



Changes in the levels and variability of halocarbons and the compliance with the Montreal Protocol from an urban view



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HIGHLIGHTS

- The variability of 7 halocarbons in Taipei was re-examined after 14 years.
- The reduced variability implies that the emissions have been largely curbed.
- Average concentrations of ODS in Taipei have approximated background levels.

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ABSTRACT

Ambient levels and variability of major atmospheric halocarbons, i.e. CFC-12, CFC-11, CFC-113, CCl₄, CH₂Cl₃, C₂HCl₃, and C₂Cl₄ in a major metropolis (Taipei, Taiwan) were re-investigated after fourteen years by flask sampling in 2012. Our data indicates that the variability expressed as standard deviations (SD) of CFC-113 and CCl₄ remained small (2.0 ppt and 1.9 ppt, respectively) for the 10th–90th percentile range in both sampling periods; whereas the variability of CFC-12, CFC-11, C₂HCl₃, and C₂Cl₄ measured in 2012 became noticeably smaller than observed in 1998, suggesting their emissions were reduced over time. By comparing with the background data of a global network (NOAA/ESRL/GMD baseline observatories), the ambient levels and distribution of these major halocarbons in Taipei approximated those at a background site (Mauna Loa) in 2012, suggesting that the fingerprint of the major halocarbons in a used-to-be prominent source area has gradually approached to that of the background atmosphere.

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1. Introduction

Chlorofluorocarbons (CFCs) have been released from Earth's surface over the past several decades, resulting in ozone depletion due to their long atmospheric lifetimes and potent catalytic properties in the stratosphere (Molina and Rowland, 1974; Carpenter et al., 2014). These entirely man-made species also strongly absorb long-wavelength infrared radiation emitted from Earth's surface and by the atmosphere, allowing them to become the third largest

contributor among long-lived greenhouse gases to the radiative forcing of the global climate next to carbon dioxide and methane (Ramanathan, 1975; Wuebbles et al., 1999; IPCC, 2013; Butler and Montzka, 2015). After implementation of the 1987 Montreal Protocol and its subsequent amendments (UNEP, 1987, 1992), production of these ozone-depleting substances (ODS) was largely restricted or phased out in most developed (non-A5) and developing (A5) nations. As a result of a significant reduction in emissions on the global scale, the tropospheric concentrations of CFCs and some other synthetic halocarbons, such as methyl chloroform (CH₃CCl₃) and carbon tetrachloride (CCl₄), no longer increase and all have declined for at least a decade, as reported by long-term background monitoring networks (Prinn et al., 2005; Rigby et al., 2013; Carpenter et al., 2014). Their inter-hemisphere gradients also

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shrank drastically (Prinn et al., 2000). Furthermore, the radiative forcing from CFCs showed a negative trend since 1990–2000s (IPCC, 2013; Rigby et al., 2014). Other halocarbons such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), which are considered to be low-ozone-depleting-potential or as ozone-safe substitutes, gradually replaced CFCs in the application demands for refrigeration, air-conditioning, aerosol propulsion, and thermal-insulating foam production. Though the threats of ozone depletion are diminishing, the net forcing of halocarbons and related compounds still remains positive and is increasing due to the steeply increasing concentrations of the CFC replacements (HCFCs and HFCs) and other fully fluorinated halogens (e.g. PFCs, SF₆, and NF₃) in the post-Montreal Protocol era (Weiss et al., 2008; Rigby et al., 2010, 2014; Daniel et al., 2011; Li et al., 2011; Laube et al., 2012; IPCC, 2013).

Even though attention has shifted to the CFC-replacements in the last decade, the remaining atmospheric CFC abundance, which was responsible for about 76% of synthetic halocarbon radiative forcing in 2012 (Rigby et al., 2014), still outweighs the combined replacements. Moreover, despite background monitoring showing various degrees of decline for the Montreal Protocol-restricted halocarbons, the decline rates are still important from the perspectives of ozone layer recovery and the radiative forcing produced by the ODS (Weatherhead and Andersen, 2006; IPCC, 2013). As a result, it is always useful to periodically scrutinize CFC emissions to affirm the effectiveness of the regulatory phase-out policies.

Taiwan is not party to the Montreal Protocol, but has voluntarily strived to comply with the control measures set to the non-A5 countries since the mandate was ratified (Tsai, 2006). In addition to stringent domestic regulations to phase out ODS, field measurements have also been conducted to provide feedback to the regulatory agency for effectiveness assessment. For instance, both random and on-site measurements in urban or industrial areas were used to assess the effectiveness of the abatement of CFC emissions (Wang et al., 2000; Chang et al., 2001; Zhang et al., 2010, 2014). Li et al. (2011) utilized interspecies correlation to suggest the successful phase-out of CFCs and their growing replacement with HCFCs and HFCs in Taiwan based on in-situ measurements during the period 2007–2008. On site in-situ measurements conducted in Taipei in 2005 also suggested minimal emissions of CFC-12, CFC-11, and CFC-113 (Chang et al., 2008). While the on-site in-situ measurements are a useful means to examine emissions manifested as “noise” or variability in concentrations, the concentration variability revealed from the random sampling over large populated source areas can further complement the in-situ data in divulging spatial emission conditions (Hurst et al., 1998; Wang et al., 1998; Chen et al., 1999). As a result, Taipei, the largest and the most economically viable metropolitan area in Taiwan, served as the test ground for re-assessment of the variability of these primary CFCs in 2012. The analytical technique and sampling approach were kept as similar as possible to the first inspection of this kind conducted in 1998, 14 years ago, in order to minimize bias. By comparing the variability of the change in the concentrations, the overall emission status for the compliance with the Montreal Protocol for the major ODS over time can be better understood.

2. Experimental

Two sample collections were conducted in August 1998 and February 2012 in Taipei. Fig. 1 illustrates the sampling sites in the Taipei basin. To avoid over-influence from nearby point sources, sampling was carried out in open fields such as parks and schoolyards, and was as evenly and randomly distributed as possible. The sampling locations, time of day, and the analytical

methods in 1998 and 2012 were almost identical. Spatial distributions of the seven target halocarbons (CFC-12, CFC-11, CFC-113, CCl₄, CH₃CCl₃, C₂HCl₃, and C₂Cl₄) in the metropolis were then interpolated or extrapolated from the randomly distributed sampling sites. Two time periods (i.e., 5:00–6:15 A.M. and 5:45–7:00 P.M.) were chosen to pose a contrast, with the early morning as a city baseline when traffic, business, and domestic activities were minimal, and the evening hours when conditions were busy and brisk. The sampling days in 1998 and 2012 were deliberately selected for calm weather with low wind speeds less than 1 ms⁻¹, which is in favor of registering any release from nearby point sources during sampling and can minimize seasonal disturbance arising from the synoptic weather conditions. Air samples were collected in 2-L stainless steel canisters purchased from University of California, Irvine (UCI) (Blake et al., 1992).

2.1. 1998 collection

In the 1998 study, 56 and 53 samples were collected between 5:45 and 6:15 A.M. and between 5:45 and 6:15 P.M., respectively. The ambient temperatures were 24.6–26.9 °C and 28.7–31.3 °C during the morning and evening sampling period, respectively. Air samples were analyzed by a gas chromatograph equipped with electron capture detection (GC/ECD, Varian 3400 CX). A PC-controlled automated valve system with an online cryo-trap was built to enrich the target halocarbons. A 300 mL aliquot of air was drawn consistently from the canister to the system for sample preconcentration, which was performed by a cryo-trap made of a piece of stainless steel tubing (1/8 in. × 10 cm) packed with glass beads. During cryo-trapping, the trap was cooled by purging liquid nitrogen (LN₂) to the setpoint of –170 °C into the trap housing. During injection, the stainless steel trap was short-circuited by a high electrical DC current (30 A; 4 V) for thermal desorption of the analytes into GC. A DB-1 column (J&W Scientific, 60 m × 0.32 mm × 1.0 μm) was used for separation. The reproducibility of this system was evaluated with a replicate precision of about 1–2% for the seven halocarbons. Details of this automated system can be found in literature (Wang et al., 1999). Pressurized air (~700 kPa) filled in a 30-L Aculife-treated cylinder (Scott Specialty Gases, San Bernardino, CA) was used as the reference mixture, with its absolute calibration scales for the target gases aligned to those used in UCI (Wang et al., 1995).

2.2. 2012 collection

In the 2012 study, 52 and 53 samples were collected between 5:00 and 6:00 A.M. and between 6:00 and 7:00 P.M., respectively. The ambient temperatures were 18.0–21.5 °C and 20.0–23.8 °C during the morning and evening sampling period, respectively. Canister air samples were analyzed by an automated GC–MS system (3800-GC and Saturn 2200-MS, Varian), which is a laboratory version of the one described in our previous study (Wang et al., 2012). The pre-concentration and chromatographic techniques for enriching and separating the halocarbons were similar to those applied in the 1998 study. The GC oven was cooled with LN₂ and maintained at –15 °C for 1 min initially, ramped to 0 °C at 7.5 °C min⁻¹, ramped to 140 °C at 5 °C min⁻¹, ramped to 180 °C at 20 °C min⁻¹, and finally maintained at 180 °C for a further 15 min. Internal standards were blended with each sample aliquot to back-correct the analytical drift to safeguard stability. Precision was assessed to be less than 1.5% for the seven target halocarbons. Calibration of C₂HCl₃ was made with a commercial standard (Linde SPECTRA Environmental Gases, USA), which exhibited a difference within 10% from the UCI standard. A tertiary standard purchased from National Oceanic and Atmospheric Administration/Earth System Research Laboratory/Global Monitoring Division

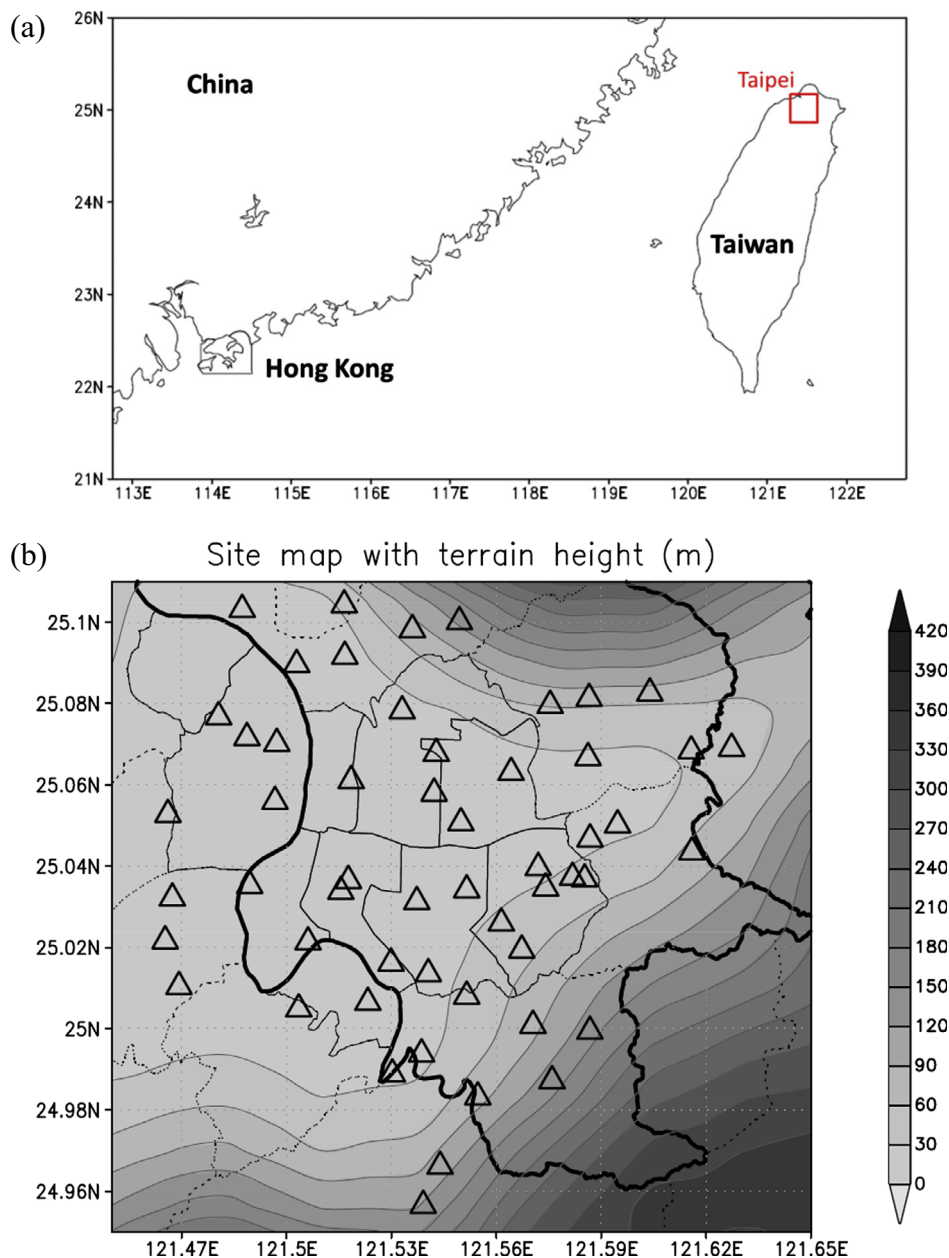


Fig. 1. (a) Geographic location of the Taipei metropolis and (b) locations of respective sampling sites with terrain height.

(NOAA/ESRL/GMD) in 2010 was employed for the calibration of the rest six halocarbons in the 2012 collection. This scale was inter-compared with that used by UCI, and the halocarbons showed good agreements within $\pm 4\%$ except for C_2Cl_4 (Hall et al., 2014).

3. Results and discussion

The sampling and analytical variables were deliberately kept as similar as possible to reveal changes in the emission status between the two collections 14 years apart. Thus, morning (5:00–6:15 A.M.) and evening (5:45–7:00 P.M.) samples were collected consistently at the same sites within a day for both collections, the degree of data scattering for the seven ODS between the two collections periods was then examined and compared (box whisker plots in Fig. 2; statistics in Table 1). Seven halocarbons, i.e., CFC-12, CFC-11, CFC-113, CCl_4 , CH_3CCl_3 , C_2HCl_3 , and

C_2Cl_4 , are discussed as follows using concentration variability to determine their emission status and their overall compliance with the Montreal Protocol. The seven major halocarbons subject to the phase-out implemented since 1996 are categorized by their applications and discussed in the following sections.

3.1. CFC-113 and CCl_4

Trichlorotrifluoroethane (CFC-113) was conventionally used as a deflux solvent in the electronic industry. Carbon tetrachloride (CCl_4) was primarily used as a chemical intermediate to produce CFCs, particularly for CFC-12 and CFC-11. These two compounds are rarely seen in household applications. In our previous study, there was minimal variability in CFC-113 and CCl_4 compared with other studied ODS from the samples collected either in Taipei or in potential source areas, i.e., a high-tech, electronic industrial park, reflecting the overall success of the phase-out of these two ODS

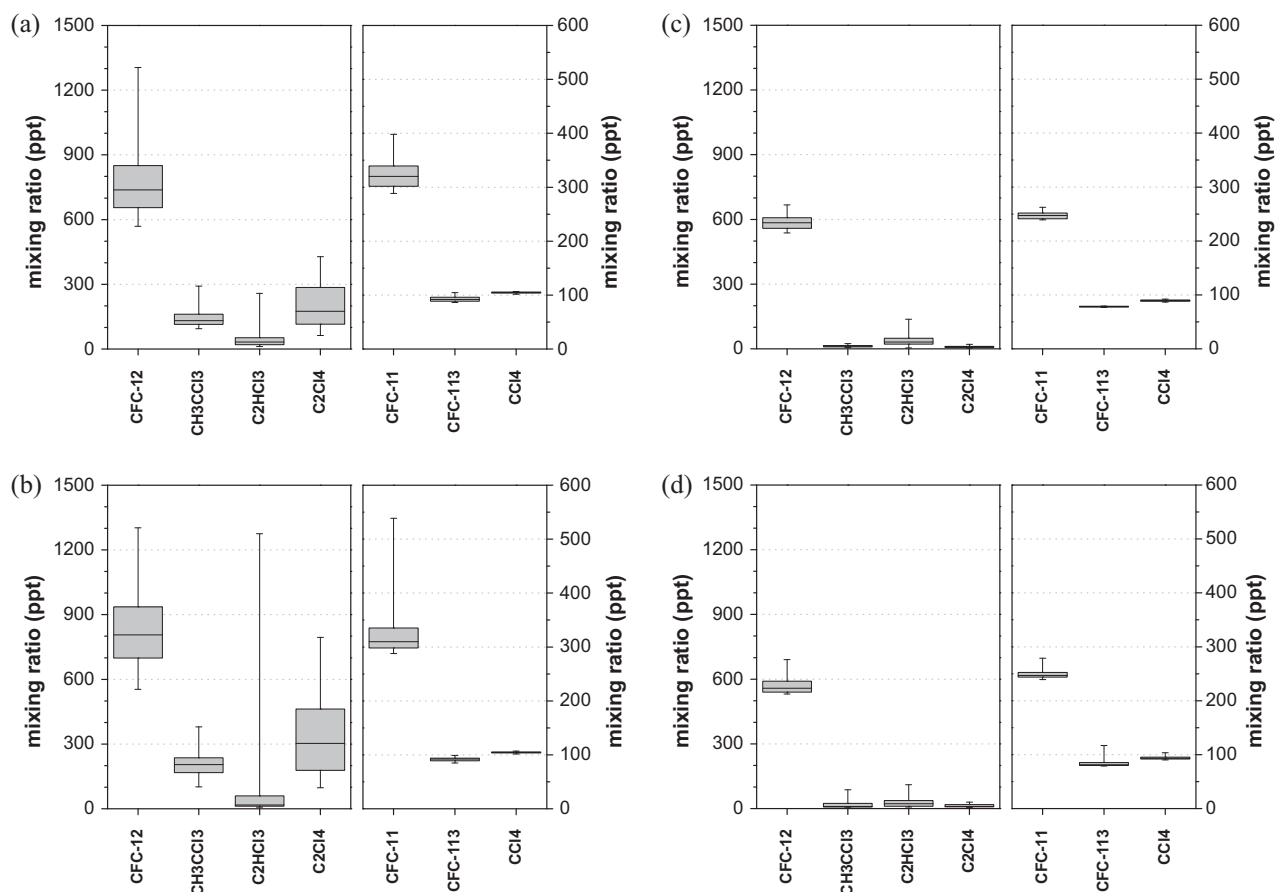


Fig. 2. Concentration distribution of the seven halocarbons for (a) 56 samples collected between 5:45 and 6:15 A.M., (b) 53 samples collected between 5:45 and 6:15 P.M. in the 1998 collection, (c) 52 samples collected between 5:00 and 6:00 A.M., and (d) 53 samples collected between 6:00 and 7:00 P.M. in the 2012 collection. Whiskers define the outlying 5% of the data. The box represents 25–75% of the data. The median or the 50th percentile is the line within the box.

Table 1

Statistics for the seven halocarbons from Taipei collections made in 1998 August and 2012 February, respectively.

Compound	Atmospheric lifetime	Analytical Precision (RSD, %)	1998 August (N = 109)						2012 February (N = 105)					
			Overall				10th–90th		Overall				10th–90th	
			Min (ppt)	Max (ppt)	Mean (ppt)	1 σ SD (ppt)	Mean (ppt)	1 σ SD (ppt)	Min (ppt)	Max (ppt)	Mean (ppt)	1 σ SD (ppt)	Mean (ppt)	1 σ SD (ppt)
CFC-12	100 years ^a	1.0	538.0	11201.9	975.1	1272.8	780.5	120.0	524.0	1211.2	588.0	77.7	576.0	30.2
CFC-11	45 years ^a	1.2	278.5	836.6	334.0	71.4	319.0	20.1	238.7	285.5	249.3	9.6	247.7	4.9
CFC-113	85 years ^a	1.5	84.7	107.8	92.6	4.9	92.1	3.0	75.8	136.1	82.2	9.5	79.8	2.0
CCl ₄	26 years ^a	0.7	100.0	108.3	104.4	1.5	104.5	1.0	86.3	104.4	91.8	3.6	91.4	1.9
CH ₃ CCl ₃	5 years ^a	1.0	88.6	442.6	179.5	71.7	169.3	44.4	5.6	125.4	18.0	20.1	12.8	5.7
C ₂ HCl ₃	4–7 days ^b	0.8	5.8	19712.4	286.5	1893.0	39.9	40.6	2.1	1533.8	54.3	157.5	29.4	15.5
C ₂ Cl ₄	3–4 months ^b	0.9	62.4	2335.6	303.4	317.5	241.8	110.4	3.2	295.2	14.3	28.6	10.6	4.2

^a IPCC (2013).

^b Simmonds et al. (2006).

only a few years after the complete phase-out was put to action in 1996. Such a finding suggests that the solvent-type ODS had been replaced successfully (Wang et al., 2000). However, the need for a confirmation of whether such a “quiet” condition can be maintained or was just a coincidental phenomenon motivated the 2012 sampling. As shown in Table 1, CFC-113 and CCl₄ exhibited the smallest deviation of concentration among all the target halocarbons in the 1998 collection. The 1 σ standard deviations (SD) for CFC-113 and CCl₄ in 2012 were estimated to be 2.0 ppt and 1.9 ppt, respectively, which approximate the SD of 1998 (3.0 ppt and 1.0 ppt, respectively) for the 10th–90th percentile range based on

over 100 samples for each collection period. Minimal variability was also found for both the morning and evening data of CFC-113 and CCl₄ for the 1998 and 2012 collections as illustrated in Fig. 2. As a result, the recent 2012 collection re-confirmed the findings of 1998 that the emissions of these two compounds have been successfully phased out. Consumption records of CFCs show zero demand for CFCs including CFC-113 and CCl₄ since 1996 (see Supplementary Materials). Moreover, since CCl₄ is both an ODS and a hazardous chemical (a confirmed carcinogen), the import and usage of this compound is subject to the most stringent regulations of all chemicals on the island (Taiwan EPA, 2013). As a

result, our findings of small variability for both CFC-113 and CCl_4 appear to be in agreement with the trading records.

3.2. CFC-12 and CFC-11

CFC-12 and CFC-11 are the most abundant halocarbons in the atmosphere, contributing approximately 55% to the total chlorine from long-lived gases in the troposphere (Carpenter et al., 2014). Until now the two compounds also exerted the largest radiative forcing among all halocarbons due to their prominent atmospheric burden, which was estimated to be 7.6% of all well-mixed greenhouse gases based on the NOAA Annual Greenhouse Gas Index in 2014 (Butler and Montzka, 2015). CFC-12 and CFC-11 are commonly released from applications such as aerosol spray, foam blowing, and refrigeration (McCulloch et al., 2001, 2003). As shown in Table 1, the variability of CFC-11 concentrations has reduced considerably compared to the variability observed 14 years earlier. This reveals a SD of 4.9 ppt (relative standard deviation (RSD) = 2.0%) for the 10th–90th percentile range, which is only slightly greater than its analytical precision of 1.2%. The reduced variability was also observed for CFC-12 (Table 1), which was the main refrigerant used in the air conditioners of older vehicles (manufactured or imported before mid-1994 in Taiwan). The rapid

decline in variability for CFC-12 suggests that the number of these refrigeration units diminished considerably during the period 1998–2012. Nowadays modern cars use HFC-134a as the refrigerant (McCulloch et al., 2003), which is the most abundant HFC in the background atmosphere with an estimated concentration of 67.5 ppt in 2012 (Montzka et al., 2015). Nevertheless, CFC-12 is still the single most abundant ODS in the atmosphere (Carpenter et al., 2014). The vehicle registration records show that cars made before 1995 accounted for about 62% of vehicles in 1998, the year when our first collection was conducted. This percentage dropped to only 12% in 2012 (Taiwan Ministry of Transportation and Communications, 2014). The dramatically reduced yet substantial number of old vehicles remaining on the streets even in 2012 may explain the relatively larger data spread for CFC-12 compared to the data spread of CFC-11, CFC-113 and CCl_4 in the 2012 collection.

Because one of the major applications of CFC-12 and CFC-11 is refrigeration, it is expected that the old refrigeration units using these two compounds may cause more release in summer (Lee and Chiou, 2007). To verify the assertion, a summer dataset obtained in 2013 comprising 38 locations in Taipei was employed (Chang et al., 2014). The results revealed the variability of CFC-12 and CFC-11 expressed as SD to be 7.3 ppt and 4.1 ppt, respectively,

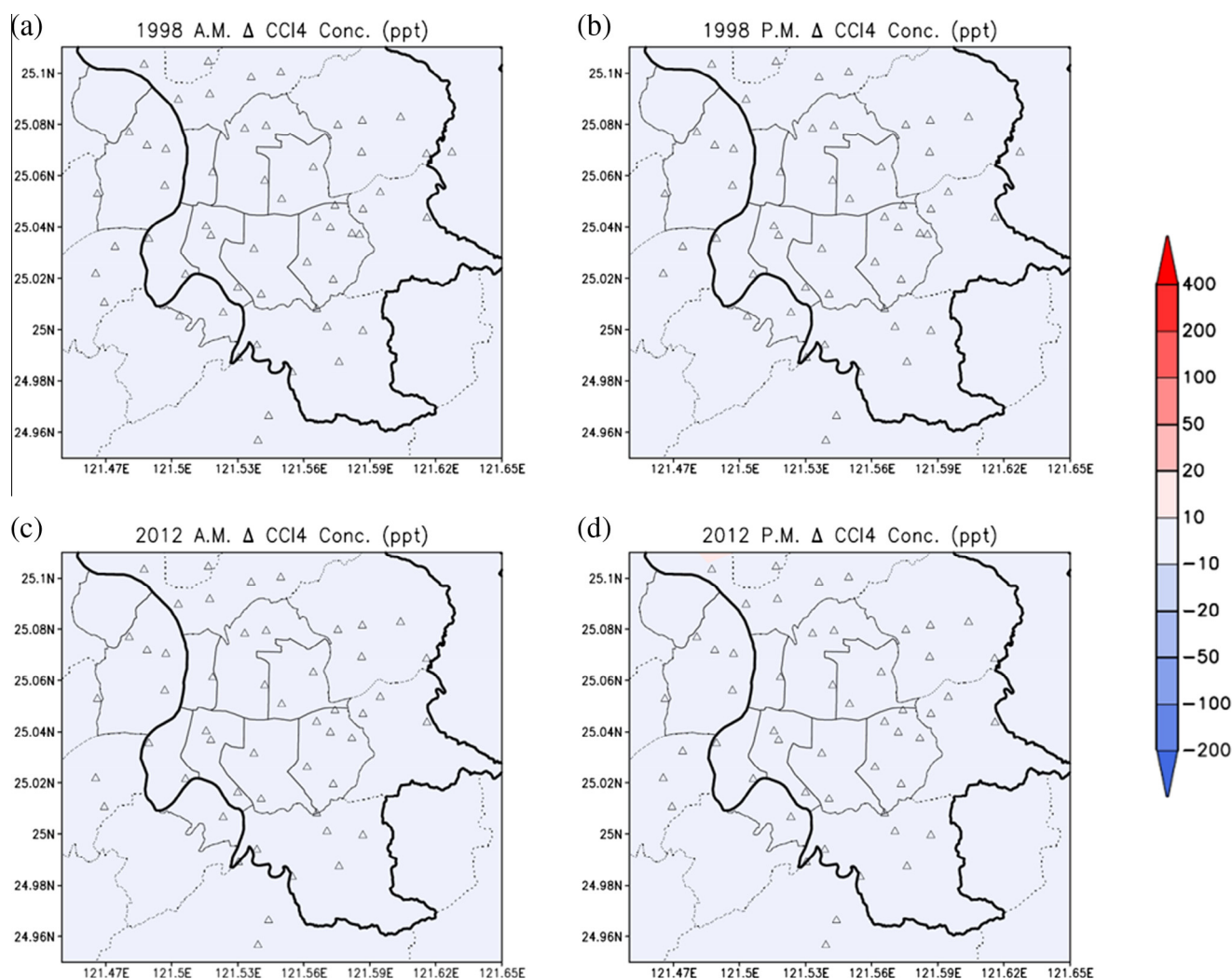


Fig. 3. Contour plots of ΔCCl_4 from samples collected in Taipei. The Δ represents the difference between an air sample and the median value calculated from all samples within the 10th–90th percentile range of each collection. Same definition applies to Fig. 4. The medians of CCl_4 concentrations are 104.4 ppt, 104.4 ppt, 89.6 ppt, and 93.3 ppt for (a) morning and (b) evening in 1998, and (c) morning and (d) evening in 2012, respectively.

for the 10th–90th percentile range, which were even lower than the SD observed in winter 2012 (Table 1), suggesting that the seasonal variation in emissions for the two most susceptible compounds has become quite small due to dramatically reduced emissions.

The availability of CFC-12 in the market supplied from smuggling may have contributed to the slower-than-expected process for car owners to give up their old cars. Customs records show that seized smuggled CFC-12 is often the largest in percentage among various seized ODS, accounting for 63% of the total seized ODP tonnage, followed by Halons (23%) and CFC-11 (9%) (Taiwan EPA, 2009). For instance, the seized CFC-12 amounted to approximately 30 metric tons on the island in 2010 (see Supplementary Materials). Smuggling of CCl_4 and CFC-113 were also found but in much smaller quantities. In addition, there were approximately 4 metric tons of CFCs annually used in manufacturing metered-dose inhalers in Taiwan, which were classified as an essential use and could be exempted from the Montreal Protocol no later than 2010. It is speculated that older vehicles tend to leak more refrigerant than newer ones and that remaining old vehicles with leaky air conditioners at tropical latitudes can easily access illegal CFC-12. These two processes, if occurring, would be counter-forces to the decline of atmospheric CFC-12.

Both the SD of CFC-12 and CFC-11 measured in 2012 (overall and 10th–90th in Table 1) were consistently smaller than those in 1998, implying emissions diminished considerably over time.

3.3. CH_3CCl_3 , C_2HCl_3 , and C_2Cl_4

As shown in Table 1, in contrast to the long-lived CFCs mentioned above, our field collections in Taipei showed that the mean concentrations of the shorter-lived halocarbons, i.e., methylchloroform (CH_3CCl_3) and tri- and tetrachloroethene (C_2HCl_3 and C_2Cl_4), had drastically decreased to less than one fifth of what they were 14 years earlier (Wang et al., 2000). CH_3CCl_3 is the fastest declining compound of the target ODS due to both the phase-out and its relative short lifetime of about 5 years (Carpenter et al., 2014). In Table 1, the mean concentration of CH_3CCl_3 dropped drastically from 179.5 ppt in 1998 to 18.0 ppt in 2012. The variability (SD) of CH_3CCl_3 also decreased noticeably from 44.4 ppt to 5.7 ppt for the 10th–90th percentile range in the 14 years. The three compounds, CH_3CCl_3 , C_2HCl_3 , and C_2Cl_4 , are predominately used as a metal degreaser (e.g., CH_3CCl_3) and/or dry cleaning fluid (e.g., C_2Cl_4) in industrial applications. Note that a small quantity of C_2Cl_4 emission was found in flue gas with estimated emissions of about 19 Gg yr^{-1} released from coal-fired power plants into the

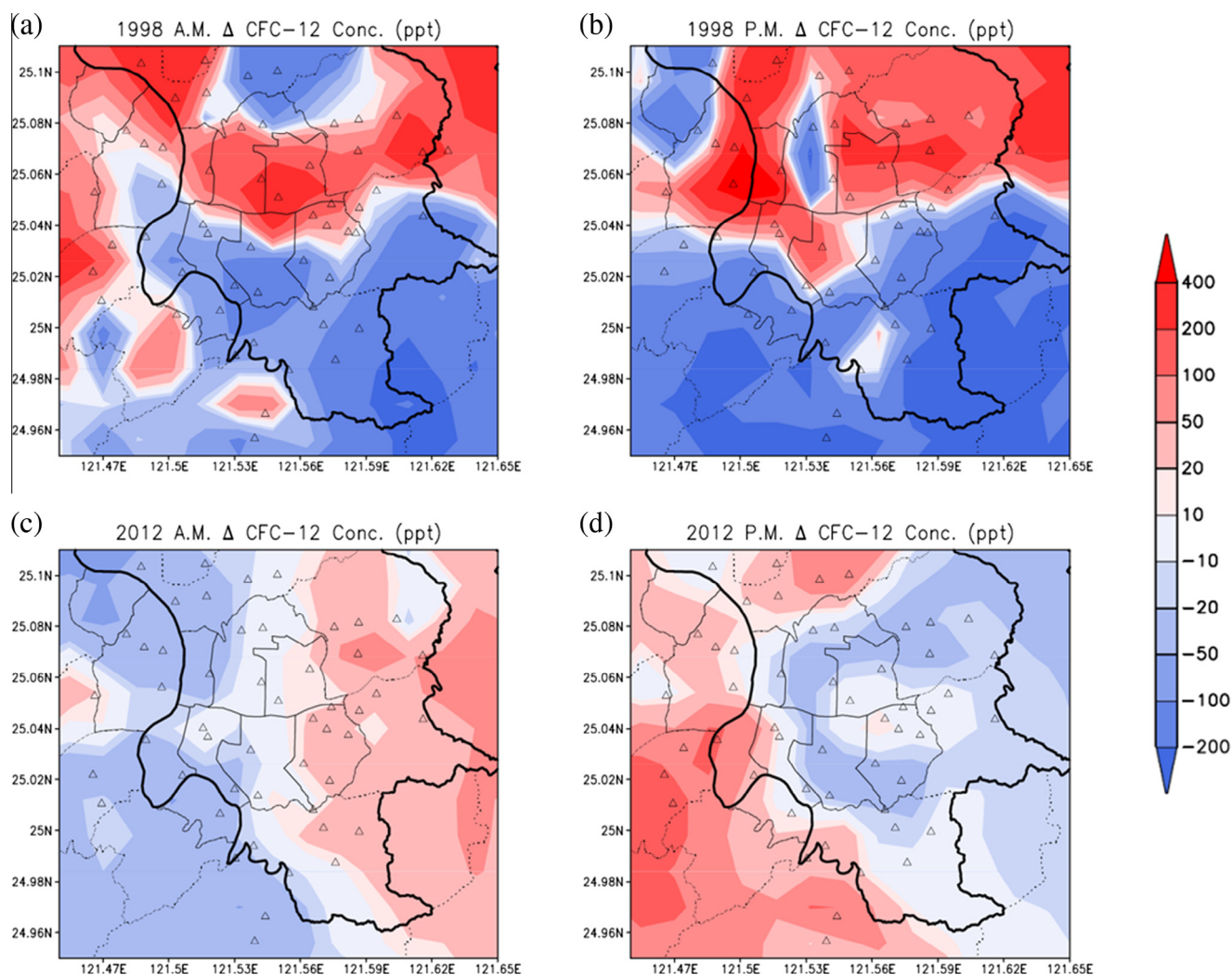


Fig. 4. Contour plots of $\Delta\text{CFC-12}$. The medians are 737.2 ppt, 806.2 ppt, 584.1 ppt and 557.7 ppt for (a) morning and (b) evening in 1998, and (c) morning and (d) evening in 2012, respectively.

atmosphere (McCulloch et al., 1999). Only a negligible amount ($<0.014 \text{ Gg yr}^{-1}$) of global natural emissions of CH_3CCl_3 released from biomass burning was suggested (Simpson et al., 2007). C_2HCl_3 and C_2Cl_4 have natural sources from seawater algae and microbial activities in the oceans or salt lakes (Abrahamsson et al., 1995; Weissflog et al., 2005). However, these natural sources are not expected to be significant compared to their anthropogenic counterparts. Because of their relatively high reactivity with OH radicals (lifetimes of 4–7 days for C_2HCl_3 and 3–4 months for C_2Cl_4), both C_2HCl_3 and C_2Cl_4 exhibit distinct seasonal cycles with pronounced inter-hemispheric gradients (Simmonds et al., 2006; Montzka et al., 2011). Though C_2HCl_3 and C_2Cl_4 are not controlled ODS, their background levels have drastically declined due to reduction in usage (Simmonds et al., 2006). In our Taipei collections, they also showed substantial declines in both absolute concentrations and variability over 14 years (Table 1). Unlike CH_3CCl_3 , C_2HCl_3 , and C_2Cl_4 , they are not controlled by the Montreal Protocol, but by the reduction acts in the USA, EU, and many other countries that identify them as probable carcinogens (IARC, 1995). Listed as one of the class 1 and 2 toxic substances by the Taiwan government (Taiwan EPA, 2013), these two compounds decreased in usage on the island at very rapid rates (see Supplementary Materials).

3.4. Spatial distributions of selected halocarbons in the Taipei basin

Random sampling with sufficient spatial coverage over a heavily populated area can provide an unbiased and effective detection of the emissions for the target species. Since more than 50 samples were collected within a 30 min time period for both the morning and evening collections, a “snap-shot” effect was deliberately created by making contour plots from interpolation and extrapolation of 50 more samples. “Hot spots” or the spatial inhomogeneity can then be easily detected from these snap-shots (Figs. 3 and 4). For instance, the homogeneity of CCl_4 concentrations appears to remain unchanged over 14 years, as illustrated in Fig. 3. In comparison, the spatial inhomogeneity of CFC-12 can be easily seen in Fig. 4. However, the concentrations of CFC-12 became more evenly distributed and therefore more spatially homogeneous in 2012 compared to the results of 1998. Similar results can also be found for other halocarbons; however, due to space limitations, their contour plots are shown in Supplementary Materials. In general, shorter-lived halocarbons such as CH_3CCl_3 , C_2HCl_3 , and C_2Cl_4 (see Supplementary Materials) displayed considerably more pronounced spatial inhomogeneity than the other fully halogenated compounds for the 1998 results. However, such inhomogeneity has greatly diminished into a more homogeneous condition 14 years later.

3.5. Comparison with background data at Mauna Loa

In theory, the reduced variability or the increased homogeneity over time for the aforementioned ODS caused by the decreased emissions should make their ambient levels gradually coincide with the background levels. For this purpose, a section (4–5 days) of the NOAA/ESRL/GMD in-situ data of CFC-12, CFC-11, CCl_4 , and CH_3CCl_3 at Mauna Loa (MLO) (19.54°N , 155.58°W ; 3397 m a.s.l.) around our sampling times was exploited to serve as the background reference (Elkins et al., 1993). For CFC-113 and C_2Cl_4 , their monthly averages from air samples collected at MLO in the same month of our sampling times were also used as the reference (Montzka et al., 1996). This remote site was chosen because its latitude approximates Taipei's in the Northern Hemisphere. In fact, which Northern Hemisphere site we choose is largely irrelevant since the background levels for nearly all ODS have converged in recent years as emissions have decreased (Rigby et al., 2013).

Aligning the urban measurements with background observations is another way of viewing the existence of emissions. As an illustration, all the Taipei data were compared with 4–5 days of in-situ data from MLO for CFC-12 and CCl_4 arranged in a sequence increasing from low-to-high (Fig. 5). The MLO data in 1998 and 2012 served as the true background levels at the time of observations, which showed negligible variability ($\text{SD} < 2.0 \text{ ppt}$ and $< 0.4 \text{ ppt}$ for CFC-12 and CCl_4 , respectively). By contrast, the Taipei data of CFC-12 showed a rather large gradient in both sampling periods, reiterating that emissions were relatively pronounced. Nevertheless, despite the large difference in the gradient between the two Taipei datasets, the lowest 1–2 data points of each Taipei dataset were found to be nearly identical to the MLO levels within the analytical precision ($< 2\%$), suggesting that these minimum data points are no different from the background air from the CFC-12 concentration perspective (Fig. 5a). The highest concentrations of CFC-12 were generally found in more prosperous areas with higher likelihood of CFC-12 leakage from older vehicles; whereas the minimum concentrations were mostly found in less congested areas. In contrast to CFC-12, the Taipei CCl_4 data resembled the MLO data, except that the 2012 data exhibited a slightly larger gradient than that of 1998, possibly due to residual emissions from a landfill site, since 8 samples collected near the site showed unusually high concentrations of CCl_4 ($\geq 98.05 \text{ ppt}$) (Fig. 5b). Again, the lowest data points coincided with the MLO data to mark the background levels of CCl_4 at the time of sampling.

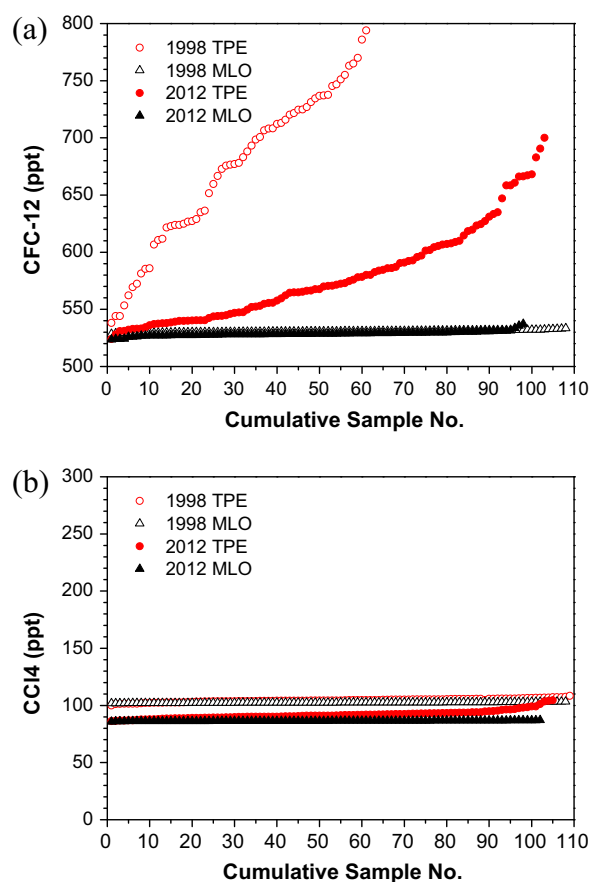


Fig. 5. (a) CFC-12 and (b) CCl_4 concentrations in an increasing order from the 1998 and 2012 Taipei (TPE) collections in comparison with the background measurements at Mauna Loa (MLO) from the NOAA/ESRL/GMD network. Approximately 4–5 days of MLO continuous data ($N \approx 100$) are used for comparison.

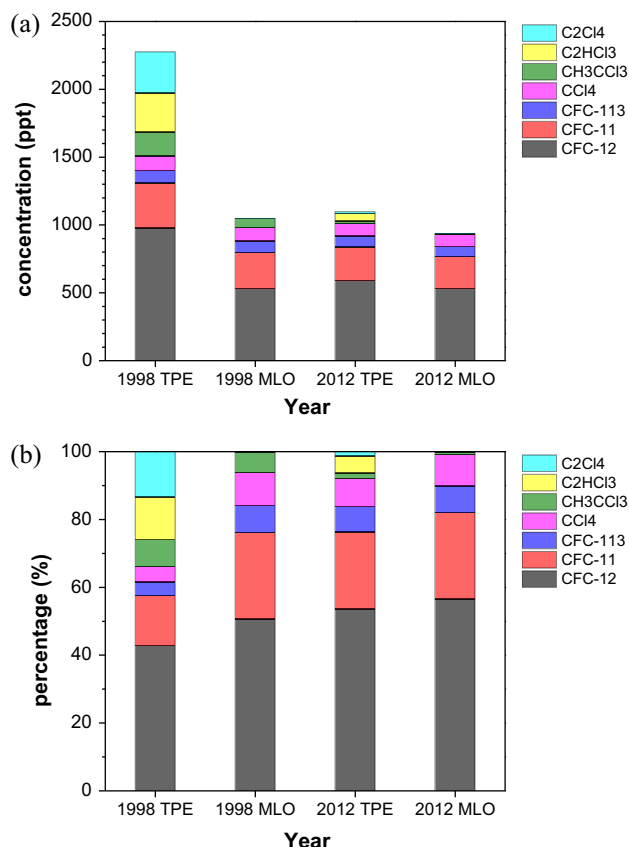


Fig. 6. (a) Cumulative concentrations and (b) percent contributions of the mean values for the seven halocarbons in the 1998 and 2012 Taipei (TPE) collections compared with those of the measurements at Mauna Loa (MLO). CFC-12, CFC-11, CCl₄, and CH₃CCl₃ are the hourly data using a GC-ECD at MLO, whereas CFC-113 and C₂Cl₄ are the flask air sampling data analyzed by GC-MS. No measurements of C₂HCl₃ are available from MLO during these periods. The data at MLO are the same as those in Fig. 5.

Fig. 6 illustrates the cumulative concentrations and percentage distributions of the seven halocarbons in Taipei and MLO using their mean values. Note that the CFC-113 and C₂Cl₄ data are the results of flask air samples collected at MLO and analyzed by NOAA/ESRL/GMD using GC-MS in the same month of our experiments in Taipei (Montzka et al., 1996, 2011). However, no measurements of C₂HCl₃ are available from MLO during these periods. Despite these analytical issues, the fraction of C₂HCl₃ and C₂Cl₄ is small (<2%) compared to the total amount of halocarbons in the background atmosphere. The concentrations of C₂HCl₃ and C₂Cl₄ in the Northern Hemisphere were estimated to be 1–5 ppt and 5–15 ppt, respectively (Ko et al., 2003). Simmonds et al. (2006) also reported average concentrations of 1.2 ppt for C₂HCl₃ and 4.94 ppt for C₂Cl₄ observed at Mace Head in 2004, with no distinct trend for C₂HCl₃ and a small decline in C₂Cl₄ at a rate of -0.18 ± 0.05 ppt yr⁻¹ from 1995 to 2004. A recent update by Montzka et al. (2011) reported the mean level of about 1.7–3.0 ppt for C₂Cl₄ in the Northern Hemisphere in 2008. As shown in Fig. 6a, the mean concentrations of the primary ODS in Taipei have approximated those at MLO after 14 years.

With regard to the concentration of the halocarbons, the most short-lived halocarbons of the seven, CH₃CCl₃ and C₂Cl₄, decreased the most over 14 years, by 81% and 95%, respectively. CFC-12 and CFC-11 remained the largest contributors to the atmospheric halocarbons, as the sums of CFC-12 and CFC-11 amounted to about 58% and 76% of the total halocarbon concentrations measured in Taipei in 1998 and 2012, respectively (Fig. 6b). In addition, the

contributions of the primary ODS in Taipei approximated that at MLO in 2012, implying that the fingerprint of the ODS in the urban air of Taiwan has gradually approached to that of the background atmosphere.

4. Conclusions

In this study, seven major halocarbons in the Taipei metropolitan area showed various degrees of decline in both their concentrations and variability when comparing the measurements of 1998 with those of 2012. We found that CFC-113 and CCl₄ showed small spatial variability in both 1998 and 2012, whereas the variability of other halocarbons considerably decreased in the 14 years. Through comparison of the decreased variability, the concentrations approached background levels measured at MLO. The fingerprint of atmospheric halocarbons in the Taipei area, which used to be markedly different from that of the background atmosphere in 1998, became quite similar in 2012. Our findings of the fingerprint of the ODS gradually approaching that of the background atmosphere in a major metropolitan area with a quarter of the nationwide population provide strong indication to suggest that the country has successfully phased out major ODS and also dramatically reduced the use of hazardous halocarbons of C₂HCl₃ and C₂Cl₄.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.06.070>.

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