

## Preface



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Budgets and cycles are important tools for the study of atmospheric chemistry. They complement the observations of atmospheric gases and particles that reflect the combined influences of rates of emission, atmospheric transport, and loss by transformation and deposition. As the different components of the budgets are determined, the cycles of the atmospheric species become established. The budget and cycle of atmospheric carbon (e.g., Bolin, 1983; Tans, et al., 1990), central to the discussions leading to the Kyoto Protocol, is but one of many examples of the value of such investigations.

Inventories of emissions to the atmosphere are crucial components of good budgets. In some cases, especially where well-quantified human activities dominate, the inventory compilation is relatively straightforward, if laborious. The result has been relatively reliable inventories for such species as  $\text{CF}_2\text{Cl}_2$  (AFEAS, 1996). In other cases, especially where natural sources play major roles, the inventory development activity is much more complex, involving both rigorous accounting and pathbreaking biogeochemistry. Although sometimes poorly constrained, the resulting inventories provide important information concerning limitations in our understanding of the biogeochemistry of these compounds, and thereby point to areas where future research is needed (e.g.,  $\text{N}_2\text{O}$ ; Bouwman and Taylor, 1996).

Species or groups of species with dominant natural sources and, in addition, high reactivity pose a particularly difficult inventory problem. In these cases, ambient concentrations exhibit great spatial and temporal variability, and thus field observations are unable to provide the same level of guidance that is available for more stable entities. Reactive atmospheric chlorine (RAC) is perhaps the archtypical example.  $\text{HCl}$ , one of its major constituents, is measured in the atmosphere only with great difficulty, and the chlorine atom itself is so reactive and its atmospheric concentrations so low that its presence must be inferred rather than established by measurement. Nevertheless, RAC is known to occur in the troposphere, both as a consequence of direct emissions (Graedel and Keene, 1995) and of multi-phase chemistry (Gard et al., 1998; Spicer et al., 1998). In complementary studies, recent laboratory work has

identified previously unanticipated and/or unquantified sources of RAC (Seisel et al., 1997; Oum et al., 1998). Furthermore, RAC has been suggested; to be highly significant to tropospheric (e.g., Chameides and Stelson, 1992) and ocean surface (e.g., Coale et al., 1996) chemistry, at least under some conditions. Establishing the RAC budget and cycle is therefore of substantial interest.

The series of papers that follows this overview describes research that has led to the first global, gridded inventory of reactive chlorine emissions to the atmosphere. This project is a component of the [Global Emissions Inventory Activity](#) (GEIA; Graedel, 1994), which in turn is a component of the International Global Atmospheric Chemistry Programme. The RAC inventory has been developed along GEIA principles: an international and intercontinental working group, a  $1^\circ \times 1^\circ$  spatial resolution, and, with these papers, publication in the refereed scientific literature.

The individual papers report gridded global emission inventories as a function of source type for major reactive chlorine species in the troposphere. The species considered include particulate chlorine, hydrochloric acid ( $\text{HCl}$ ), nitryl chloride ( $\text{ClNO}_2$ ), methylchloride (chloromethane,  $\text{CH}_3\text{Cl}$ ), chloroform (trichloromethane,  $\text{CHCl}_3$ ), methyl chloroform (1,1,1-tri-chloroethane,  $\text{CH}_3\text{CCl}_3$ ), perchloroethene (tetrachloro-ethene,  $\text{C}_2\text{Cl}_4$ ), trichloroethene ( $\text{C}_2\text{HCl}_3$ ), methylene chloride (di-chloro-methane,  $\text{CH}_2\text{Cl}_2$ ), and the hydrochlorofluorocarbon (HCFC) chlorodifluoromethane ( $\text{CHClF}_2$ ). Four major classes of source types were considered: Oceanic and terrestrial biogenic emissions (Khalil et al., 1999); sea-salt production and dechlorination (Erickson et al., 1999); biomass burning (Lobert et al., 1999); and anthropogenic emissions from industrial sources and coal combustion (Aucott et al., 1999; McCulloch et al., 1999 a,b). The individual inventories for each source type were integrated into species-specific composite inventories; budget closure was assessed based on inversion modeling and related approaches and major areas of uncertainty identified (Keene et al., 1999). We anticipate that these results will provide critical input data for future modeling studies, as well as a useful perspective in planning future measurement programs.

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