{FCClF}_2$ (CFC-113), CH_3CCl_3 , and CCl_4 , which accounts for more than 80% of the total atmospheric chlorine loading, began to slow-down or even decline (6–12). Although trends in background data are clear signs of changes in global-scale emissions, they provide little information that can be used to evaluate regional or national compliance with the Montreal Protocol. Abundance trends determined from measurements at fixed sites proximate to source regions are dependent upon the method of extracting background data from "noisy" records (7). Thus, the trends in the noise or variability are sensitive indicators of changes in their regional emissions (13). By analogy, the concentration variability determined from random sampling in potential source areas also reveals another form of emission condition (14–17). Overall, the concentration variability of anthropogenic halocarbons, spatial or temporal, has become smaller in recent years than in the pre-Protocol era.

In contrast to halocarbons, concentrations of volatile organic compounds (VOCs) are highly variable, with most

atmospheres containing a complex mixture of hundreds, possibly thousands, of different species. These atmospheric VOCs can have profound impact in urban air quality (18). When associated with the chemistry of the nitrogen oxides, VOCs are important in the photochemical production of tropospheric ozone. Numerous VOCs have also received considerable attention for their adverse effects on human health and are listed in the Title III of the Clean Air Act Amendments of 1990. Hence, a series of EPA methods is designed to target these VOCs (19–21).

Most VOC measurement techniques involve the use of high-resolution capillary chromatography (GC) in conjunction with various GC detectors, including flame ionization detector (FID), photoionization detector (PID), or mass spectrometer (MS). Given the complexity involved in the chromatographic analysis of VOCs, it is justifiable to explore new techniques of quality control or standardization procedure to reduce artifacts or systematic errors in the analysis.

Conventionally, monitoring the long-term stability of an analytical system or eliminating systematic errors in VOC analysis requires a procedure involving both external and internal references. However, artifacts or systematic errors can be easily introduced when the preservation of the standards loses its integrity due to chemical reactions, surface adsorption, contamination, or leakage (22–24). This is of particular concern for remote in-situ setups, for which replenishing the reference air or having a mechanism to add internal standards could be a challenging task. In this work, the variability of trace gases based on time-series and simultaneous sample collection in various environments was investigated, and a simple technique of quality control was explored using halocarbons of little atmospheric variability as reference in trace gas analysis.

Experimental Section

1. Sampling. Air samples were collected in 2-L stainless steel canisters, some purchased from UC, Irvine (25, 26), with the rest being self-fabricated in a similar procedure to UCI's. Two urban, one industrial, and one coastal collection were made between 1996 and 1998. The two urban studies were performed in August 1996 and August 1998, respectively, in the Taipei metropolitan area. This metropolitan area has a population of more than 5 million in a basin area of about 300 km². For the 1996 collection, time-series samples were taken for 3 days at five sites with three samples taken each day at each site. This three-day collection was to evaluate the temporal variability of halocarbons. For the 1998 collection, 54 samples were randomly collected at different sites between 5:00–5:30 A.M., and another 55 samples were collected at the same sites between 5:30–6:00 P.M. Since the anthropogenic halocarbons are industrial or human activity related, the sampling at dawn represents a low emission condition within a day, whereas the sampling in the evening, when the city activity peaks, should pose a contrast to the morning condition for anthropogenic emissions. The design of the 1998 collection was to obtain a near simultaneous sampling for assessing the area variability of trace gases. All urban samples were collected in open fields, such as parks and schoolyards, to avoid over-influence from nearby point sources (14).

For the background studies, 65 air samples were collected along the coastline of Taiwan during 3 days in August 1997. Additionally, 25 samples were collected in an industrial park for the purpose of surveying the fugitive CFC emissions from manufacturing electronic products.

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2. Analytical Instrumentation and Sample Analysis. In the early setup, the analytical system consisted of a Vairan 3400 cx gas chromatograph equipped with a flame ionization detector (FID) and an electron capture detector (ECD). Two capillary columns were connected in parallel to an adjustable Y-splitter, with the PLOT column (Chrompack, 50 m, 0.53 mm i.d., $df = 10\ \mu\text{m}$) connected to the FID for separating and detecting C_2 – C_7 hydrocarbons. A DB-624 column (J&W Scientific, 75 m, 0.53 mm i.d., and $df = 3\ \mu\text{m}$) was connected to the ECD for halocarbon analysis. A 360 mL aliquot of air (STP) from the canister was transferred to a cryogenic trap for sample preconcentration and cryo-focusing. After injection, the temperature of the GC oven was ramped from -10 to $200\ ^\circ\text{C}$ in 27.5 min and maintained at $200\ ^\circ\text{C}$ for another 17.5 min. More than 30 halocarbons and nonmethane hydrocarbons (NMHCs) were quantified from each injection. This system was used to analyze the coastal, industrial, and the first urban collections.

In a later setup, a computer controlled fully automated valve system with an online cryo-trap was built in-house, which could accommodate several canisters for continuous analysis. This system provided better precision than the earlier setup. Details of this automated system can be found elsewhere (27). Approximately 300 mL of sample air was drawn consistently from each canister for each aliquot. After cryo-trapping, the injection flow was split to two columns located in two separate GCs with a split ratio of 1:1. A DB-1 column (J&W Scientific, 60 m, 0.32 mm i.d., and $df = 1.0\ \mu\text{m}$) was used in the Varian 3400 GC. The outlet of this column was further split into two 0.1 mm i.d. uncoated columns of unequal length with the smaller flow (about 1/3) going into the ECD and the larger flow (about 2/3) going to the FID, to separate C_4 – C_{12} hydrocarbons. A second PLOT column (HP, 50 m, 0.32 mm i.d., $df = 8.0\ \mu\text{m}$) was connected to a second FID in an HP-6890 to separate C_2 – C_7 hydrocarbons. The 109 samples collected in an urban environment were analyzed by this system, in which continuous analysis was performed within 5 days. GC/MS analysis further confirmed hydrocarbon speciation. Figure 1 displays typical ECD and FID chromatograms from the later setup.

A 30-L reference cylinder (Aculife treated, provided by Scott, San Bernardino, CA) filled with urban air to about 700 kPa was assayed every 3–6 runs. Absolute calibration scales for the measured gases are tied to those of UC, Irvine (28).

Results and Discussion

Ambient concentrations of numerous trace gases were measured from 244 samples collected in three different environments, i.e., urban, industrial, and coastal, with the urban collections consisting of both time-series and simultaneous samples. Individual mixing ratios for these samples are not listed due to space limitations. Figure 2 displays the time-series result of one site for three selected gases from the 1996 urban collection. Many measured gases exhibit significant concentration variations except for CFC-113 and CCl_4 , which are tightly linked to urban activities. The 1s relative standard deviation (RSD) for the 48 samples taken from all five sites is about 4% for CCl_4 and 8% for CFC-113. In addition to this time series study, the second urban collection made in 1998 was to investigate area dependence and concentration variability of trace gases by sampling at more than 50 sites within a short time period, as shown by the box-whisker plots in Figure 3 for selected halocarbon. Again, both CFC-113 and CCl_4 were found to have little concentration variability with 1s RSD = 1.4% for CCl_4 and 4.8% for CFC-113 for all of the morning and afternoon samples combined (109 samples). We believe the narrower concentration ranges for CCl_4 and CFC-113 with this collection than the time-series one is not only due to the improved analytical precision (1 σ precision = 1.1% for CCl_4 and 1.8% for CFC-

113 for 1998 collection vs 2.4% for CCl_4 and 2.8% for CFC-113 for 1996 collection) but also due to the reduction in emissions over the 2 year period.

Minimum concentrations of CFC-12 observed in either time-series or simultaneous study were close to 600 pptv, roughly about 100 pptv above the northern hemispheric background values. This compound is primarily used as a refrigerant in older vehicles (manufactured or imported prior to mid-1994 in Taiwan). As estimated, over half of the total registered 1 million passenger cars in Taipei still use CFC-12. Consequently, leakage of CFC-12 is not localized but widespread and thus elevates CFC-12 concentrations in the basin.

Methylchloroform and tri- and tetrachloroethene are conventionally used as a degreasing or dry cleaning solvents, hence, their emissions are more stationary than those of CFC-12. Our previous study found clear area-dependence for CH_3CCl_3 , and elevated concentrations were detected mainly in suburban areas in close proximity to factories (14). Variability of CH_3CCl_3 is slightly larger in the late afternoon (Figure 3b) than in the early morning (Figure 3a), possibly due to heavier industrial activities. Compared to our simultaneous survey made a year earlier (14), its variability was substantially reduced, implying the ban on this substance may have taken effect. The variability difference for tri- and tetrachloroethene between morning and evening measurements is even more dramatic. The applications for these two compounds resemble those of CH_3CCl_3 but are not regulated by the Montreal Protocol. However, voluntary reduction in emissions of these two compounds occurred in the United States and Europe in light of toxicity concerns (13, 29). Tri- and tetrachloroethene are emitted into the atmosphere over Taipei primarily through their use as dry cleaning solvents. The demand for these two compounds has not decreased in Taiwan. In fact, significant increase in consumption was observed for $\text{CCl}_2=\text{CCl}_2$ for the period 1995–1997. Owing to their relative high reactivity arising from reacting with HO radicals and, to a less extent, Cl radicals ($\tau \approx 7$ days for $\text{CHCl}=\text{CCl}_2$; $\tau \approx 4$ months for $\text{CCl}_2=\text{CCl}_2$), their background mixing ratios are low (28, 30–33). Hence, spatial concentration variability is more pronounced than other long-lived CFCs due to large concentration gradient between source and background environments. Because morning and afternoon samples were collected at the same sites, the difference in concentration range reflects the variation in emission between the two periods.

Chlorofluorocarbon-113 was primarily used as a deflux agent in the electronics industry. In the post-Montreal Protocol era, electronic products are not supposed to be cleaned by CFC-113. Instead, other alternative agents, such as water- or hydrocarbon-based solvents, replaced CFC-113 in the cleaning process. Herein, sampling near a potential source area, an electronics industrial park, was made to verify whether CFC-113 is still used in the domestic electronic industry, see Figure 4. The tight concentration distribution of CFC-113 indicates that CFC-113 is no longer used. Discussions with EPA of Taiwan and industrial personnel confirmed that the CFC-113 has been replaced from production process to avoid heavy tariffs under the Montreal Protocol. In contrast, both $\text{CCl}_3\text{H}=\text{CCl}_2$ and $\text{CCl}_2=\text{CCl}_2$ are widely used in the semiconductor plants as cleaning solvents, and, as a result, large concentration variability was observed.

Another useful indicator of usage and release, other than the import figures, is to compare with the background levels. Figure 5 presents the background sampling results for 65 samples collected along the Taiwan coastline. Moderate traffic on the coastal highways somewhat elevated CFC-12 levels for some samples, particularly in harbor areas. In general, the mixing ratios for other measured halocarbons in coastline collection are substantially more uniform than

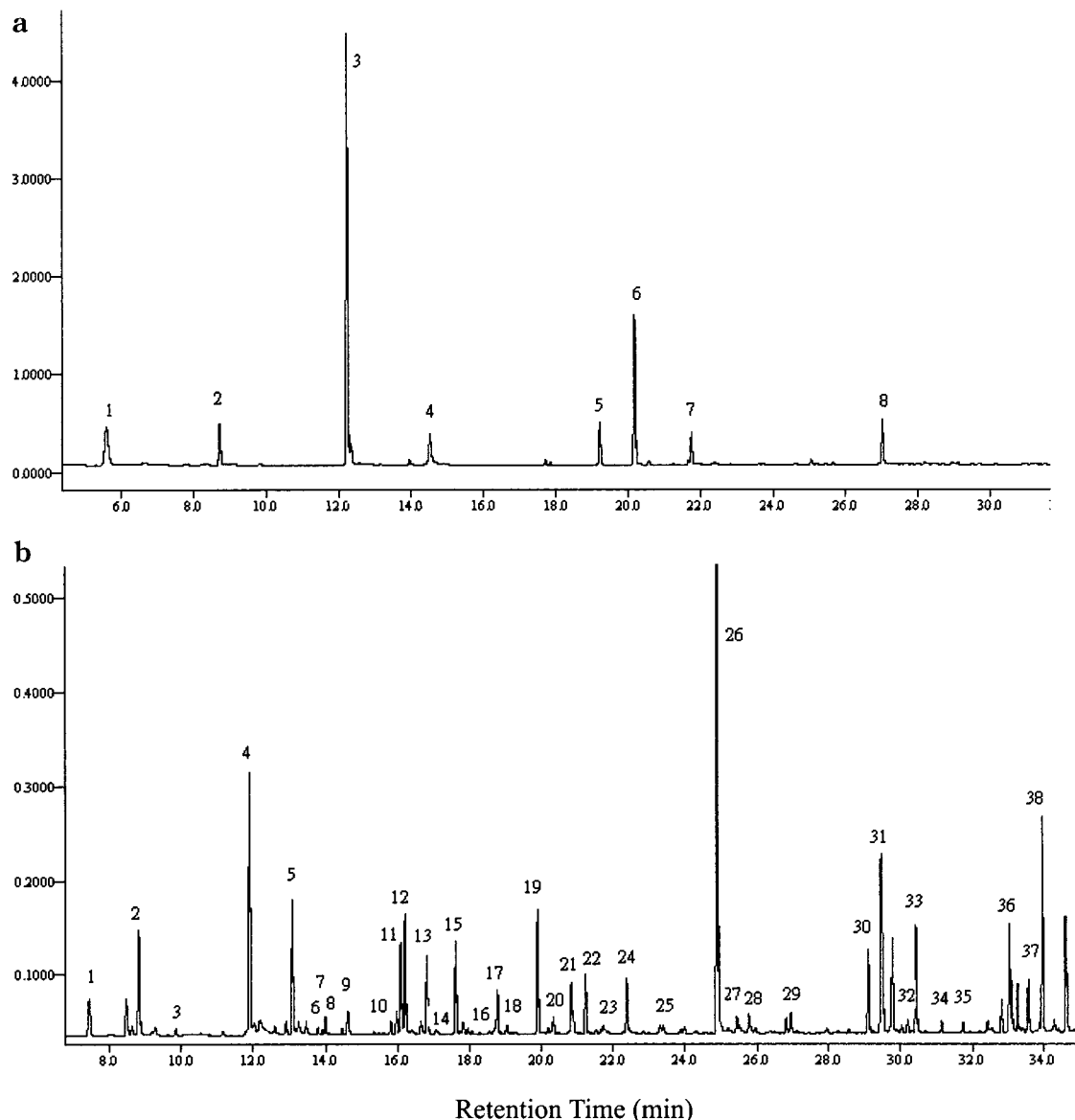


FIGURE 1. a. Separation of halocarbons on DB-1 column for a typical sample collected in Taipei City. Peak assignments: (1) CFC-12, (2) H-1211, (3) CFC-11, (4) CFC-113, (5) CH_3CCl_3 , (6) CCl_4 , (7) CHCl_3 , and (8) C_2Cl_4 . b. Separation of nonmethane hydrocarbons on the DB-1 column for a typical sample collected in Taipei City. Peak assignments: (1) isobutane, (2) butane, (3) 2-butane, (4) 2-methylbutane, (5) pentane, (6) *trans*-2-pentene, (7) *cis*-2-pentene, (8) 2-methylbutane, (9) 2,2-dimethylbutane, (10) cyclopentene, (11) 1-pentene, (12) 2-methylpentane, (13) 3-methylpentane, (14) 2-methyl-1-pentene, (15) hexane, (16) 3-hexene, (17) methylcyclopentene, (18) 2,4-dimethylpentane, (19) benzene, (20) cyclohexane, (21) 2-methylhexane, (22) 3-methylhexane, (23) 2,2-dimethylhexane, (24) heptane, (25) methylcyclohexane, (26) toluene, (27) 2-methylheptane, (28) 3-methylheptane, (29) octane, (30) ethylbenzene, (31) 1,3-dimethylbenzene, (32) styrene, (33) 1,2-dimethylbenzene, (34) nonane, (35) 1-methylethylbenzene, (36) propylbenzene, (37) 1,2,4-trimethylbenzene, and (38) 1,3,5-trimethylbenzene.

in the urban collections, and the comparison are more dramatic for shorter-lived halocarbons, i.e., CH_3CCl_3 , $\text{CCl}_2\text{H}=\text{CCl}_2$, and $\text{CCl}_2=\text{CCl}_2$. More importantly, with the exception of CFC-12, the coastal levels are close to the reported northern hemispheric values (9, 11, 28, 30, 31). This result helps illustrate that the air masses, having picked up halocarbons from inland cities, get diluted with cleaner air as they move away from inland cities and eventually blend into the background.

For the above four sample collections in urban, industrial, and coastal environments, mixing ratios of CFC-113 and CCl_4 were consistently uniform and, more importantly, close to reported background levels. Similar results have also been reported for measurements made in Porto Alegre, Brasil in Southern Hemisphere with a population of 3.4 million, in which the average concentration for CCl_4 is 103 ± 16 pptv, also very close to the reported background value, indicating

no local emissions for CCl_4 (17). Note that the north-to-south concentration gradient has diminished in recent years due to reduced global emissions, therefore the concentrations in the S.H. can be directly compared to those in the N.H.

Carbon tetrachloride is mainly used as a chemical intermediate for the production of CFCs, particularly for CFC-11 and CFC-12, which accounted for nearly 80% of the total CCl_4 production. To comply with the Montreal Protocol, production of CFC-11 and CFC-12 was completely ceased in 1991 in Taiwan. The fact that CFC-113 and CCl_4 were never domestically produced, and the amount imported to Taiwan has dropped to zero is a positive indicator of its complete phaseout in industrial applications in Taiwan. Furthermore, the concentration ranges of CFC-113 and CCl_4 are not significantly different from their analytical precision, particularly for the 1998 urban collection.

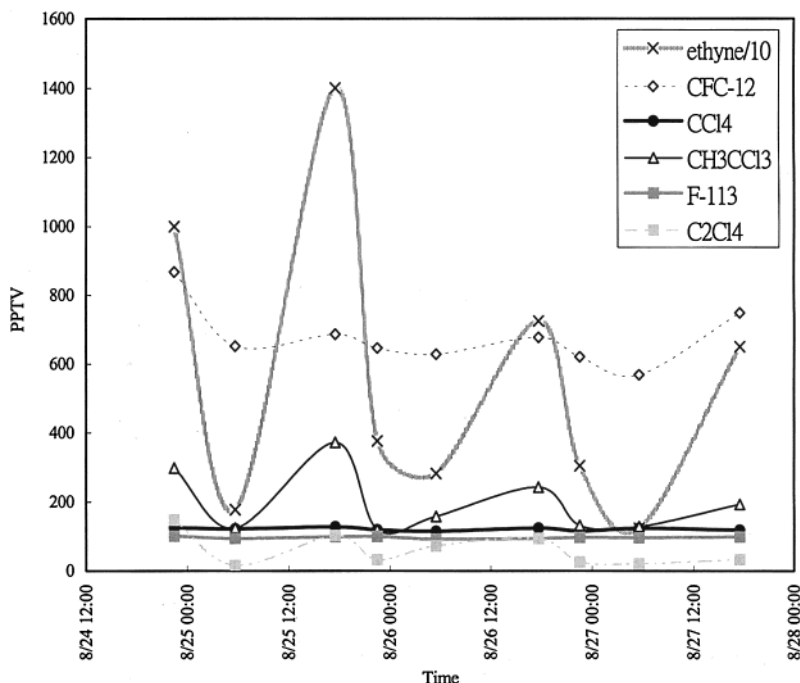


FIGURE 2. Time series samples collected on campus of Taiwan University in 1996. Collection started at Saturday 10:30 P.M. and ended at Tuesday 5:30 P.M. Ethyne mixing ratios are scaled down by 10-fold to be compared with mixing ratios of halocarbons.

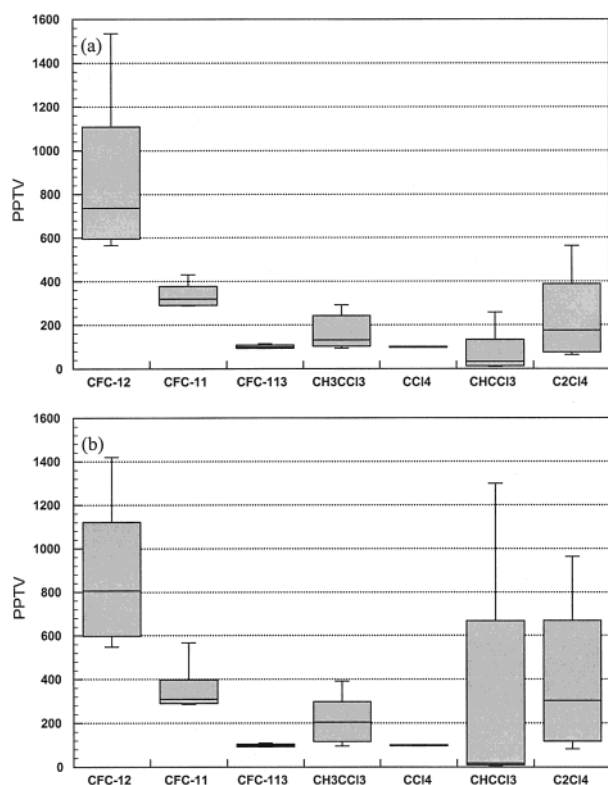


FIGURE 3. Concentration distribution of halocarbons for the 56 samples collected between 5:00 and 5:30 A.M. (a) and the 53 samples collected between 5:30 and 6:00 P.M. (b) in Taipei City. Whiskers define the outlying 5% of the data. The box represents 10–90% of the data. The median or the 50th percentile is the line within the box. Same definition applies to Figures 4 and 5.

We explored the feasibility of applying the homogeneous property associated with atmospheric CFC-113 or CCl_4 as reference compounds to quality control the analysis of other trace gases, of which the concentration variability and species complexity are significantly greater, see Table 1. This is illustrated using the 1998 urban collection of 109 samples,

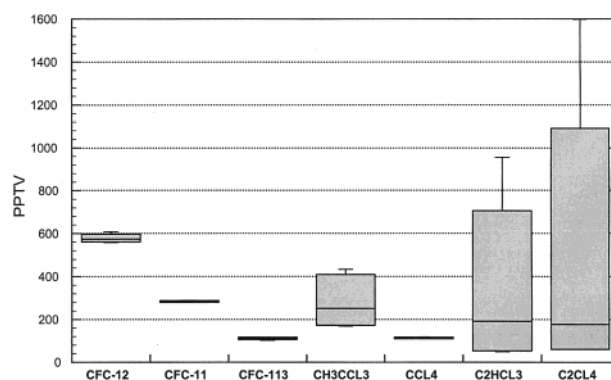


FIGURE 4. Concentration distribution of halocarbons for the 25 samples collected in an electronic industrial park.

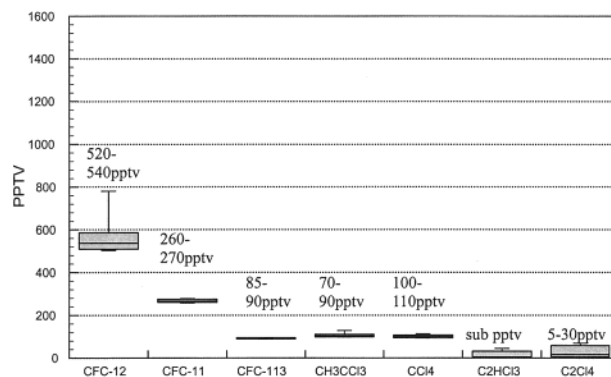


FIGURE 5. Concentration distribution of halocarbons for the 65 samples collected along the coastline of Taiwan. Northern hemispheric background values are marked above the boxes, which can be found in our cited refs 7, 10, 11, 13, 15, 17, 19, 26.

which were analyzed continuously during a 5-day period. Figure 6 displays the mixing ratios of CFC-113 and CCl_4 for the samples along with the CCl_4 mixing ratios for the bracketing reference aliquots. The CCl_4 concentration in the reference air was deliberately enhanced in order to facilitate precision comparison of CCl_4 between the external reference

TABLE 1. Precision and Concentration Statistics for Selected Trace Gases for the 109 Samples from 1998 Taipei Collection^a

	compound	1s% (n = 17)	median (pptv)	min. concn (pptv)	max. concn (pptv)	10% percentile (pptv)	90% percentile (pptv)	10%percentile/ 90%percentile
1	CCl ₂ F ₂ (CFC-12)	0.62	721.7	67.7	10826.6	1062.2	566.4	1.9
2	CCl ₃ F(CFC-11)	0.68	304.6	270.0	831.2	374.8	280.4	1.3
3	C ₂ Cl ₃ F ₃ (CFC-113)	1.21	118.1	90.0	141.3	124.7	106.0	1.2
4	CH ₃ CCl ₃	0.87	181.7	100.0	495.4	311.0	117.6	2.6
5	CCl ₄	1.11	104.4	100.0	108.3	106.5	102.4	1.0
6	CHCCl ₃	0.81	447.2	146.3	12850.0	5674.8	177.4	32.0
7	C ₂ Cl ₄	0.65	2776.6	903.8	9418.7	7593.6	1123.3	6.8
8	ethane	0.85	7343.0	3083.5	24278.5	11222.0	3586.5	3.1
9	ethene	0.65	11214.0	1904.0	42672.5	28014.5	3528.5	7.9
10	ethyne	0.58	11605.0	3006.0	44262.0	29458.0	3629.5	8.1
11	propane	0.90	5467.0	1339.5	12939.0	10110.0	2283.0	4.4
12	propene	0.63	3351.0	747.5	12618.5	9225.0	1295.0	7.1
13	isobutane	0.74	255.0	37.7	1084.0	466.4	91.1	5.1
14	<i>trans</i> -2-butene	0.66	464.0	81.0	1614.0	1058.0	159.5	6.6
15	<i>cis</i> -2-butene	0.89	354.0	68.0	1331.5	811.5	126.0	6.4
16	1-butene	0.58	689.0	145.5	2190.0	1762.5	249.5	7.1
17	2, 2-dimethylpropane	1.11	567.0	87.0	3042.0	1601.0	142.0	11.3
18	1,3-butadiene	1.08	554.0	122.0	2423.0	1649.5	193.0	8.5
19	1-pentene	0.60	392.0	142.5	1129.0	783.5	190.0	4.1
20	2-butyne	0.94	134.0	21.5	538.0	342.5	45.5	7.5
21	propyne	1.45	324.0	80.0	1320.0	807.0	128.5	6.3
22	isobutene	1.87	2017.0	433.0	8376.0	6161.5	824.5	7.5
23	2-methyl-1-propene	0.89	200.8	29.1	2942.8	683.0	64.6	10.6
24	butane	0.87	716.6	103.9	3912.6	1322.5	256.9	5.1
25	2-methylbutane	0.65	1337.2	203.2	22662.6	4205.1	406.4	10.3
26	pentane	1.45	117.3	17.5	1628.3	340.4	34.0	10.0
27	2-methylpentane	0.81	446.3	26.1	9883.8	1579.5	108.7	14.5
28	3-methylpentane	0.88	250.2	25.3	5550.2	915.1	64.5	14.2
29	hexane	0.92	4530.0	522.4	8624.5	14046.1	1282.6	11.0
30	methylcyclopentane	1.69	170.1	20.9	3852.4	558.7	39.2	14.3
31	benzene	1.75	597.7	93.5	8525.9	2215.0	179.9	12.3
32	cyclohexane	1.47	66.9	9.3	891.2	175.1	18.6	9.4
33	3-methylhexane	0.85	150.4	23.3	2296.3	420.6	52.6	8.0
34	heptane	1.41	59.7	9.6	1263.4	232.4	17.4	13.4
35	toluene	1.41	2786.7	330.0	42745.0	11786.3	766.6	15.4
36	octane	1.50	363.0	117.6	12382.1	1123.6	178.3	6.3
37	ethylbenzene	3.11	204.2	19.1	1418.8	625.8	46.1	13.6
38	1,3-dimethylbenzene	2.17	417.7	35.8	3960.4	1549.8	105.9	14.6
39	styrene	1.73	201.9	63.5	2236.6	755.2	82.7	9.1
40	propyl benzene	1.46	86.7	12.3	443.4	302.3	18.2	16.6
41	1,2,4-trimethylbenzene	1.87	131.5	35.3	639.1	394.1	44.8	8.8
42	1,3,5-trimethylbenzene	1.58	166.1	30.2	1004.1	557.3	34.1	16.3

^a Precision was assayed by continuous analysis of a reference air ($n = 17$), in which the halocarbon mixing ratios were below 1 ppbv and hydrocarbon mixing ratios were close to the median values of the 109 samples.

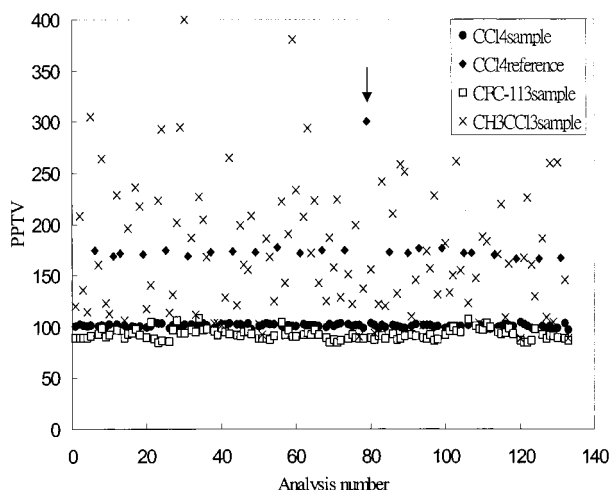


FIGURE 6. Mixing ratios of CFC-113 (solid circles) and CCl₄ (empty boxes) observed in the 109 samples, along with the CCl₄ mixing ratios for the bracketing reference air aliquots (solid diamonds). CH₃CCl₃ mixing ratios (crosses) in the 109 samples are also shown to pose a contrast to CFC-113 and CCl₄. The reference aliquot indicated by the arrow was caused by computer malfunction.

air and the samples. Interestingly, the 24 reference aliquots exhibit a slightly larger deviation than the 109 samples with

1s RSD being 1.8%, despite that all aliquots were all drawn from the same 6-L canister filled from a pressurized cylinder. Closely examining our procedure revealed that the pressure of the reference canister did not remain constant, but depleted as aliquots were repeatedly drawn, and was replenished from a cylinder when its pressure dropped to a low level. This pressure inconsistency affected the precision of the mass flow controller, whereas the initial pressure inside all sample canisters was equivalent to the atmosphere when sampling. The outlier of the reference aliquots in Figure 6 was caused by computer malfunction, and, therefore, the cold-trap was left with a previously trapped sample. The tight distribution of CCl₄ concentrations suggests that the analytical system was very stable and did not exhibit any noticeable systematic errors throughout the 5-day analysis period. Figure 6 also displays the mixing ratios of CFC-113 in the 109 samples. The slightly larger variation with CFC-113 than CCl₄ implies that CCl₄ can more effectively serve as a quality control reference than CFC-113. This very constant CCl₄ observation suggests that CCl₄ could be used as an "intrinsic" internal standard to provide a more direct reference. By doing so, no additional internal standards and fewer external reference runs are then needed. Thus, the CCl₄ concentration can instantaneously validate the analytical quality of a given sample. In fact, few samples from our past collections showed CCl₄ mixing ratios below or above 3

standard deviations from the mean, demonstrating that this quality control concept based on CCl_4 concentration is feasible.

Although the atmospheric burden of CCl_4 is declining at a rate of 0.7pptv/yr (12), the rate is rather slow owing to its long lifetime and minor emissions. As a result, samples collected over a short time period, e.g., days or weeks, can have a nondetectable decline, which makes the use of CCl_4 as an internal reference highly applicable.

In practice, measuring ambient halocarbons including CCl_4 requires the use of an electron capture detector, which is more sensitive to fully halogenated hydrocarbons than other GC detectors, such as the FID, PID, or MS. Applying GC/MS to measure halocarbons along with other ambient VOCs may require trapping significantly more sample air than the amount of air used in our study (300 mL).

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