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A quantitative assessment of distributions and sources of tropospheric halocarbons measured in Singapore

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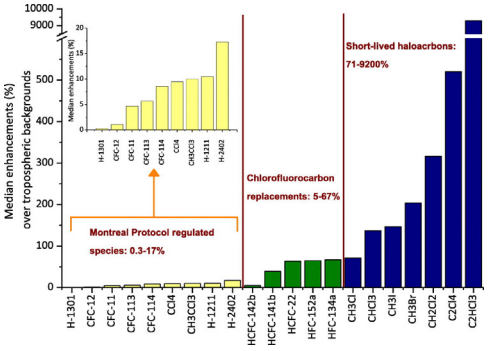
HIGHLIGHTS

- First ground-based atmospheric measurements of 26 halocarbons in Southeast Asia
- Montreal Protocol regulated species are close to global backgrounds.
- Chlorofluorocarbon replacements show significant enhancements above baseline.
- Transported peat-forest burning smoke affects selected short-lived halocarbons.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reports the first ground-based atmospheric measurements of 26 halocarbons in Singapore, an urban-industrial city-state in Southeast (SE) Asia. A total of 166 whole air canister samples collected during two intensive 7 Southeast Asian Studies (7SEAS) campaigns (August–October 2011 and 2012) were analyzed for C_1-C_2 halocarbons using gas chromatography-electron capture/mass spectrometric detection. The halocarbon dataset was supplemented with measurements of selected non-methane hydrocarbons (NMHCs), C_1-C_5 alkyl nitrates, sulfur gases and carbon monoxide to better understand sources and atmospheric processes. The median observed atmospheric mixing ratios of CFCs, halons, CCl_4 and CH_3CCl_3 were close to global tropospheric background levels, with enhancements in the 1–17% range. This provided the first measurement evidence from SE Asia of the effectiveness of Montreal Protocol and related national-scale regulations instituted in the 1990s to phase-out ozone depleting substances (ODS). First- and second-generation CFC replacements (HCFCs and HFCs) dominated the atmospheric halocarbon burden with HFC-134a, HCFC-22 and HCFC-141b exhibiting enhancements of 39–67%. By combining near-source measurements in Indonesia with receptor data in Singapore, regionally transported peat-forest burning smoke was found to impact levels of several NMHCs (ethane, ethyne, benzene, and propane) and short-lived halocarbons (CH_3I, CH_3Cl, and CH_3Br) in a subset of the receptor samples. The strong signatures of these species near peat-forest fires were potentially affected by atmospheric dilution/mixing during transport

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and by mixing with substantial urban/regional backgrounds at the receptor. Quantitative source apportionment was carried out using positive matrix factorization (PMF), which identified industrial emissions related to refrigeration, foam blowing, and solvent use in chemical, pharmaceutical and electronics industries as the major source of halocarbons (34%) in Singapore. This was followed by marine and terrestrial biogenic activity (28%), residual levels of ODS from pre-Montreal Protocol operations (16%), seasonal incidences of peat-forest smoke (13%), and fumigation related to quarantine and pre-shipment (QPS) applications (7%).

1. Introduction

Chlorofluorocarbons (CFCs) and their first- and second-generation replacement products, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), are entirely anthropogenic in origin and were developed in the 1930s and continued evolving through the 1980s for domestic and industrial applications as refrigerants, solvents, propellants, and foam blowing agents. Because of their chemical inertness, the only realistic sink mechanism of tropospheric CFCs upon their release is transport to the stratosphere. Here, CFCs are photolyzed by UV radiation producing Cl atoms that catalytically destroy stratospheric O_3 (Kim et al., 2011 and references therein). Halons, a separate group of bromine-containing halocarbons primarily used as fire suppression agents, undergo similar troposphere-stratosphere transport. This is followed by photolytic production of Br, which is more efficient than Cl on a per-atom basis in destroying stratospheric O_3. Consequently, halons are known to have higher ozone depletion potentials (ODP) as compared to CFCs. In contrast, HCFCs and HFCs are partially removed in the troposphere upon reaction with OH, and are less significant contributors to stratospheric O_3 depletion (Kim et al., 2011). Overall, O_3 depletion since the 1970s, primarily attributed to these ozone depleting substances (ODS), is estimated to contribute a non-trivial globally averaged radiative forcing (RF) of -0.15 ± 0.10 W m^{-2} (IPCC/TEAP, 2005). In addition, these halocarbons exert a considerable influence on global direct radiative forcing owing to their ability to absorb long-wave (IR) radiation and their long atmospheric lifetimes (on the order of decades to centuries). Global increases in industrially produced ODS and non-ODS halocarbons from 1750 to 2000 are estimated to exert a positive RF of $+0.33 \pm 0.03$ W m^{-2}, corresponding to ~13% of the total RF exhibited by all greenhouses gases (IPCC/TEAP, 2005).

In view of the environmental impacts described above, the production and use of these and other ODS such as CCl_4 and CH_3CCl_3 were regulated by the Montreal Protocol (MP) in 1989 and its subsequent amendments, imposing a complete ban on CFCs for developed and developing countries by 1996 and 2010, respectively. On the other hand, HCFCs are allowed to undergo step-wise reduction between 2004 and 2030 for developed countries and between 2013 and 2040 for developing countries (Keller et al., 2012). In the post-MP era, long-term ground-based measurements at remote locations have reported gradually decreasing or stabilizing trends for tropospheric CFCs, CCl_4 and CH_3CCl_3 (Prinn et al., 2016; ESRL, 2016), showing the general effectiveness of the global phase-out of these ODS. However, such trends insufficiently reflect the effectiveness of MP regulations at a regional scale or in individual countries where information on halocarbons is mostly derived based on national or regional bottom-up emission inventories. These inventories could have inherent uncertainties arising from inaccuracies in assigning halocarbon usage data among end-use sectors based on production data, overlooked leakage from existing stockpiles, and unreported production (Fang et al., 2012 and references therein). The uncertainties can be minimized through ambient measurements at regional and local scales, thereby assessing the effectiveness of the MP and relevant national regulations on spatial scales that cannot be inferred from globally averaged remote location data. In addition, such ambient measurements can serve as the first step in developing top-down emission estimates using inversion algorithms coupled with atmospheric dispersion models (Hurst et al., 2006; Stohl et al., 2009; Keller et al., 2012). These regional-scale estimates can consequently provide a unique and independent tool to evaluate official emission inventories (Keller et al., 2012).

To date, atmospheric halocarbons in Asia have mainly been measured in East Asia, especially Japan and the Pearl River Delta (PRD), China (Palmer et al., 2003; Yokouchi et al., 2005a; Chan and Chu, 2007; Guo et al., 2009; Vollmer et al., 2009; Stohl et al., 2010; Zhang et al., 2010, 2014; Shao et al., 2011; Li et al., 2014; Wu et al., 2014). A fraction of these studies reported top-down halocarbon emission estimates using inverse modelling (Vollmer et al., 2009; Stohl et al., 2010), the CO tracer method (Palmer et al., 2003; Guo et al., 2009; Shao et al., 2011; Fang et al., 2012; Zhang et al., 2014) or the HCFC-22 tracer method (Fang et al., 2012; Wu et al., 2014). Aircraft-based measurement campaigns have been conducted in the region centering over the Indonesian archipelago (BIBLE A; Elliott et al., 2003), Java (BIBLE B; Choi et al., 2003), the northwestern and western Pacific basin extending near Borneo (NASA PEM-West A and B; Blake D.R. et al., 1996, 1997), Thailand and Malaysia (CARIBIC, Leedham Elvidge et al., 2015). In comparison, relevant measurements focusing exclusively on Southeast (SE) Asia are almost nonexistent except for an early ship-based report on marine-derived halocarbons (Yokouchi et al., 1997) and a more recent land-based study of 4 short-lived halocarbons from the Malaysian Borneo (Robinson et al., 2014).

To enhance our understanding of halocarbon levels in SE Asia, two ground-based measurement campaigns were conducted in 2011–2012 in Singapore, an urban-industrial city-state characterized by a warm and humid tropical environment. This work was part of the 7 Southeast Asian Studies (7SEAS) campaign investigating burning smoke of peat-forest and agricultural residue in the Maritime Continent. Another major objective of the study was to investigate the effects of industrial emissions on halocarbon levels. Singapore is a major center for chemical, petrochemical, pharmaceutical, electronics and other manufacturing industries that are clustered in industrial areas/estates across the mainland as well as on nearby islands. In addition, the close proximity to industrial areas in neighboring countries (e.g., Malaysia (N and NE of Singapore) and Indonesia (W-SW of Singapore)) implies possible mixing of regional emission plumes with local ones and could potentially affect observed halocarbon levels.

This work quantified a total of 26 atmospheric halocarbons – one of the largest suites reported in the past ~10 years and higher than the 9 to 16 halocarbon species typically characterized by studies across the world (Reimann et al., 2008; Keller et al., 2012; Artuso et al., 2010). A list of halocarbons measured in this study along with their major uses/sources, atmospheric lifetimes, ODPs, 100-y global warming potentials (GWPs) and applicable phase-out timelines are provided in Table S1 (Supplementary material). The halocarbon dataset is supplemented by measurements of 7 non-methane hydrocarbons (NMHCs; ethane, ethyne, propane, i-butane, n-butane, benzene and toluene), 7 alkyl nitrates (C_1-C_5 $RONO_2$), 2 sulfur gases (carbonyl sulfide and dimethyl sulfide; OCS and DMS), and carbon monoxide (CO) to better understand sources and atmospheric processes. These observations enable an evidence-based assessment of – i) the effectiveness of MP and related national regulations on ODS levels; ii) the influence of the growth in use of first- and second-generation CFC replacements; and iii) the relative impacts of