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Estimated emissions of chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons based on an interspecies correlation method in the Pearl River Delta region, China

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HIGHLIGHTS

- The bank emissions of CFCs still exist.
- The concentrations and emissions of HCFCs and HFCs have significantly increased.
- The PRD region makes a great contribution to the China's halocarbon emissions.

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ABSTRACT

Although many studies have been conducted in recent years on the emissions of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) at the large regional (such as East Asia) and national scales, relatively few studies have been conducted for cities or metropolitan areas. In this study, 192 air samples were collected in the Pearl River Delta (PRD) region of China in November 2010. The atmospheric mixing ratios of six halocarbons were analyzed, including trichlorofluoromethane (CFC-11, CCl_3F), dichlorodifluoromethane (CFC-12, CCl_2F_2), monochlorodifluoromethane (HCFC-22, $CHClF_2$), 1,1-dichloro-1-fluoroethane (HCFC-141b, CH_3CCl_2F), 1-dichloro-1,1-fluoroethane (HCFC-142b, CH_3CClF_2), and 1,1,1,2-tetrafluoroethane (HFC-134a, CH_2FCF_3), and their emissions were estimated based on an interspecies correlation method using HCFC-22 as the reference species. The results showed no significant change in the regional concentration and emission of CFC in the past 10 years, suggesting that the continuous regional emission of CFC has had no significant effect on the CFC regional concentration in the PRD region. Concentrations and emissions of HCFCs and HFCs are significantly higher compared to previous research in the PRD region ($P < 0.05$). The largest emission was for HCFC-22, most likely due to its substitution for CFC-12 in the industrial and commercial refrigeration subsector, and the rapid development of the room air-conditioner and extruded polystyrene subsectors. The PRD's ODP-weighted emissions of the target HCFCs provided 9% (7–12%) of the national emissions for the corresponding species. The PRD's GWP-weighted emissions of the target HCFCs and HFC-134a account for 10% (7–12%) and 8% (7–9%), respectively, of the national emissions for the corresponding species, and thus are important contributions to China's total emissions.

1. Introduction

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) are all man-made chemical substances used in many industrial and commercial fields, such as refrigeration, foam blowing, metered dose inhalers, and fire extinguishing, as well as solvents (Metz et al., 2005). CFCs and HCFCs are of great concern due to their high ozone depletion potential (ODP) (Montzka et al., 2011). Moreover, CFCs, HCFCs, and HFCs are greenhouse gases, and HFCs are included among the Kyoto Protocol (KP) targets (Solomon et al., 2007). Therefore, studies estimating their emissions have become the focus of academics and policy makers. Under the control of the Montreal Protocol (MP), CFCs have been phased out on a global scale (Montzka et al., 2011). The phase-out of HCFCs was requested to begin in 1996 by non-Article 5 parties (mainly developed countries), but it was not until 2013 that Article 5 parties (mainly developing countries) were requested to take action (UNEP, 2009). Influenced by phase-

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out progress and market demand, significant differences were found among countries for the emissions of CFCs, HCFCs, and HFCs (Li et al., 2011). Studying the atmospheric mixing ratios (in units of parts per trillion volume, pptv, in this paper) and emissions of these species in a particular country or region can help to track the implementation effectiveness of the MP and KP, and can provide basic information for multi-scale environmental studies and policy making.

The interspecies correlation method has been widely used in recent years, applying aircraft monitoring or high-frequency measurements at remote sites to estimate the emissions of CFCs, HCFCs, and HFCs in large regions (such as East Asia) or for entire countries (Blake et al., 2003; Kim et al., 2010; Li et al., 2011; Palmer et al., 2003; Yokouchi et al., 2005, 2006). However, the observational data from a remote background site are not suitable for estimating emissions in smaller areas using the interspecies correlation method because distinguishing the individual contribution of different source areas in the same airflow direction is difficult. An improved method was to use the interspecies correlation method, but based on local atmospheric data, as shown by Shao et al. (2011), in estimating halocarbon emissions in the Pearl River Delta (PRD) region in 2004.

The PRD region is one of the most densely populated and highly developed metropolitan areas in China, and also features a large manufacturing industry (Streets et al., 2006). Its regional air quality has been worsened by rapid urbanization and industrialization, and halocarbon emissions in this area are of special international interest. Observational studies were widely carried out when CFCs were being phased out, as the consumption of CFCs was allowed in China until 2010 (Chan and Chu, 2007; Chan et al., 2006; Fang et al., 2012; Guo et al., 2009; Shao et al., 2011; Zhang et al., 2006a,b, 2010). A great deal has changed in the past few years, but recent halocarbon emissions have not been reported yet for the PRD region. In this study, 192 whole air samples were collected in the PRD region in November 2010, and the interspecies correlation method was applied to estimate the emissions of six halocarbons, including trichlorofluoromethane (CFC-11, CCl_3F), dichlorodifluoromethane (CFC-12, CCl_2F_2), monochlorodifluoromethane (HCFC-22, $CHClF_2$), 1,1-dichloro-1-fluoroethane (HCFC-141b, CH_3CCl_2F), 1-dichloro-1,1-fluoroethane (HCFC-142b, CH_3CClF_2), and 1,1,1,2-tetrafluoroethane (HFC-134a, CH_2FCF_3). This latest study will help to track the implementation effectiveness of the MP in this region.

2. Method

2.1. Sampling and analysis

The PRD region is located in southern China and consists of nine administrative areas in Guangdong Province, with an area of about 42,000 km^2 (Streets et al., 2006). In this region, we selected three sampling sites, including one urban site in Guangzhou (23.130°N, 113.260°E) and two rural sites in Heshan (22.711°N, 113.548°E) and Wanqingsha (22.711°N, 112.927°E), respectively (Fig. 1). All three sites were on the top of a hill or on the roof of a high building to minimize the influence of any proximate emission sources. In total, 192 air samples were collected in 3.2-L electro-polished stainless-steel canisters, which had been cleaned and evacuated by a canister cleaner (3100A; Entech, Irvine, CA, USA) before shipment to the sampling sites. The restricted grab sampler (39-RS-x; Entech), which has a 5-μm Silonite-coated metal particulate filter, was placed on the inlet of the canister to completely eliminate dust and particulate intrusion during sampling. At each sampling site, one sample was collected at 09:00 (local time) and another at 13:00 (local time) on each day between November 9 and 29, 2010. Moreover, on 3 of these days (November 19, 20, and 27) more intensive sampling was conducted, which included collection of an additional five to seven samples at each site.

A cryogenic pre-concentration system (7100A; Entech) was connected with a gas chromatography/mass spectroscopy (GC/MS) system (Saturn 2100; Varian, Palo Alto, CA, USA) to analyze the six target

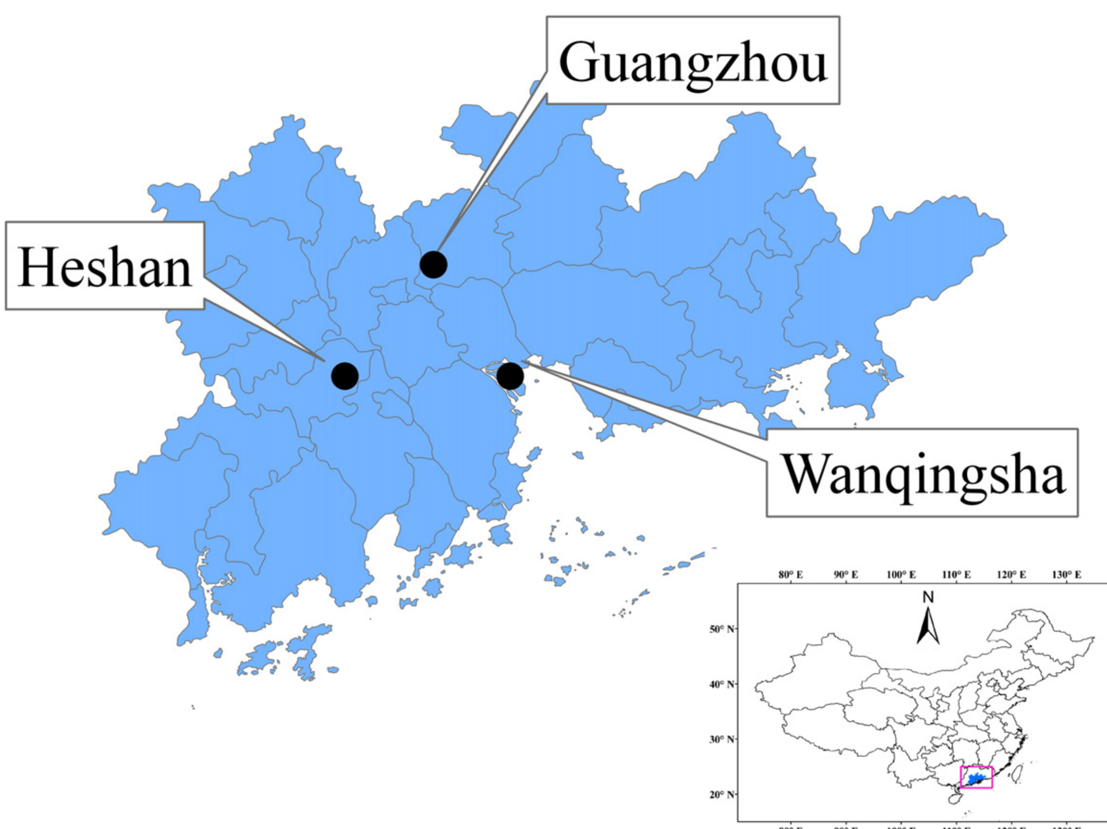

Fig. 1. Map showing the locations of three sampling sites in the PRD region.