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Chloroform, carbon tetrachloride and methyl chloroform fluxes in southern California ecosystems

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ABSTRACT

Chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), and methyl chloroform (CH_3CCl_3) are important carriers of chlorine to the stratosphere and account for an estimated 15% of the total organic chlorine in the troposphere, roughly equivalent to chlorine load due to methyl chloride (CH_3Cl). The tropospheric burden of chlorine has declined since 1994, largely due to the restriction of CH_3CCl_3 and CCl_4 use as specified by the Montreal Protocol. However, few field studies have been conducted on the terrestrial-atmosphere exchange of these chlorinated hydrocarbons, leading to uncertainties about the natural cycling of these trace gases. This work shows the results of 75 flux measurements conducted in a variety of southern California ecosystems, including coast sagebrush, chamise chaparral, creosote bush scrub, shoreline, and coastal salt marsh. We find no evidence of a significant soil sink in these ecosystems but rather a small net source of $CHCl_3$ and possibly CCl_4.

1. Introduction

Anthropogenic chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) contribute the majority of chlorine to the stratosphere and amount to ~68% or 2.34 ppb (parts per billion) of the total chlorine in the troposphere (Clerbaux and Cunnold, 2007). In addition to the CFCs and HCFCs, several other chlorocarbons reach the stratosphere, including CH_3Cl (methyl chloride, chloromethane), CH_2Cl_2 (methylene chloride, dichloromethane), $CHCl_3$ (chloroform, trichloromethane), CCl_4 (carbon tetrachloride, tetrachloromethane) and CH_3CCl_3 (methyl chloroform, 1,1,1-trichloroethane), which together account for nearly the remaining balance of chlorine. Since 1994, the total atmospheric chlorine burden has been decreasing, owing in large part to the decline of CH_3CCl_3 and CCl_4, two chlorocarbons regulated by the Montreal Protocol. Whereas the primary sink of CCl_4 is photodissociation in the stratosphere, the primary sink for CH_3CCl_3, CH_3Cl, $CHCl_3$ and CH_2Cl_2 is oxidation by hydroxyl radical (OH) in the troposphere (Clerbaux and Cunnold, 2007). In fact, background methyl chloroform concentrations are used to derive averaged tropospheric OH concentrations (Montzka et al., 2000; Prinn et al., 1995). This approach assumes an accurate knowledge of industrial production and emission rates as well as an understanding of the geographic distribution and strengths of any additional sources or sinks.

The recently estimated atmospheric lifetimes of $CHCl_3$, CCl_4 and CH_3CCl_3 are 0.5 yrs, 26 yrs and 5 yrs, respectively (Clerbaux and Cunnold, 2007; O'Doherty et al., 2001). Atmospheric lifetimes are useful to guide regulatory decisions as well as to test our understanding of the atmospheric chemical processes, and estimating lifetime requires an accurate account of global burdens, sources and sinks. While CCl_4 and CH_3CCl_3 are primarily anthropogenic in origin (McCulloch and Midgley, 2001; Singh et al., 1976), $CHCl_3$ has large natural and anthropogenic sources

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and is not a Montreal Protocol gas (Laturnus et al., 2002). Large uncertainties are associated with the atmospheric budgets of these compounds, with significant discrepancies between estimated global source and sink strengths and their regional distributions (Clerbaux and Cunnold, 2007; Khalil and Rasmussen, 1999; O'Doherty et al., 2001).

Several recent studies have reported a potentially significant terrestrial sink for CCl_4 (Happell and Roche, 2003; Happell and Wallace, 1998; Liu, 2006; Wang et al., 2007), CH_3CCl_3 (Happell and Wallace, 1998; Kutsuna et al., 2000; Wang et al., 2006), and even $CHCl_3$ (Wang et al., 2007). If these sinks are indeed significant relative to atmospheric destruction processes, then their estimated lifetimes would need to be reduced and their source and sink budgets reassessed. For CCl_4, it is already difficult to reconcile a 26 yr atmospheric lifetime with observed background concentrations, which require annual emissions that are much larger than known sources (Clerbaux and Cunnold, 2007). A globally significant soil sink would exacerbate the imbalance. In this study, we report net fluxes of $CHCl_3$, CCl_4, and CH_3CCl_3 from a variety of southern California shrubland and coastal ecosystems to better understand the relative importance of these ecosystems in the global budgets of these compounds.

2. Field sites and methods

Between 1997 and 2000, 75 flux chamber measurements were conducted through different seasons at southern California ecosystems ranging from the inland desert to the shore of the Pacific Ocean. The study sites included three shrublands, two coastal salt marshes, and a sandy beach. The shrubland communities included creosote bush scrub at the Boyd Deep Canyon Desert Reserve (33°39′N, 116°22′W, $n=11$) located ~110 km from the coast; chamise chaparral at the Elliott Chaparral Reserve (32°53′N, 117°7′W, $n=14$) located ~15 km from the coast; and coastal sage scrub at the Scripps Coastal Reserve (32°52′N, 117°15′W, $n=16$) located on a coastal bluff. The coastal salt marsh studies were conducted at the Mission Bay marsh (32°47′N, 117°13′W; $n=14$) and the San Dieguito lagoon (32°58′N, 117°15′W, $n=18$). The beach study site was at the Scripps Institution of Oceanography (SIO) (32°52′N, 117°15′W, $n=2$).

The climate of southern California is Mediterranean, with wet mild winters and dry warm summers. The shrubland growing season extends from the beginning of winter rains to spring/early summer, whereas the salt marsh growing season extends from late winter through summer (Zedler et al., 1992). The shrubland study plots covered a variety of vegetation, with an emphasis on the most common species present in their respective ecosystems. Measurements were made during growing and non-growing seasons and over a range of soil moisture conditions.

The coastal salt marsh study plots were selected according to predominant vegetation communities along the vertical zonation of the marsh. Hence measurements ranged from the upper marsh, which was inundated during the highest high tides, down to the tidal channels that were only exposed during low tides. Plots were measured several times between June 1998 and June 1999. The beach chamber sites were conducted during low tide and included one site with sand only and another site with decaying kelp and surf grass deposited on the sand: *Macrocystis pyrifera* (45 g dry wt), *Phyllospadix torreyi* (28 g dry wt), and *Egregia menziesii* (12 g dry wt).

Net fluxes were measured using a large (850 L) two-component static flux chamber (Rhew et al., 2001) during daylight hours, and enclosures were 30–40 min in duration. Most shrubland and all salt marsh flux measurements were conducted using a dark chamber (aluminum lid), although five shrubland sites were also measured with a clear-top chamber (acrylic lid) to test for the effect of sunlight. Clear-topped chambers used an internal air chiller (ice water pumped through a small radiator mounted on the inside wall) to modulate chamber temperatures. Beach flux measurements also used this clear lid and cooling system. For each chamber experiment, three 6-L air samples were drawn from the chamber into previously evacuated silica-lined stainless steel canisters (Restek Corp, Bellefonte, PA), and ambient air samples were also collected. Control experiments were conducted on the dark ($n=4$) and light ($n=4$) chambers by placing them over a solid aluminum surface. Net fluxes ± s.d. (nmol m^{-2} d^{-1}) for dark and light control chambers, respectively, were 0.5 ± 0.6 and -1.3 ± 5.8 for $CHCl_3$, -0.6 ± 0.8 and 0 ± 0 for CCl_4, and 0 ± 0 and -0.9 ± 1.3 for CH_3CCl_3.

Samples were measured using a gas chromatograph (HP 5890 Series II) equipped with a custom-built thermostatted gas sampling module. The instrument includes three separate chromatographic configurations and detectors to measure CH_4; N_2O and CCl_2F_2 (F-12); and $CClF_3$ (F-11), CH_3CCl_3, $CHCl_3$ and CCl_4, respectively. The instrumentation and standards (SIO 1998 calibration scale) were developed for the Advanced Global Atmospheric Gases Experiment to optimize the accuracy and precision at near ambient concentrations, with peak area precisions (1 σ) of 3.26% for $CHCl_3$, 0.23% for CCl_4, 0.39% for CH_3CCl_3 and 0.06% for CH_4 (Prinn et al., 2000). Fluxes were determined by applying a linear least squares fit to the measured dry air mole fractions versus time of sampling, and multiplying by the number of moles of air in the chamber. Flux errors were calculated using slope uncertainties (based on 68% confidence intervals for the regression coefficients) propagated with estimated errors of the number of moles of air in the chamber. All reported fluxes are net fluxes, and fluxes were treated as zero when the r^2 value of the curve fit <0.7. Minimum detectable fluxes based on instrumental precision and typical field conditions are estimated at 1.1 nmol m^{-2} d^{-1} for $CHCl_3$, 0.5 nmol m^{-2} d^{-1} for CCl_4, 0.9 nmol m^{-2} d^{-1} for CH_3CCl_3 and 2.5 μmol m^{-2} d^{-1} for CH_4; all measured net fluxes smaller than this magnitude are also treated as zero. Fluxes of CH_3Cl, CH_3Br and CH_4 were also measured at these sites and are reported elsewhere, along with further details of specific chamber sites (Rhew et al., 2000, 2001, 2002).

Statistical analyses were conducted with JMP IN software Version 5.1 (SAS Institute Inc.). Biome-averaged net fluxes were tested for statistical significance from zero