

Anthropogenic emissions of trichloromethane (chloroform, CHCl₃) and chlorodifluoromethane (HCFC-22): Reactive Chlorine Emissions Inventory



M.L. Aucott,¹ A. McCulloch,² T.E. Graedel,³ G. Kleiman,⁴ P. Midgley,⁵ and Yi-Fan Li⁶

Abstract. Anthropogenic emissions of trichloromethane (CHCl₃, chloroform) in 1990 have been estimated with a variety of methods specific to the source category. The largest source category for CHCl₃ was found to be pulp and paper manufacturing, responsible for an estimated 30 ± 8 Gg yr⁻¹ reactive chlorine in the form of CHCl₃. Water treatment of various types was estimated to contribute another 19 ± 12 Gg. Manufacturing facilities of products other than pulp or paper and other relatively minor sources were estimated to emit an additional 13 ± 5 Gg yr⁻¹, for a total of 62 ± 25 Gg yr⁻¹ reactive chlorine in the form of CHCl₃. The global flux of chlorodifluoromethane (HCFC-22) is well characterized from industrial and regulatory data to have been 195 Gg in 1990, equivalent to 80 ± 0.6 Gg yr⁻¹ as active chlorine. The fluxes of reactive chlorine from CHCl₃ and HCFC-22, distributed globally in a 1° latitude times 1° longitude grid, revealed areas highest in emissions.

1. Introduction

The Reactive Chlorine Emissions Inventory (RCEI) has been organized under the auspices of the International Global Atmospheric Chemistry Program's Global Emissions Inventory Activity (GEIA) [Graedel and Keene, 1999]. The first objective of the project has been to develop global emissions inventories by source type for major reactive chlorine species in the troposphere and to map these emissions on a global a 1° x 1° latitude x longitude grid. Anthropogenic emissions estimates of two of these reactive chlorine compounds, trichloromethane (chloroform, CHCl₃) and the hydrochlorofluorocarbon, chlorodifluoromethane, (HCFC-22), are developed and discussed in this paper. The fluxes developed herein, in the form of arrays of emissions from individual grid squares, are also available from the GEIA Website at <http://groundhog.sprl.umich.edu/geia/rcei>.

CHCl₃ is present in the atmosphere at background concentrations that are apparently stable in the region of 15 picomoles (pmol) mol⁻¹ [Fraser *et al.*, 1994]. The concentration of HCFC-22 was 88 pmol mol⁻¹ in 1990, growing at 7 pmol mol⁻¹yr⁻¹ [Sanhueza, 1995]. The principal removal process for both compounds is reaction with atmospheric hydroxyl radicals and the resulting estimated atmospheric lifetimes are about 0.5 years for CHCl₃ [Albritton *et al.*, 1995] and 13 years for HCFC-22

[Sanhueza, 1995]. There are uncertainties associated with these compound reaction rates with hydroxyl radicals, and there are temporal and spatial variations in tropospheric concentrations of hydroxyl radicals. These considerations add uncertainties to budgets of atmospheric gases, particularly those of relatively short-lived species such as CHCl₃ when viewed at regional or smaller scales.

Globally, the CHCl₃ flux into the atmosphere, which is required to maintain the observed concentration, is estimated from the above concentration and lifetime to be ~0.6 Tg yr⁻¹. CHCl₃, which is emitted from both anthropogenic and natural processes, is produced intentionally and used as a feedstock in chemical manufacturing, mainly to produce HCFC-22. It is also used as a solvent and extractant in various manufacturing and laboratory procedures. It is created as a by-product during the delignification of wood pulp, the bleaching of paper, and the disinfection of water with chlorine and chlorine-containing compounds. CHCl₃ is also present in trace quantities in the gases released from combustion and has been observed in gases produced from anaerobic decomposition of organic material.

There are no known natural sources of HCFC-22. Although concentrations of the chemically similar dichlorodifluoromethane (CFC-12) and trichlorofluoromethane (CFC-11), which were higher than in ambient air, have been detected in volcanic vents, HCFC-22 was not found, even when the vent contained a substantial concentration of its chemical precursor CHCl₃ [Isodorov, 1990]. On the other hand, HCFC-22 is widely used as a refrigerant, and all of the material so used will eventually be released into the environment unless specific steps are taken to recover and reuse or destroy the charges in each piece of equipment. Most emissions into the environment are a result of leaks from refrigeration equipment during use, servicing or final disposal rather than being from the chemical plants in which it is produced. Some 0.195 Tg yr⁻¹ is estimated to have been so emitted into the atmosphere in 1990 [Midgley and McCulloch, 1997].

These compounds are among the significant carriers of organically bound chlorine into the atmosphere. This work sets out

¹New Jersey Department of Environmental Protection, Trenton.

²ICI Chemicals & Polymers Ltd., Runcorn, England.

³School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut.

⁴Center for Global Change Science, Massachusetts Institute of Technology, Cambridge.

⁵M and D Consulting, Leinfelden Musberg, Germany.

⁶AES, Environment Canada, Downsview, Ontario.

Copyright 1999 by the American Geophysical Union.

Paper number 1999JD900053.

to catalog the anthropogenic components of these fluxes and to assign geographical distributions to them. Each compound has a different pattern of geographical distribution for its emissions. CHCl₃ emission distribution is significantly influenced by point sources at paper mills and chemical and pharmaceutical plants, whereas the emission pattern of HCFC-22 tends to follow the distributions of population and affluence.

For fluxes of either compound to be of real value in the modeling of atmospheric processes, such as the reactive chlorine compound cycles, geographical distribution on a far finer scale than semihemispherical is required. This way, regional variations in concentration can either be traced to regional sources or be accounted for by regional variations in atmospheric chemistry. The calculation and distribution of the industrial components of the fluxes of CHCl₃ and HCFC-22 are described here; oceanic and biogenic fluxes are discussed by *Khalil et al.* [1999].

2. Estimation Procedures and Results for Specific Source Categories: CHCl₃

2.1. Pulp and Paper Manufacture

Chloroform is produced as a by-product during the delignification of wood and other cellulose pulps and the bleaching of paper by chlorine. Other chlorine-containing oxidants used in these processes, such as chlorine dioxide (ClO₂) also generate CHCl₃ [*Juuti et al.*, 1996]. Several reports [*National Council for Air and Stream Improvement (NCASI)*, 1988; *Ayres*, 1992; *Blum*, 1996; *U.S. Environmental Protection Agency (USEPA)*, 1984] provide information on the magnitudes of these emissions. Calculations based on these reports, including an extrapolation of U.S. estimates to global estimates, suggest that yearly global emissions are in a range from 10 to 70 Gg yr⁻¹ CHCl₃, with an approximate median of 30 Gg yr⁻¹, or 27 Gg yr⁻¹ reactive chlorine [*Aucott*, 1997]. Extrapolation of 1990 U.S. CHCl₃ emissions from pulp and paper manufacturers as reported on the U.S. Toxics Release Inventory (TRI) [*USEPA*, 1995] also provides a global estimate of 27 Gg yr⁻¹ reactive chlorine in the form of CHCl₃ [*Aucott*, 1997]. These emissions are expected to be localized to areas where wood is pulped and paper made and not dispersed among the population at large. Hence not only is an emission function required to relate CHCl₃ emissions to the quantity of pulp and paper manufactured but also the geographical locations of individual plants.

The TRI data appear consistent with the other reports noted above. Because these data are based on actual reports by discrete facilities and because they provide a convenient method of locating at least the larger pulp and paper manufacturing sources of CHCl₃ in the United States, the TRI was used in this work as the basis for development of a CHCl₃ emission factor for global paper and pulp mills. This factor, modified to adjust for differing amounts of chlorine used in various regions, was then combined with addresses and output quantities of mills throughout the world as listed in the International Phillips' 1997 Paper Directory [*Miller Freeman Information Services (Miller Freeman)*, 1996] (henceforth referred to as "the directory") to provide the global distribution of emissions.

In developing the emission factor, quantities from pulp and paper manufacturers in the 1990 TRI were totaled. In 1990, 9.97 times 10⁹ grams of CHCl₃ were reported released to the environment from paper or pulp manufacturing facilities, which

represents 90 % of all TRI CHCl₃ environmental releases. These facilities transferred 2.6 × 10⁸ g to sewage treatment plants and another 4.9 × 10⁷ g to nonincinerating treatment or disposal facilities, which include evaporation ponds and lagoons. It is assumed that virtually all of CHCl₃, transferred to these treatment and disposal facilities, was ultimately released to the atmosphere.

Facility addresses in the TRI were compared with addresses reported in the directory. Output quantities, considered to be the sum of the paper/board and pulp outputs, were determined for each mill listed in the directory. The total output was found to be 90.3 million metric tons per year. (Although the output quantities listed may be more akin to capacity than to actual production; it is assumed that these quantities are representative of production. It is also assumed that they are reported consistently in the directory for all mills listed regardless of country or region.) Most of the mills reporting in the TRI were found in the directory. The total output of mills that appeared in both the TRI and the directory was ~ 34 million metric tons per year. A comparison of the output quantities of mills in both lists and those that appeared only in the directory revealed that it is primarily the smaller mills that do not appear in the TRI. An exclusion of some smaller mills is not surprising, because the TRI threshold is 25,000 pounds for chemicals manufactured, which includes by-product production.

The CHCl₃ released from these unlisted mills was estimated with a process of several steps. First, the mills listed in the directory were sorted into groups based on output quantity. The mills that appeared in both the TRI and the directory were also sorted into groups. Inspection of the resulting histograms suggested that facilities could be characterized as either "large" or "small," with large having an output greater than 300,000 t yr⁻¹ and small having an output less than 300,000 t yr⁻¹. There were 381 small facilities listed in the directory, and they accounted for 31.8 million t yr⁻¹, or 35%, of the total U.S. output. In the group of facilities that also appeared in the TRI, however, small facilities represented only 21% of the total output of the TRI facilities. It was concluded that if all small facilities had in fact reported on the TRI, the total releases from this group would have been greater by a factor of 35/21, or 1.67.

When the releases and transfers to sewage treatment plants from the small group were augmented by multiplying by 1.67, the total releases and sewage treatment transfers from the facilities, which were listed in the directory and which also appeared on the TRI, grew overall by a factor of 1.22. There were also mills that appeared on the TRI but could not be found in the directory. It was assumed that this group also excluded a similar portion of small mills, and so total releases and sewage treatment facility transfers from this group were similarly augmented by multiplying by 1.22. This brought the estimated total U.S. CHCl₃ emission from paper and pulp mills to 1.25 × 10¹⁰ g yr⁻¹.

Dividing this total by the 90.3 million metric tons of output generated an emission factor of 0.138 kg t⁻¹. This factor thus represents an average CHCl₃ emission per metric ton of "output," as indicated in the directory, for all U.S. facilities. It is lower than the draft EPA emission factor of 0.195 kg t⁻¹ of air-dried pulp for CHCl₃ emission from facilities that bleach with chlorine (*USEPA*, 1996b), very likely because it represents all facilities including those that use no chlorine or chlorine compounds.

Much variation exists in the ratio of CHCl₃ releases to output among the paper mills that report on the TRI. Figure 1 is a distribution of these mills sorted into groups based on grams of CHCl₃ released per metric ton of directory-listed output. The range

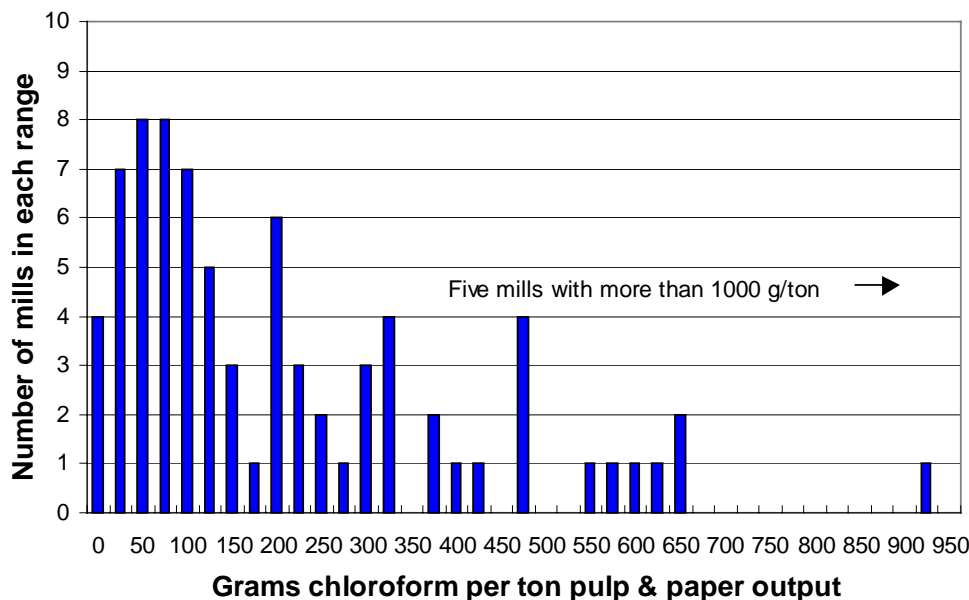


Figure 1. Distribution of paper and pulp mills, grouped by grams of CHCl₃ released per ton of directory-listed output. Based on data from the 1990 U.S. Toxics Release Inventory [USEPA, 1994] and International Phillips' 1997 Paper Directory [Miller Freeman, 1996], as described in the text.

is from 0.02 to 1.78 kg t⁻¹. Nearly 80 % of these mills released less than 0.4 kg CHCl₃ per ton of output, but some released over 1 kg per ton of output. An earlier study [NCASI, 1988] also found wide variation in the rate of CHCl₃ generated by pulp mills, ranging from 0.06 kg t⁻¹ to 1.35 kg t⁻¹ per air dry ton of bleached pulp. This study revealed that the mill emission rates were a function of a variety of factors, especially the presence of hypochlorite stages in bleach lines and the addition of hypochlorite to extracted stages. Other process-specific parameters, including temperature, wood species, flow rates, and pH also affected CHCl₃ emission rates. Many of these factors cannot be characterized without on-site analyses and measurements.

Because of this wide range of CHCl₃ generation, uncertainty exists with the emission factor. The uncertainty range was explored by considering the ratio of emissions to output for each facility, which reported on the TRI for which an output quantity was also listed in the directory, finding the mean ratio, and using a Ttest to establish the critical value for the standard deviations from the mean. For all the facilities in this group, the mean emission factor was 0.27 kg t⁻¹, with a 95% confidence interval of ± 0.07 kg t⁻¹. Since the overall factor, based on estimated total U.S. emissions and directory-listed output as discussed above, was only 0.138 kg t⁻¹, the confidence interval was correspondingly reduced to ± 0.04 kg t⁻¹. Because the emission factors appear to have a non-normal distribution, this confidence limit must be considered approximate.

2.2. Global Data set for Pulp and Paper Manufacture

While the directory [Miller Freeman, 1996] provides a comprehensive listing of pulp and paper mills throughout the world, it does not seem to have complete coverage. In particular, the production in Russia and the Peoples' Republic of China is considerably less than that reported in UN statistics [United

Nations (UN), 1995]; one conclusion is that there are facilities in these countries that are not listed.

This was investigated further by comparing the national capacities for paper only, from the directory list, with national gross domestic products (GDPs) in U.S. dollars at merchant rates of exchange, as reported in UN [1995]. It is clear from Figure 2 that nations with higher GDPs tend to make more paper. The fitted relationship:

$$P_i = 13.23 \times E_i \quad R^2 = 0.93 \quad (1)$$

where P_i is the paper production of country I , as Gg in 1990, and E_i is the gross national product of that country, in 10⁹ U.S. dollars, is shown in Figure 2, together with its 95% confidence limits; although the usefulness of the confidence limits is questionable for a database with such a skew toward zero. Nevertheless, the values that are very wide of the line can be explained in terms of nations whose paper production is a very large component of their GDP, such as Finland, or the reverse, in the case of France, Italy, and the United Kingdom.

The paper productions of China and Russia reported to the UN are also plotted in Figure 2, as points a - d. For China, points c and d, the value at point c is unexpectedly high. This is most likely a problem with the GDP, which was converted at merchant rates to derive point c and may be unreasonably low. An alternative conversion, at "equivalent purchasing power" gives an equally large error in the opposite sense, point d on Figure 2. It is likely that an intermediate treatment of GDP would result in a point close to the fitted line. For Russia, the two different conversions of GDP derive points a and b, which show good agreement. Consequently, UN production figures were used: for both Russia and China, the paper-making capacity reported in the directory was augmented by an amount sufficient to bring it up to the paper production reported in UN [1995]. The pulp capacity reported in the directory was subsequently added in.

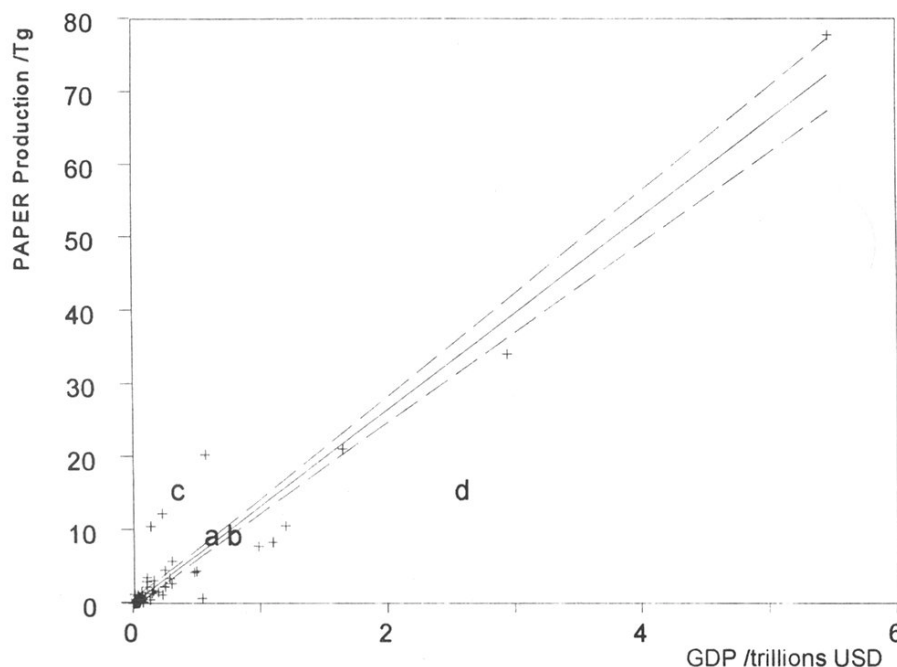


Figure 2. National paper-making capacities compared with gross domestic products for 1990. The solid line is the linear fit to the data, as in equation (1) and the dashed lines its 95% confidence limits. Production reported to the United Nations for Russia (points a and b) and China, (points c and d), are compared with two different treatments of gross domestic product, as described in the text.

2.3. Chloroform Emissions from Pulp and Paper Manufacture in Different Regions

To extend the U.S. emission factor to other regions, a transfer function was developed describing chlorine usage per ton of output in the U.S. pulp and paper industry. The function was then compared to the regional totals of pulp and paper manufacture, calculated from national outputs as reported in the directory and the relevant regional consumption of chlorine, in order to develop regional weighting functions. Regional CHCl_3 emission factors were then the product of the U.S. emission factor, established from the TRI, and these weighting functions.

The pulp and paper-producing nations comprising each region are listed in Table 1. The information on chlorine production capacity for these regions of the world [Roberts, 1992] was compared with data describing the fraction of chlorine used in each region for pulp and paper manufacture [Ayres and Ayres, 1997]. It was assumed that the product of this fraction and the chlorine production capacity represented the total chlorine used in each region by the pulp and paper sector. This assumption will be affected by underutilization of the chlorine capacity and by trade in chlorine between regions, but the first effect should be similar for each region, to a first approximation, and trade in chlorine between regions can be expected to be very small compared to regional use. Hence the functions, used in a relative sense, should be robust.

The regional CHCl_3 emission factors developed in this way are recorded in Table 1, together with the regional CHCl_3 emissions. The lower factors for Asia/Pacific and Europe are consistent with reported conversions to chlorine-free paper manufacture [Kirschner, 1997; Ondrey and Parkinson, 1997]. Furthermore, the

wide variation in the base data set from U.S. mills readily encompasses these low values.

2.4. Distributing the Emissions from Pulp and Paper Mills

For the United States, the 1.03×10^{10} grams of CHCl_3 emissions to air, surface water, and treatment and disposal plants from the pulp and paper industry, which were reported to the Toxic Release Inventory (TRI) were distributed according to the latitude and longitude designated in the TRI. The additional 2.4×10^9 g, estimated to be emitted from facilities that did not report to the TRI, were distributed on exactly the same pattern. In effect, the individual emissions in the TRI were augmented by 23%. This distribution pattern was chosen on the rationale that the additional facilities would most likely be in the same locality as those that had the requirement to report. The alternative distributor, population, would have resulted in more dispersion of the releases with most of the emissions in cities. This is almost the opposite of the CHCl_3 emission pattern reported in the TRI.

Emissions throughout the rest of the world were distributed according to the address of the mill listed in the directory, using the Times Atlas of the World [Times, 1983]. In the instances where the address was insufficient to identify a location, the output was distributed on the same pattern as the rest of the nation's production.

For China and Russia the directory output was divided into two categories, that recorded in the directory and the additional augmentation, as discussed above. The directory records were distributed geographically as in the rest of the world. The augmentation quantity was distributed using the assumption that

Table 1. Pulp and Paper Producing Countries and the Regional Emission Factors for CHCl₃

| Region | Africa | Pacific Rim | EasternEurope | Indian sub-continent | Near East | North America | South and Central America | Western Europe |
|--------------|--------------|--------------|---------------|----------------------|-----------|---------------|---------------------------|----------------|
| Nat'l. comp. | Algeria | Australia | Albania | Bangladesh | Iran | Canada | Argentina | Austria |
| | Algeria | Australia | Albania | Bangladesh | Iran | Canada | Argentina | Austria |
| | Angola | China | Bosnia | India | Iraq | Cuba | Bolivia | Belgium |
| | Cameroon | Hong Kong | Bulgaria | Nepal | Israel | Dom. Rep. | Brazil | Denmark |
| | Egypt | Indonesia | Croatia | Pakistan | Jordan | Jamaica | Chile | Finland |
| | Ethiopia | Japan | Czech Rep. | Sri Lanka | Kuwait | Mexico | Colombia | France |
| | Kenya | Korea (N) | Hungary | | Lebanon | U.S. | Costa Rica | Germany |
| | Libya | Korea (S) | Macedonia | | Syria | | Ecuador | Greece |
| | Madagascar | Malaysia | Poland | | Turkey | | El Salv. | Ireland |
| | Morocco | Myanmar | Romania | | | | Guatemala | Italy |
| | Mozambique | New Zealand | Former USSR | | | | Panama | Luxmbg. |
| | Nigeria | Phillippines | Serbia | | | | Paraguay | Nethlnds. |
| | South Africa | Singapore | Slovakia | | | | Peru | Norway |
| | Sudan | Taiwan | Slovenia | | | | Uruguay | Portugal |
| | Tanzania | Thailand | | | | | Venezuela | Sweden |
| | Tunisia | Viet Nam | | | | | | Switzlnd. |
| | Uganda | | | | | | | U.K. |
| | Zaire | | | | | | | |
| | Zambia | | | | | | | |
| | Zimbabwe | | | | | | | |
| REF | 0.052 | 0.053 | 0.25 | 0.145 | 0.154 | 0.138 | 0.111 | 0.025 |
| RRCE | 0.30 | 4.0 | 4.2 | 0.90 | 0.60 | 15.8 | 1.5 | 2.6 |

REF, Regional emission factor, g CHCl₃ kg⁻¹ pulp and paper; RRCE, Regional reactive chlorine emission in form of CHCl₃, Gg yr⁻¹

sparsely populated grid squares could not support a paper/pulp mill and that such mills are unusual in the middle of cities. Thus a pair of filters was applied to the population data: in China, weeding out any with less than 100,000 and more than 500,000 inhabitants and, in Russia, weeding out any with less than 20,000 or more than 1,000,000 inhabitants. These numbers were chosen partly, so they did not exclude any of the mills characterized in the directory at the bottom end. The distribution that results is thus that of grid squares where there could possibly be a paper or pulp mill rather than those in which a mill's presence is confirmed.

The global total CHCl₃ emission from the pulp- and paper-manufacturing sector is estimated to be 34 Gg yr⁻¹, or 30 Gg yr⁻¹ of reactive chlorine. The uncertainty, based on U.S. emission factors per mill as reported on the TRI, as discussed above, is estimated as ±8 Gg yr⁻¹ reactive chlorine.

2.5. Drinking Water and Waste Water Treatment

Chloroform and other trihalogenated methanes are created when water is treated with chlorine through the so-called haloform reaction involving humic compounds [Larson and Weber, 1994]. Trihalomethanes have been found to be ubiquitous in waters treated with chlorine, and concentrations in excess of 100 ppb [Larson and Weber, 1994; Howard, 1990] are regularly observed. Because of its relatively lower humic content, waste water generates less CHCl₃ when treated with chlorine than drinking water sources [USEPA, 1984]. Because of its relatively low solubility in water and relatively high vapor pressure, the CHCl₃

generated in water can be expected to partition into the atmosphere [Ballschmiter, 1992] and fluxes of CHCl₃ have, indeed, been observed from potable water [Keating et al., 1997] and sewerage [Haas and Herrmann, 1996]. For annual accounting it can be safely assumed that these emissions were contemporary with generation of the CHCl₃.

The quantity of CHCl₃ emitted is a function of rate at which the water is treated with chlorine or chlorine-containing compounds and the quantity of water treated. With the exception of the United States, water use per head of population in individual treated water areas appears remarkably similar [van der Leeden, 1975]. The developed world uses 40-300 L/capita/d; those who are supplied with water in the developing world use 30-200 L/capita/d [van der Leeden, 1975]. The UN statistics [UN, 1995] show that while the fraction of the population served with safe drinking water is correlated with gross domestic product (GDP) per capita, the relationship is not linear. There appears to be a cut-point at about \$2000 per capita. Above this value there are only one or two nations with less than 100% coverage of treated water. Below it the average coverage is 55.8%. It is assumed that the more sparsely populated areas are those without treated water.

For each nation with a 1990 GDP [UN, 1995] of less than \$2000 per head, the grid squares were filtered out in order of population density until the total population remaining was equal to the number of people in each nation reported as supplied with treated water [UN, 1995], or the average for that region if no value for that nation was given. For nations with a GDP of greater than \$2000 per capita, it was assumed that 100% of the water used per

person was treated.

To convert the water usage into CHCl₃ emissions, a global emission factor per head of population was developed on the basis of quantities of water used. Usage per capita in the United States is about 570 L/d [van der Leeden, 1990]. The U.S. EPA emission factor of 41 grams CHCl₃ per 10⁶ L of chlorine-treated water [USEPA, 1984], coupled with this water usage quantity, suggests a daily CHCl₃ flux of about 2.3 × 10⁻² g/person. The lower amounts of water used in the rest of the world suggest a daily CHCl₃ flux of about 4.2 × 10⁻³ g/person from this source. These rates translate to overall quantities of about 2 Gg CHCl₃ yr⁻¹ for the United States and 7 Gg yr⁻¹ for the rest of the world. Assuming that the quantity of publicly supplied water and treated wastewater is approximately the same, and using an emission factor of 14 g per 10⁶ L of chlorine-treated wastewater [USEPA, 1984], the CHCl₃ produced globally from waste watertreatment totals 3 Gg yr⁻¹. These sources together total 12 Gg yr⁻¹ (11 Gg yr⁻¹ reactive chlorine). This was distributed as the product of the appropriate annual CHCl₃ flux per capita and the population served with treated water in each gridsquare, calculated as described above.

The uncertainty in this estimate can be approached by comparing the U.S. EPA CHCl₃ emission factor with the observed average CHCl₃ concentration of U.S. drinking water of ~13 ppb [Krasner *et al.*, 1989]. Assuming that this concentration represents all the CHCl₃ produced during water treatment and that it is all ultimately released to the atmosphere, this figure leads to a U.S. CHCl₃ emission 60% lower than the 2 Gg yr⁻¹ discussed above. Indeed, it may be that the 41 g per 10⁶ L factor is too high, which is consistent with the report that drinking water is typically treated with a lower rate of chlorine today than formerly (C. Weisel, Rutgers University, personal communication, 1997). However, it is possible that in other regions of the world, higher rates of chlorine treatment prevail. Assuming a 60% uncertainty on both the lower and the upper end suggests that globally, 12 ± 7 Gg yr⁻¹ (11 ± 7 Gg yr⁻¹ chlorine) are produced from this source.

2.6. Chloroform Emissions from Cooling Water and Other Water Treatment

Water used in cooling towers and other heat exchangers is typically treated with chlorine to remove slime organisms and other biota such as mussels. Little information is available on the quantity of CHCl₃ produced in this manner. CHCl₃ is also expected to be released from swimming pools treated with chlorine-containing compounds, such as calcium hypochlorite, and from laundry bleaching with compounds including sodium hypochlorite. Because cooling waters are typically drawn from rivers, which probably have similar humic matter content to drinking water sources, it is assumed that the drinking water treatment CHCl₃ emission factor also applies to cooling waters. It is also assumed that the same rate of CHCl₃ production results from the other uses.

Apportionment of estimated quantities of chlorine used for cooling water and other water treatment, based on U.S. data [Jolley *et al.*, 1978; Anderson, 1993; *Chemical Marketing Reporter (CMR)*, 1995a,b; *Charles River Associates (CRA)*, 1993] suggests that approximately 70% as much CHCl₃ is released from cooling and other water treatments as from drinking and wastewater treatment [Aucott, 1997]. Assuming that a similar apportionment is valid globally and that a similar uncertainty exists as for drinking and wastewater treatment, 8 ± 5 Gg reactive

chlorine in the form of CHCl₃ are released from cooling and other water treatments. These emissions were distributed evenly among the global population served with treated water.

2.7. Other Industrial CHCl₃ Emissions

The principal use for CHCl₃ is as the chemical feedstock from which HCFC-22 is produced; relatively small amounts leak into the environment from the manufacturing process. It is also a by-product from other chlorinated hydrocarbon processes and similarly small amounts leak into the environment from there. The largest source of emissions is from other manufacturing processes, particularly in the pharmaceuticals industry, in which CHCl₃ is used as a solvent or process agent. Altogether, the global release from industrial sources is 11 Gg yr⁻¹, or about 10 Gg yr⁻¹ of potentially reactive chlorine. The uncertainty associated with this estimate is likely to be modest, of the order of 20%.

The function to estimate chloroform emissions from HCFC-22 manufacture was derived from the U.S. Toxic Release Inventory [USEPA, 1994]. A total of 419 Mg of CHCl₃ emissions from HCFC manufacturers are listed in this compilation, and the ratio of this value to the calculated U.S. production of HCFC-22 was used as an emission function for other countries. Built into this function are some significant assumptions: that containment of CHCl₃ in other nations is the same as that in United States and that the chemical feedstock fraction of HCFC-22 is constant among nations.

Production of HCFCs is reported by countries as part of the process of monitoring implementation of the Montreal Protocol. Results are reported as national totals of HCFC production and consumption in ODP tons (metric tons multiplied by the ozone depletion potentials of the individual compounds) [Ozone Secretariat, 1997]. In 1990 the principal compound in this data set was HCFC-22, accounting for 95% of HCFC production [Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), 1997]. For this work, estimates of national manufacture of HCFC-22 in 1990 were derived from the UN database, assuming the fraction accountable to HCFC-22 was constant, globally.

HCFC-22 is a significant raw material for fluoropolymers, but the quantities manufactured for this should not be included in the report to the UN. They will represent an additional component that will also involve CHCl₃ emissions. If this additional fraction in the United States is representative of all nations, then their CHCl₃ emissions from total HCFC-22 manufacture will be well represented using the emission function.

Robustness of the treatment can be illustrated by comparing the UN data set to that developed by AFEAS. The latter [AFEAS, 1997], from which production for feedstock is rigorously excluded, but which does not show national data, reports the total HCFC-22 production as 219.5 Gg in 1990. The equivalent number calculated by summing the national data in the UN compilation [Ozone Secretariat, 1997] is 236.5 Gg. This suggests an overreporting of only 8% in the UN data, much less than the average additional 35% of HCFC-22 that is used as a chemical feedstock but not reported in the AFEAS compilation [Midgley and Fisher, 1993]. Because the total production of HCFC-22 indicated by AFEAS, which excludes production of raw material, so closely matches the total production of HCFC-22 indicated by the UN data, there can be confidence that the UN data also largely exclude production of raw material. Therefore the UN data, which

do contain national data, can safely be used in this analysis.

The defined emissions from US facilities were distributed from the data in the TRI. Those calculated for other countries by the method described above were assigned to the production facilities reported by *Linak and Yau* [1995] in developed nations and *Alperowicz and Cox* [1987], with additional personal communication from ICF Inc., in Asian and European centrally planned economies. The facility in India is known to the authors to be in the state of Gujarat.

Other industrial CHCl₃ emissions were also calculated using a function derived from the data in the TRI and reported U.S. consumptions of CHCl₃, 672 Mg total emissions from a consumption of 10 million lbs (or 4.54 Gg) [*Linak and Yau*, 1995]. The total consumption of CHCl₃ in western Europe, reported by *Linak and Yau* [1995], was split among countries according to the productive capacity recorded. Japanese, Mexican, and Canadian consumptions were taken directly from the same reference. Consumption in eastern European countries was estimated using the information of *Alperowicz and Cox* [1987] for Poland, Romania, and Russia. No evidence for uses elsewhere in the world has been found.

Emissions of CHCl₃ from each region were then the product of the emission function and the regional consumption. For the European Union, the calculated emissions of CHCl₃ were 6.2 Gg, of which 5.9 Gg were from non-HCFC-related uses. The relatively large emissions are a consequence of the large (40 Gg) non-HCFC use reported by *Linak and Yau* [1995].

To develop a distribution model for the industrial CHCl₃ emissions, the data in the TRI were examined. These relate to 41 individual facilities with CHCl₃ emissions from general chemical use and 19 facilities with emissions from HCFC-22 production. Some 32 unique grid squares are represented, 10 of which contained, or were adjacent to grid squares that contained, sites in both sets. This is 60 times greater than the number that would have resulted from a random distribution of facilities among the more populous grid squares, and this was taken to confirm the view that population density is not a good distributor for chemicals manufactured on the scale of CHCl₃ used principally in other chemical (or related) processes. Locations of emissions associated with HCFC-22 production are known; consequently, all industrial CHCl₃ emissions were distributed on the same pattern as these releases. While this will artificially concentrate the emissions (by a factor up to 3), it is more realistic than using population.

2.8. Chloroform Emissions From Landfills, Ruminants and Combustion Processes

Khalil et al. [1990] report that biogas generators, designed to anaerobically decompose wastes to generate methane, also generate CHCl₃. M. A. K. Khalil (personal communication, 1996) has provided an emission ratio of 2×10^{-5} grams CHCl₃ for each gram methane emitted from biogas generators. Assuming that the ratio of CHCl₃ to methane emissions from landfills and waste dumps is similar, the 50 Tg of methane emitted by these sources worldwide [*Bingemer and Crutzen*, 1987; *Hogan et al.*, 1991] include about 1 Gg of CHCl₃. Ruminants, most of which are domestic, appear to release about 100 Tg of methane [*Bingemer and Crutzen*, 1987; *Hogan et al.*, 1991]. If this methane also contains trace quantities of CHCl₃ in similar proportions as biogas, then perhaps 2 Gg yr⁻¹ is emitted from this source.

Table 2. Reactive Chlorine From Anthropogenic CHCl₃ Emissions, Global Totals

| Source Category | Emission Gg yr ⁻¹ Reactive Cl | Uncertainty ± Gg yr ⁻¹ Reactive Cl |
|--|---|--|
| Pulp and paper manufacturing | 30 | 8 |
| Other industrial | 10 | 2 |
| Drinking water and wastewater treatment | 11 | 7 |
| Cooling water and other water treatments | 8 | 5 |
| Other | 3 | 3 |
| Total | 62 | ± 25 |

Trace quantities of CHCl₃ have been reported in motor vehicle exhaust [*Howard et al.*, 1990] and emitted from other combustion processes. Assessment of available data on these various combustion sources [*Aucott*, 1997] suggests that the total emission from combustion sources is in the range of 0.5 Gg yr⁻¹.

The combined reactive chlorine in the form of CHCl₃ emissions from combustion sources, landfills, and ruminants, with an estimated total in the range of 3 Gg, is too low to make a significant impact on the gridded inventory and has not been considered further.

2.9. Globally Integrated Anthropogenic CHCl₃ Emission Totals

Global total anthropogenic CHCl₃ emissions and the resulting reactive chlorine emissions are as shown in Table 2.

3. Estimation of Emissions of HCFC-22

3.1 Sources

Unlike CHCl₃, the concentration of HCFC-22 in the atmosphere is increasing [*Montzka et al.*, 1996]. This increasing concentration is a consequence of both the quantities released and the removal rate that is ~25 times less than that of CHCl₃.

HCFC-22 is the most widely used substitute for chlorofluorocarbons (CFCs), particularly in refrigeration systems; there are also some minor uses (in some parts of the world) as an aerosol propellant and a significant use as the raw material from which the fluoropolymer, PTFE (polytetrafluoroethylene), is manufactured. Although there are some process emissions, the predominant releases of HCFC-22 occur during use of the material. These releases are immediate in the case of aerosol propellants but are spread over several years from refrigeration equipment that, typically, has a service life of 20 years. Leakage may be semicontinuous from systems that are not hermetically sealed, with occasional emissions from incomplete recovery of the refrigerant during servicing and, possibly, emission of the whole charge of refrigerant as a consequence of accidental damage or disposal of the system.

The combined emission of HCFC-22 to the atmosphere was 195 Gg during 1990 [*Midgley and Fisher*, 1993]. By 1995 this had risen to 225 Gg, but over the period 1991-1995, production stayed virtually constant at 240 Gg yr⁻¹ [*AFEAS*, 1997]. This

reflects the high proportion of current production that is sold to replace previous losses from refrigeration systems. It also shows the mature nature of the halocarbon refrigeration market where the change from CFCs to HCFC-22 had been going on for many years, mainly for technical reasons. The phaseout of CFCs has not resulted in a sudden surge in demand for HCFC-22. The rise in production of all HCFCs, which has been reported as required by the Montreal Protocol [Oberthür, 1997; Ozone Secretariat, 1997], is consistent with most of the increase being for HCFC-141b (dichlorofluoroethane) and HCFC-142b (chlorodifluoroethane) which are used as solvents and in the manufacture of insulating foam [AFEAS, 1997].

3.2. National Emissions

The national data collected by the UN Environment Programme are reported for consumption of all HCFCs, together, as calculated ODP tons (the product of ozone depletion potential and the mass sold within the country as metric tons). Thus these reports cannot provide rigorous data on the use of an individual material, such as HCFC-22, and their value is restricted to the sort of consistency check described above. Furthermore, "consumption" in this context is defined as the net flow of material (production plus imports minus exports) for one country or economic area. It is not the same as the emission from that area; this is estimated from the sales into end uses, each of which has a distinct temporal pattern of release. Calculations of this form were performed by Midgley and Fisher [1993] for their estimates of global releases of HCFC-22.

It has been shown that the global total emissions of a refrigerant such as CFC-12 can be distributed among countries on the basis of the national fraction of the global GDP [McCulloch *et al.*, 1994] and this technique was extended to the emissions of HCFC-22 [Midgley and McCulloch, 1997]. This work showed that HCFC-22 was emitted from some 110 countries, predominantly in the developed Northern hemisphere. The larger emissions came from the United States (82 Gg), the European Union (35 Gg), the former USSR (21 Gg), and Japan (13 Gg), with smaller emissions from developing nations such as China (2 Gg) and India (3 Gg).

3.3. Distribution Within Each Nation

Given the estimate of national quantities emitted, a function to distribute emissions geographically within each country is still necessary. HCFC-22 is used principally in retail and commercial cold stores and in smaller-scale air conditioning systems (particularly hermetic "window units"), and so it is likely to be used most heavily in the most populated areas. Emissions are almost certain to have the same geographical distribution as use; relatively little HCFC-22 is used in mobile systems. Thus the national emissions estimated by Midgley and McCulloch [1997] were distributed by population density, as reported by Li [1996].

4. Discussion

The anthropogenic fluxes of reactive chlorine in the form of CHCl₃ and chlorodifluoromethane have been distributed in 1° latitude x 1° longitude grid squares using various methods as described for the particular source categories discussed above (Plates 1 and 2). The distribution for CHCl₃ shows large point sources within the United States, Europe, and Japan. In the United States, these are primarily pulp- and paper-manufacturing

facilities, while in Europe and Japan, the point sources represent estimated releases from chemical manufacturers and related industries. There are also large regional emissions of CHCl₃ in Europe, the former USSR, China, and the Indian subcontinent associated with pulp and paper manufacture. In the absence of the facility specific emission data that are available only for the United States, these emissions have been distributed on the basis of known locations of pulp and paper manufacturers, apportioned by region based on output quantities and chlorine use, as described above.

The distribution for HCFC-22 essentially tracks the distribution of air conditioning and refrigeration equipment. Hence it follows the pattern of population in industrialized regions.

Significant seasonal variations of the anthropogenic source of each compound are not expected. In the case of CHCl₃, most of the emissions are associated with large continuous-process industrial operations such as paper mills or chemical production plants. Somewhat higher emissions in summer and fall of CHCl₃ emissions from water treatment have been observed [Howard *et al.*, 1990], likely due to increased humic content of source waters. Emissions of HCFC-22 are expected to be relatively constant throughout the year because they are primarily a function of the design of equipment and the way that it is maintained and, as a rule, do not depend on operating conditions.

There is a small upward trend in HCFC-22 emissions amounting to less than 3% yr⁻¹ over the period 1990-1995. On the other hand, there may be a downward trend in industrial CHCl₃ emissions. CHCl₃ releases from all facilities reporting in the U.S. TRI show a consistent decline from 1988 to 1994, dropping over this period from 12.3 Gg to 5.2 Gg [USEPA, 1996a]. This decrease almost certainly reflects process improvements and substitution of nonchlorine bleaching by the pulp and paper industry as well as other changes. On the basis of the 1990 data used in this analysis, the pulp and paper and other industrial sectors contribute two thirds of the anthropogenic CHCl₃ emission. If the decline, evident from the TRI, in CHCl₃ release from the United States is mirrored globally, total anthropogenic releases of this chemical are lower today than the quantity estimated in this work for 1990.

The estimated 62 ±25 Gg yr⁻¹ anthropogenic source of reactive chlorine in the form of CHCl₃ discussed herein should be compared with natural and biomass burning sources. Natural sources are estimated to contribute 0.5 Tg Cl per year in the form of CHCl₃ [Khalil *et al.*, 1999]. This is 8 times as much as the anthropogenic source. Biomass burning sources of CHCl₃ [Lobert *et al.*, 1999] are estimated to contribute 2 Gg Cl. The global budget of CHCl₃ is discussed by Keene *et al.* [1999]. Keene, *et al.* compare the latitudinal distribution of estimated integrated annual CHCl₃ emissions with modeled sinks using an inversion modeling approach. This comparison reveals substantial regional discrepancies. Globally, however, the overall imbalance between integrated emissions and sinks is relatively small.

5. Summary

As part of the Reactive Chlorine Emissions Inventory (RCEI) project to estimate and map global emissions of reactive chlorine compounds (see other articles in 1999), estimates of anthropogenic emissions of CHCl₃ and HCFC-22 as of 1990 have been developed and plotted on a global 1° latitude x 1° longitude grid.

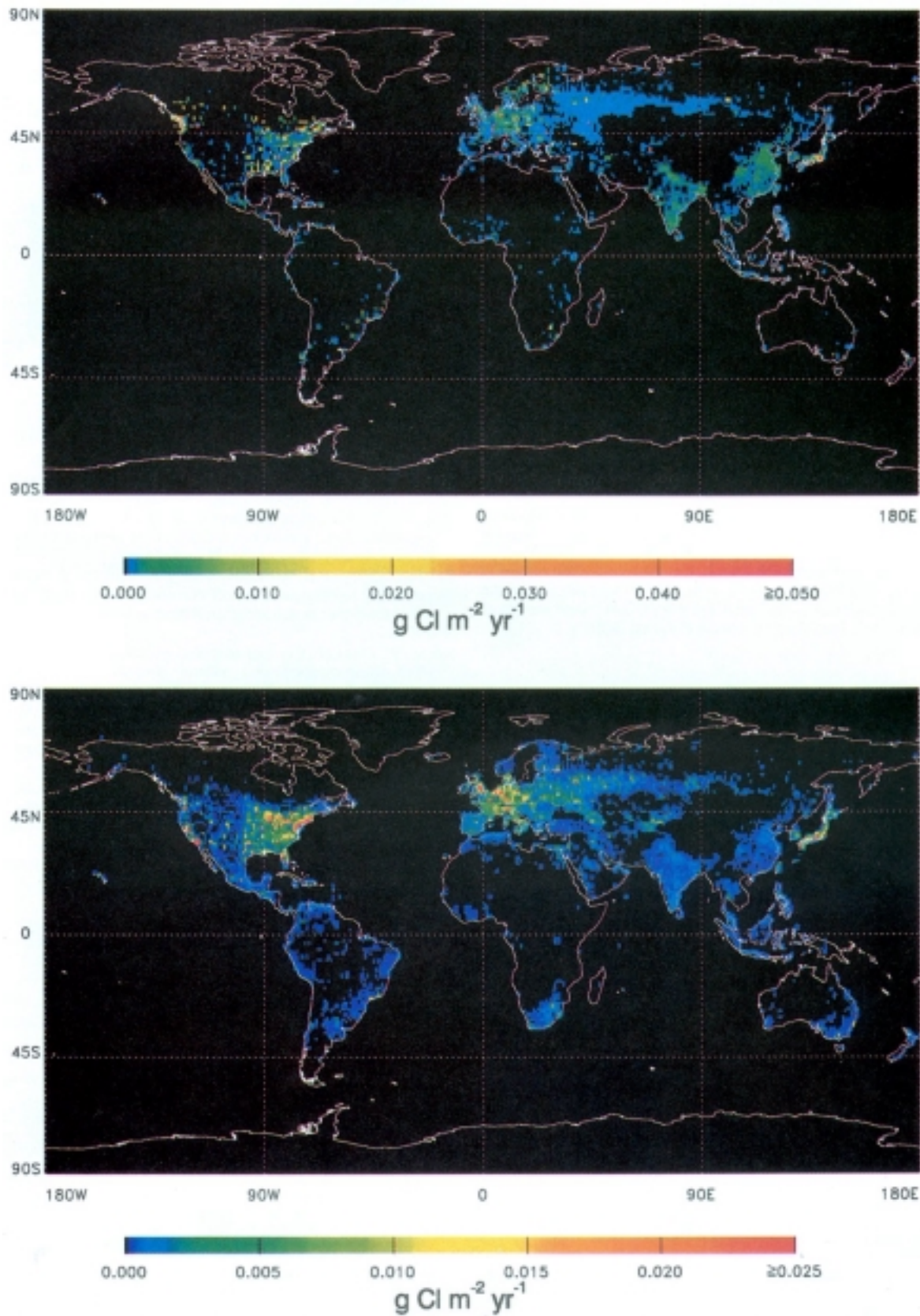


Plate 1. Anthropogenic emissions of CHCl₃ (above) and HCFC-22 (below), distributed globally in 1° x 1° latitude x longitude grid squares.

Global anthropogenic emissions of reactive chlorine in the form of CHCl₃ are estimated as 62 ± 25 Gg yr⁻¹. This is consistent with a recent North American anthropogenic CHCl₃ source estimate of 17 ± 6 Gg yr⁻¹ [Bakwin et al., 1997], based on a series of atmospheric measurements. A global anthropogenic flux in this range is much too low to account for the observed global background concentrations. It is clear that other sources, probably including oceanic, terrestrial, and biomass burning, must make major contributions to the global source total. Although anthropogenic sources of CHCl₃ are relatively insignificant at a global level compared to other sources, it should be noted that industrial or other releases of CHCl₃, concentrated at specific point sources, may have severe local or regional impacts.

1990 emissions of HCFC-22 are estimated as 80 ± 0.6 Gg yr⁻¹ active chlorine. This compound almost certainly has no significant natural sources. Its atmospheric concentration and rate of increase appear consistent with the anthropogenic flux described in this work and with the estimated atmospheric removal rate.

Acknowledgments. We thank anonymous referees for helpful comments. Financial support was provided by the Chemical Manufacturers' Association via the Chlorine Chemistry Council and from the European Chemical Industry (CEFIC) via Euro Chlor. This work is part of the Reactive Chlorine Emissions Inventory (RCEI), a subgroup of the Global Emissions Inventory Activity (GEIA), itself part of the International Global Atmospheric Chemistry (IGAC) core project of the International Geosphere-Biosphere Program (IGBP).

References

- Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), *Production, Sales and Atmospheric Release of Fluorocarbons through 1995*, Washington, D.C., 1997.
- Albritton, D., R. Derwent, I. Isaksen, M. Lal, and D. Wuebbles, Radiative forcing of climate change: Trace gas radiative forcing indices, chap. 2, in *Climate Change 1995, The Science of Climate Change*, edited by J.T. Houghton, L.G. Meira Filho, B.A. Callander, N. Harris, A. Kattenberg, and K. Maskell, Cambridge Univ. Press, New York, 1995.
- Alperowicz, N., and A. Cox, *On Course to Reform: The East European chemical industry, 1986-90*, Chemicon Surv. Ltd., London, 1987.
- Anderson, E., Chlorine producers fight back against call for chemical's phaseout, *Chem. Eng. News*, 71, 11, 1993.
- Aucott, M., 1997, *Chlorine atoms and the global biogeochemical chlorine cycle: Estimation of the global background tropospheric concentration of chlorine atoms and discussion of key aspects of the chlorine cycle*, Ph.D. dissertation, Rutgers Univ., New Brunswick, N.J., 1997.
- Ayres, E., Whitewash: Pursuing the truth about paper, *World Watch*, 5, 17-25, 1992.
- Ayres, R. U., and L. W. Ayres, The life cycle of chlorine, part II: Conversion processes and use in the European chemical industry, *J. Ind. Ecol.*, 1, 65-89, 1997.
- Bakwin, P. S., D. F. Hurst, P. P. Tans, and J. W. Elkins, Anthropogenic sources of halocarbons, sulfur hexafluoride, carbon monoxide, and methane in the southeastern United States, *J. Geophys. Res.* 102, 15,915-15,925, 1997.
- Ballschmiter, K., Transport and fate of organic compounds in the global environment, *Angew. Chem. Int. Ed. Engl.*, 31, 487-515, 1992.
- Bingemer, H. G., and P. J. Crutzen, The production of methane from solid wastes, *J. Geophys. Res.*, 92, 2181-2187, 1987.
- Blum, L., Recommendations of the paper task force: The minimum impact bleached kraft pulp mill, in Proceedings of the conference on *The Future Uses of Chlorine: Issues in Education, Research and Policy*, Mass. Inst. of Technol., Cambridge, Mass., 1996.
- Charles River Associates (CRA) Inc., *Assessment of the Economic Benefits of Chlor-Alkali Chemicals to the United States and Canadian Economies*, Boston, Mass., 1993.
- Chemical Marketing Reporter (CMR), Chemical profile: Calcium hypochlorite, Schnell, New York, 1995a.
- Chemical Marketing Reporter (CMR), Chemical profile: Chlorine, Schnell, New York, 1995b.
- Fraser P., M. Gunson, S. Penkett, F.S. Rowland, U. Schmidt, and R. Weiss, Measurements, Chap. 1, in *Report on Concentrations, Lifetimes and Trends of CFCs, Halons and Related Species*, edited by J. Kaye, S. Penkett, and F. Ormond, NASA Ref. Publ. 1339, 1994.
- Graedel, T. E., and W. C. Keene, Preface, *J. Geophys. Res.*, 8331-8332, 1999.
- Haas, B.S., and R. Herrmann, Transport of chlorinated hydrocarbons between sewage and sewer atmosphere, *Water Sci. Technol.*, 34 (3-4), 557-564, 1996.
- Hogan, K., J. Hoffman, and A. Thompson, Methane on the greenhouse agenda, *Nature*, 354, 181-182, 1991.
- Howard, P. (Ed.), *Handbook of Environmental Fate and Exposure Data for Organic Chemicals, vol. II, Solvents*, Lewis, Boca Raton, Fla., 1990.
- Isodorov V.A., I.G. Zenkhevich, and B.V. Ioffe, Volatile organic compounds in sulfatitic gases, *J. Atmos. Chem.*, 10, 329-340, 1990.
- Jolley, R. L., G. Jones, W. W. Pitt and J. E. Thompson, Chlorination of organics in cooling waters and process effluents, in *Water Chlorination: Environmental Impact and Health Effects*, edited by R.L. Jolley, vol. 1, Butterworth-Heinemann, Newton, Mass., 1978.
- Juuti, S., T. Vartiainen, P. Joutsenoja and J. Ruuskanen, Volatile organochlorine compounds formed in the bleaching of pulp with ClO₂, *Chemosphere*, 33 (3), 437-448, 1996.
- Keating, G.A., T.E. McKone, and J.W. Gillett, Measured and estimated air concentrations of chloroform in showers: Effects of water temperature and aerosols, *Atmos. Environ.*, 31 (2), 123-130, 1997.
- Keene, W.C., M.A.K. Khalil, D.J. Erickson, A. McCulloch, T.E. Graedel, J.M. Lobert, M.L. Aucott, S.-L. Gong, D.B. Harper, G. Kleiman, P. Midgley, R.A. Moore, C. Seuzaret, W.T. Sturges, C.M. Benkovitz, V. Koropalov, L.A. Barrie, and Y.-F. Li, Composite global emissions of reactive chlorine from anthropogenic and natural sources: The reactive chlorine emissions inventory, *J. Geophys. Res.* 104, 8429-8440, 1999.
- Khalil, M.A.K., R.A. Rasmussen, M. Wang, and L. Ren, Emissions of trace gases from Chinese rice fields and biogas generators: CH₄, N₂O, CO, CO₂, chlorocarbons, and hydrocarbons, *Chemosphere*, 20, 207-226, 1990.
- Khalil, M.A.K., R.M. Moore, D.B. Harper, J.M. Lobert, V. Koropalov, W.T. Sturges, and W.C. Keene, Natural emissions of chlorine-containing gases: The reactive chlorine emissions inventory, *J. Geophys. Res.* 104, 8347-8372, 1999.
- Kirschner, E. M., Closing the loop: Papermakers use new chemicals and technologies to cut bleaching effluents, *Chem. Eng. News*, 75, 15-17, 1997.
- Krasner, S., M. McGuire, J. Jacangelo, N. Patania, K. Reagan, and E. Aieta, 1989, The occurrence of disinfection by-products in US drinking water, *J. Am. Water Works Assoc.*, 81, 41-53, 1989.
- Larson, R., and Weber, E., *Reaction Mechanisms in Environmental Organic Chemistry*, 433 pp., Lewis, Boca Raton, Fla., 1994.
- Li, Y.-Fan, *Global Population Distribution Database*, Can. Global Emiss. Invent. Cent., Atmos. Environ. Serv., Environ. Can., Downsview, Ontario, 1996.
- Linak E. and P. Yau, *Chlorinated Methanes in Chemical Economics Handbook*, SRI Int., Menlo Park, Calif., 1995.
- Lobert, J. M., W. C. Keene, J. A. Logan, and R. Yevich, Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory, *J. Geophys. Res.*, 8373-8389, 1999.
- McCulloch, A., P.M. Midgley, and D.A. Fisher, Distribution of emissions of chlorofluorocarbons (CFCs) 11, 12, 113, 114 and 115 among reporting and non-reporting countries in 1986, *Atmos. Environ.*, 28, 2567-2582, 1994.
- Midgley, P.M., and D.A. Fisher, The Production and release to the atmosphere of chlorodifluoromethane (HCFC-22), *Atmos. Environ.*, 27(A), 2215-2223, 1993.
- Midgley, P.M. and A. McCulloch, Estimated national releases to the atmosphere of chlorodifluoromethane (HCFC-22) during 1990, *Atmos. Environ.*, 31(6), 809-811, 1997.
- Miller Freeman Information Services (Miller Freeman), *International Phillips' 97 Paper Directory*, Miller Freeman Tech. Ltd., Kent, England, 1996.
- Montzka, S.A., J.H. Butler, R.C. Myers, T.M. Thompson, T.H. Swanson, A.D. Clarke, L.T. Lock, and J.W. Elkins, Decline in the tropospheric abundance of halogen from halocarbons: Implications for stratospheric ozone depletion, *Science*, 272, 1318-1322, 1996.
- National Council of the Paper Industry for Air and Stream Improvement (NCASI), *Results of Field Measurements of Chloroform Formation and Release From Pulp Bleaching*, Tech. Bull. 558, Nat. Council of the Paper Ind. for Air and Stream Imp., Inc., New York, 1988.
- Oberthür S., *Production and Consumption of Ozone-Depleting Substances*

- 1986-1995: *The data reporting system under the Montreal Protocol*, D. Gesell. für Tech. Zusammenarb. (GTZ) GmbH, Eschborn, Germany, 1997.
- Ondrey, G. and G. Parkinson, Closing the pulp-bleaching cycle, *Chem. Eng. 104*, 33-37, 1997.
- Ozone Secretariat, Production and consumption of ozone depleting substances 1986-1995, ISBN 92-807-1665-4, Ozone Secret. to the UN Environ. Programme, Nairobi, Kenya, 1997.
- Roberts, M., Structural changes in chlor-alkali, *Chem. Week*, 151, 36, 1992.
- Sanhueza, E., Source gases: Trends and budgets, chap.2, in *Scientific Assessment of Ozone Depletion: 1994*, edited by D.L. Albritton, R.T. Watson, and P.J. Aucamp, *WMO Rep. 37*, Global Ozone Res. and Monit. Project, World Meteorol. Organ., Geneva, 1994.
- Times, *The Times Atlas of the World: Comprehensive Edition*, Times Books, London, 1983.
- United Nations (UN), *Statistical Yearbook, 39th ed.* [CD-ROM version E.95.XVII.5], UN Publ., Geneva, 1995.
- U.S. Environmental Protection Agency (USEPA), *Locating and Estimating Air Emissions From Sources of Chloroform*, EPA-450/4-84-007c, Nat. Tech. Inf. Serv., U.S. Dep. of Comm., Springfield, Va., 1984.
- U.S. Environmental Protection Agency (USEPA), *EPA 1987-1992 toxic release inventory*, [CD-ROM version reference EPA 749/C-94-001], Off. of Pollut. Prev. and Toxics, Washington, D.C., 1994.
- U.S. Environmental Protection Agency (USEPA), *1993 toxics release inventory: Public data release*, EPA 745-R-95-010, Off. of Pollut. Prev. and Toxics, Washington, D.C., 1995.
- U. S. Environmental Protection Agency (USEPA), *1994 toxics release inventory: Public data release*, EPA 745-R-96-002, Off. of Pollut. Prev. and Toxics, Washington, D.C., 1996a.
- U.S. Environmental Protection Agency (USEPA), *Review draft: Chemical pulping emission factor development document*, Off. of Air Qual. Plan. and Stand., Emissions Stand. Div., Research Triangle Park, N.C., 1996b.
- van der Leeden, F., *Water Resources of the World*, Water Inf. Cent. Inc., Port Washington N.Y., 1975.
- van der Leeden, F., F. Troise, and D. Todd, *The Water Encyclopedia*, Lewis, Boca Raton, Fla., 1990.
-
- M. Aucott, New Jersey Department of Environmental Protection, P.O. Box 418, Trenton, NJ 08625. (maucott@igc.org)
- A. McCulloch, ICI Chemicals & Polymers Ltd., Runcorn, UK. (archie_mcculloch@ici.com)
- T.E. Graedel, School of Forestry and Environmental Studies, Yale University, New Haven, CT 06520. (thomas.graedel@yale.edu)
- G. Kleiman, Center for Global Change Science, M.I.T., Cambridge, MA 02139. (gary@jake.mit.edu)
- Pauline M. Midgley, M & D Consulting, Ludwigstrasse 49, 70771 Leinfelden, Germany. (101636.11@compuserve.com)
- Y.-F. Li, AES, Environment Canada, Downsview, Ontario, Canada (yf.li@ec.gc.ca)

(Received May 5, 1998; revised January 27, 1999;
accepted January 28, 1999.)