

Industrial emissions of trichloroethene, tetrachloroethene, and dichloromethane: Reactive Chlorine Emissions Inventory



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Abstract. The identified emissions of the title compounds come predominantly from their use in industrial and commercial processes. Trichloroethene and tetrachloroethene have also been found as byproducts of gasoline and coal combustion; these sources were also considered but shown to be insignificant compared with industrial releases. Global emissions during 1990, amounting to 0.241 ± 0.013 Tg of trichloroethene, 0.366 ± 0.020 Tg of tetrachloroethene, and 0.583 ± 0.032 Tg of dichloromethane (0.195 ± 0.010 , 0.313 ± 0.017 , and 0.487 ± 0.027 Tg as chlorine, respectively) have been assigned to individual countries and thence to a 1° latitude \times 1° longitude grid based on a combination of three data sets: regional sales data that were available on a continental scale; economic activity in the form of national Gross Domestic Products; and the population distribution within each country. For those countries where they were available, data for the quantities and locations of reported emissions were also incorporated. Uncertainty in the distributed emissions is $\pm 4\%$ relative to countries with the largest emissions. The results, which are complementary to the marine fluxes and releases from biomass burning reported by *Khalil et al.* [1999] and *Lobert et al.* [1999], respectively, are recorded here as maps and are also available from the Global Emissions Inventory Activity web site at <http://groundhog.sprl.umich.edu/geia/rcei/>. While the industrial regions of North America, Europe, and Japan are the largest sites of anthropogenic emissions, there are also significant sources in the developing nations of Asia; in contrast, anthropogenic emissions within the southern hemisphere are much smaller and more widely dispersed. The total emissions of dichloromethane appear to match the observed atmospheric concentrations, but about 25% of the flux of tetrachloroethene calculated from observations remains unaccounted, and significant extra emissions of trichloroethene are necessary to effect a balance. The known sources have been examined thoroughly in this work, and so it is reasonably certain that the additional emissions are not a deliberate result of human activity; however, there is no means of discriminating their origin unequivocally, and the missing quantities may be inadvertent byproducts of anthropogenic activities.

1. Introduction

Chlorinated hydrocarbons, trichloroethene ("Tri," "TriK," C_2HCl_3), tetrachloroethene ("Per," "Perc," C_2Cl_4), and dichloromethane (methylene chloride, CH_2Cl_2), are used in a wide variety of industrial, commercial, and consumer applications. With the exception of use as chemical feedstocks, all of the applications are potentially dispersive,

so that emissions are equivalent to the quantities sold unless specific steps are taken to capture and destroy used materials [*Midgley*, 1989]. Extensive recycling takes place within the use systems themselves and through external solvent recycling contractors, but unless they are deliberately destroyed, the materials are ultimately released into the environment whence they partition into the atmosphere [*Ballschmiter*, 1992; *Dyrssen et al.*, 1990].

Other potential sources of these chemicals in the atmosphere include the exhaust gases of gasoline fuelled vehicles [*Gilli et al.*, 1989] and the combustion of coal [*Garcia et al.*, 1992]. The quantities involved have been estimated in this work and shown to be insignificant compared to the industrial and commercial emissions and so are not included in the calculated distribution. Nonindustrial fluxes are discussed in companion papers; biomass burning is a small source, significant only for dichloromethane [*Lobert et al.*, 1999], and the most significant nonanthropogenic fluxes of these materials that have been identified are from the oceans [*Khalil et al.*, 1999].

Much of the information on emissions to the atmosphere of these chlorinated hydrocarbons has been the result of informal estimates or calculations based on atmospheric measurements. For example, *Wiedmann et al.* [1994] used an arbitrary factor to convert estimates of U.S. production of tetrachloroethene into a global value; and

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Table 1. Use and Emissions of Chlorinated Hydrocarbons During 1990 Within Geographical Groups

Geographical Group	Chlorinated hydrocarbon, kt
North America	
Canada, Puerto Rico, U.S.A.	trichloroethene: 43 tetrachloroethene: 127 dichloromethane: 157
Europe	
Andorra, Austria, Belgium, Cyprus, Denmark, Faeroe Islands, Finland, France, Germany, Greece, Greenland, Iceland, Ireland, Italy, Liechtenstein, Luxembourg, Malta, Monaco, Netherlands, Norway, Portugal, San Marino, Spain, Sweden, Switzerland, Turkey, United Kingdom	trichloroethene: 104 tetrachloroethene: 124 dichloromethane: 187
Far East	
Japan, Korea (N), Korea (S), Peoples Republic of China, Taiwan	trichloroethene: 61 tetrachloroethene: 47 dichloromethane: 103
Northern Hemisphere Tropics	
Anguilla, Antigua & Barbuda, Bahamas, Bahrain, Bangladesh, Barbados, Belize, Benin, Bhutan, British Virgin Islands, Brunei Darussalam, Burkina Faso, Cambodia, Cameroon, Cape Verde Islands, Cayman Islands, Central African Republic, Chad, Cocos Islands, Colombia, Costa Rica, Cote d'Ivoire, Cuba, Djibouti, Dominica, Dominican Republic, Egypt, El Salvador, Equatorial Guinea, Ethiopia, Gabon, Gambia, Ghana, Grenada, Guadeloupe, Guatemala, Guinea, Guinea Bissau, Guyana, Haiti, Honduras, Hong Kong, India, Indonesia, Jamaica, Kuwait, Laos, Liberia, Libya, Malaysia, Maldives, Martinique, Mauritania, Mexico, Montserrat, Myanmar, Netherlands Antilles, Nicaragua, Niger, Nigeria, Oman, Pakistan, Panama, Philippines, Qatar, Sao Tome Principe, Saudi Arabia, Senegal, Seychelles, Sierra Leone, Singapore, Somalia, Sri Lanka, St. Kitts Nevis, St. Lucia, St. Vincent & Grenadines, Sudan, Suriname, Thailand, Togo, Trinidad & Tobago, Uganda, United Arab Emirates, Venezuela, Western Sahara, Vietnam, Yemen	trichloroethene: 14 tetrachloroethene: 28 dichloromethane: 52
Other Northern Hemisphere	
Afghanistan, Albania, Algeria, Armenia, Azerbaijan, Belarus, Bermuda, Bulgaria, Croatia, Czech Republic, Estonia, Georgia, Hungary, Iran, Iraq, Israel, Jordan, Kazakhstan, Kyrgyzstan, Latvia, Lebanon, Lithuania, Moldova, Mongolia, Morocco, Nepal, Poland, Romania, Russian Federation, Slovakia, Slovenia, Syrian Arab Republic, Tajikistan, Tunisia, Turkmenistan, Ukraine, Uzbekistan, Yugoslavia	trichloroethene: 16 tetrachloroethene: 35 dichloromethane: 66
Southern Hemisphere	
Angola, Argentina, Australia, Bolivia, Botswana, Brazil, Burundi, Chile, Christmas Island, Comoros, Congo, Cook Islands, Ecuador, Fiji, French Polynesia, Kenya, Kiribati, Lesotho, Madagascar, Malawi, Mali, Marshall Islands, Mauritius, Micronesia, Mozambique, Namibia, Nauru, New Caledonia, New Zealand, Niue, Norfolk Island, Papua New Guinea, Paraguay, Peru, Reunion, Rwanda, Solomon Islands, South Africa, Swaziland, Tanzania, Tokelau, Tonga, Tuvalu, Uruguay, Vanuatu, Western Samoa, Zaire, Zambia, Zimbabwe	trichloroethene: 3 tetrachloroethene: 4 dichloromethane: 16

Koppmann et al. [1993] derived estimates of dichloromethane and tetrachloroethene emitted globally on the basis of their measurements of the concentrations of these materials over the Atlantic Ocean. Neither approach is particularly satisfactory from the point of view of using the compounds as tracers to help to develop understanding of atmospheric processes.

Estimates of emissions developed from audited sales data are of greater value in this endeavor because they are independent data with quantified and small uncertainties. Such estimates of emissions were developed by *McCulloch and Midgley* [1996] based on reported sales of trichloroethene, tetrachloroethene, and dichloromethane within six discrete geographical areas. These covered sales into all applications other than chemical feedstock throughout the world, and the reported uncertainties in the global totals were 5.5%.

The chlorinated hydrocarbons examined here have atmospheric lifetimes, toward oxidation by OH radicals, that are all substantially less than 6 months [*Prather et al.*, 1991], so that they are sufficiently reactive that the temporal (seasonal) and geographical distributions of their emissions need to be known if the data are to be used for modeling atmospheric chemistry and dynamics [*Franklin and Sidebottom*, 1996]. The seasonality of emissions was addressed by *McCulloch and Midgley* [1996]; dichloromethane was picked as the model compound which could be expected to show the greatest

seasonal trends in emissions because more of its applications are commercial and domestic than is the case with the other two chlorinated hydrocarbons. The sales of dichloromethane over a period of 2 years were examined in detail to ascertain whether there were seasonal trends. It was clear that there were no discernible trends through the year, either overall, or among end uses, or among the geographical regions into which the world was divided in the study, and it was concluded that, for these short-lived chlorinated hydrocarbons that are used in industrial and consumer applications, annual sales (and hence annual emissions) were best distributed evenly throughout the year. The seasonal trends in atmospheric measurements reported by *Wang et al.* [1995], *Rudolph et al.* [1996], and *Blake et al.* [1997] for tetrachloroethene can therefore be assumed to be due entirely to environmental phenomena, with no interference from anthropogenic emission patterns.

While releases of the compounds over a short time period are best treated as being the appropriate fraction of annual emissions (with uncertainty increasing inversely to the size of that fraction), the geographical split of anthropogenic emissions is liable to be very uneven. Factors such as population density and economic activity are likely to have considerable influences. In this work, the emissions estimated from regional sales data are distributed among countries on the basis of their economic activity as described by the national Gross

Domestic Product. From this distribution, the emissions are mapped onto a 1° latitude by 1° longitude grid over the whole of the Earth's surface, using the distribution of population within each country. At this scale, each grid square covers a region of about 100 km by 100 km, and the emissions described here are better resolved spatially than the current atmospheric models. This should help to discriminate the regional and topographical features that influence atmospheric chemistry and transport.

2. GDP as a Distribution Parameter

A previous study of chlorofluorocarbon (CFC) emissions showed Gross Domestic Product (GDP) to be a useful basis on which to distribute releases among countries [McCulloch *et al.*, 1994]. In that study, it was shown that the national fraction of the global industrial releases of CFCs in 1986 was directly proportional to the national fraction of the global total of GDPs. This gave a means to distribute among countries the global total of CFC use and releases, compiled by the *United Nations Environment Programme (UNEP)* [1990] and the *Alternative Fluorocarbons Environmental Acceptability Study (AFEAS)* [1992], using the national economic statistics of the *United Nations (U. N.)* [1990]; and a similar stratagem was adopted in this work using the more up to date economic statistics of *U. N.* [1995].

Use and emissions of trichloroethene, tetrachloroethene, and dichloromethane, individually, were calculated by McCulloch and Midgley [1996] for the geographical areas listed in Table 1 for the years 1988 to 1992, enabling the total use of chlorinated hydrocarbon solvents to be calculated for each region for each year. From the statistics of *U. N.* [1995], the "regional" GDP can be calculated for the countries as listed in Table 1 as the sum of appropriate national GDPs. While there is not a good correlation between the regional use of individual chlorinated hydrocarbons shown in Table 1 and fractional GDP (as an indicator of relative regional economic activity), there is a clear relationship between fractional GDP and the use of the three compounds combined. The regional fraction of the global total of the use of all three chlorinated hydrocarbons is directly proportional to the regional fraction of the global GDP, according to the equation

$$F_S = 1.134 \times F_E - 0.0224 \quad R^2 = 0.989 \quad (1)$$

where F_S is the fraction of the global use of all the title solvents within the region and F_E is the fraction of the global total of GDP for the nations in the region.

The fitted line and its 95% confidence limits are shown in Figure 1. The goodness of the fit to the combined use of these chlorinated hydrocarbons can be ascribed to the fact that they are mature products that are part of the fabric of industry; their combined use is governed almost wholly by economic activity. Regional differences, particularly in the types of industrial activity, dictate the preferences for individual compounds, but relative economic activity determines relative usage of all. The value of the equation lies in the fact that it allows the distribution of an independently derived usage among component groups of nations using the appropriate fraction of a total economic measure. Furthermore, the equation gives negative values at a regional fraction of GDP below $2 \pm 1\%$ of the global total. This was interpreted as providing a cutoff that could be used as a mechanism to exclude countries with low economic activity in relation to their region.

3. National Use of Trichloroethene, Tetrachloroethene and Dichloromethane

The underlying economic rationale for the relationship in equation

(1) permits extension of the treatment to the smallest scale at which there is independent usage data (the regional data given in Table 1) and to use national fractions of the regional GDP to distribute the usage of chlorinated hydrocarbons reported within each geographical region. Accordingly, a revised version of equation (1) was developed

$$R_S = \sum_j (R_S \times F_S^j) = \sum_j (R_S \times (1.134 \times F_E^j - c)) \quad (2)$$

where R_S is the regional use of each chlorinated hydrocarbon from McCulloch and Midgley [1996], F_S^j is the fraction of use within the region for nation j , F_E^j is the national fraction of regional GDP, such that $\sum_j F_S^j$ and $\sum_j F_E^j$ are both unity, and c is the cutoff constant for the region.

This equation retains the proportionality constant from equation (1). At the highest fractional GDP in the treatment, proportionality accounts for 95% of the calculated usage. The total uncertainty in total use of all three halocarbons at that point is 4% of scale, with 2.4% due to uncertainty in the slope of the line. At the other end of the scale, the situation is reversed, and the cutoff constant defines almost all of the calculated usage and accounts for 60% of its uncertainty. In order to exclude the countries within each region where usage was very small and highly uncertain, separate cutoff constants c were calculated for each of the five geographical regions. Within each region, use will range from zero to the substantial fraction accountable to the largest country. Furthermore, the buildup of regional usage is quantized, it is the accumulation of discrete step changes from each country. Consequently, the cutoff constant was fitted by removing nations from the regional group, one by one in ascending order of their fraction of the regional GDP and recalculating the fit with a fixed proportionality constant (1.134). The actual values for c that gave the best fit for equation (2) were 0.0174 for Europe, 0.0167 for the northern hemispherical midlatitudes, 0.02 for the northern hemispherical tropics and 0.016 for the southern hemisphere. For the United States and Canada and for the Far East, the cutoff constant was kept at 0.0224 because there were insufficient countries in these regions to allow the treatment to work.

4. National Emissions

Since the basic data are sales for potentially dispersive end uses, excluding both materials destroyed after use and chemical feedstocks, national emissions are the same as national use. As discussed by McCulloch and Midgley [1996], these emissions were taken to occur in the year in which the sales were reported. The calculated emissions in 1990, for each country for which the fraction of the regional GDP was above the cutoff constant, are shown in Table 2.

5. Sources Other Than Industrial

In a limited study of the exhaust gases from gasoline-fueled vehicles in Italy, Gilli *et al.* [1989] showed one and two carbon halogenated hydrocarbons to be present at up to $2450 \mu\text{g m}^{-3}$. The concentrations were proportional to the distances that had been covered by the test cars, and even the vehicle running on unleaded gasoline had $250 \mu\text{g m}^{-3}$ in the exhaust. In all cases, trichloroethene was the most abundant component and, with the exception of a very small amount of tetrachloroethene in the exhaust of a much traveled vehicle, was the only compound of interest to the work in this paper.

Global gasoline consumption in 1990 was some 730 Tg, 45% in the United States and Canada [International Energy Agency (IEA), 1992a,b]. It is estimated that approximately 300 Tg of the global usage in 1990 was leaded, and so using average emission factors from

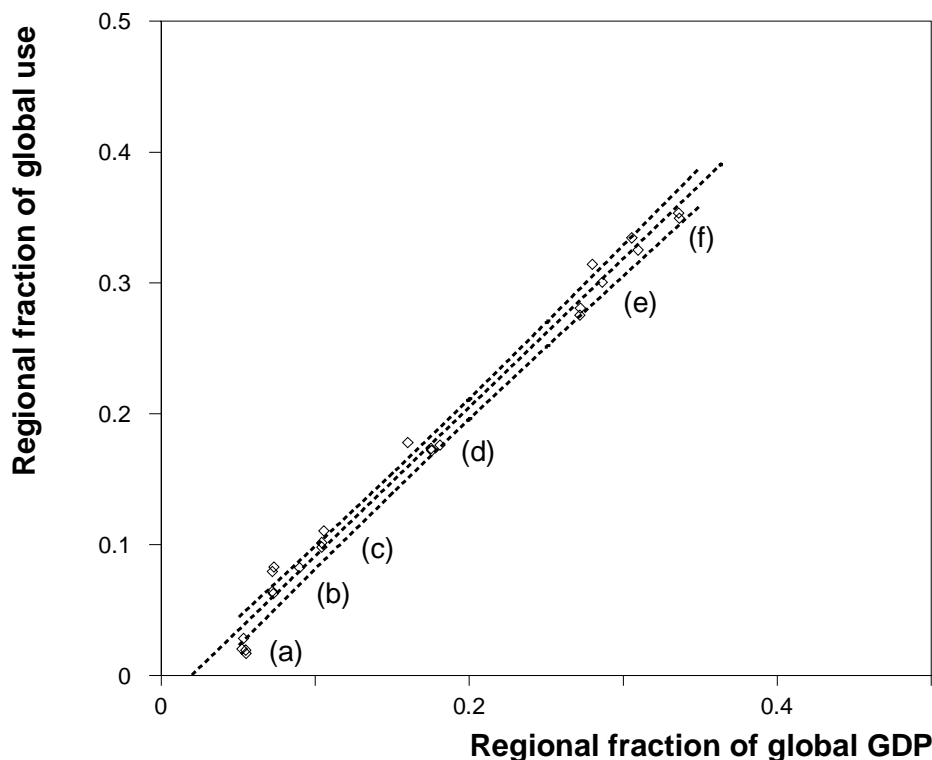


Figure 1. Comparison of use of chlorinated hydrocarbons with Gross Domestic Product. There are four points, corresponding to values for 1988 to 1991, clustered for each region: (region a), southern hemisphere; (region b), northern hemisphere tropics; (region c), other northern hemisphere (not specified in regions b, d, e or f); (region d), Far East; (region e), North America, and (region f), Europe. The dashed line shows the best straight line fit to the points, and the dotted line shows the 95% confidence limits of this line.

Gilli *et al.* [1989], the total emission of trichloroethene from gasoline engines is calculated to be about 0.003 Tg yr^{-1} (0.002 Tg yr^{-1} as reactive chlorine). Given the uncertainty in the global industrial emissions of $\pm 0.013 \text{ Tg yr}^{-1}$ in 1990 [McCulloch and Midgley, 1996], the contribution from gasoline engines is not significant and is not considered further.

Tetrachloroethene has been identified as a small but significant part of the halogen component of the flue gas from coal-fired power plant [Garcia *et al.*, 1992]. On the basis of this work the emission factor is just under $4 \times 10^{-4} \text{ g/g}$ of total chlorine content of the coal; most of the remaining chlorine being volatilized as hydrogen chloride and chloromethane. The total quantity of coal burnt in 1990 (including small-scale domestic and commercial consumption) was 4.4 Pg , with an average chlorine content of just over $1 \times 10^{-3} \text{ g/g}$ [McCulloch *et al.*, 1999], so that the tetrachloroethene released into the atmosphere from this source equals $0.0019 \text{ Tg yr}^{-1}$ ($0.0016 \text{ Tg yr}^{-1}$ of reactive chlorine). Like the trichloroethene from gasoline engines, this quantity of tetrachloroethene is much less than the uncertainty in the emissions from audited industrial production and so is not considered further here.

The most significant nonindustrial fluxes of these materials that have been identified are from the oceans. The size and extent of those fluxes are described by Khalil *et al.* [1999]; the minor flux of dichloromethane from biomass burning is described by Lobert *et al.* [1999].

6. Geographically Identified Emissions: Release Inventories

Some countries, notably the United States and Canada, require some of their industry to report geographical locations and quantities of emissions to the environment of a number of chemicals, including

trichloroethene, tetrachloroethene, and dichloromethane. Not all industrial users are required to make such reports. For example, in the United States enterprises employing less than 10 people are exempt, as are those manufacturing or processing less than 25,000 lbs/yr or otherwise using less than 10,000 lbs/yr. This results in much less than the total usage being reported in the Toxics Release Inventory (TRI) [United States Environmental Protection Agency (U.S. EPA), 1994]. For trichloroethene in the United States, 0.01788 Tg were reported for 1990, compared to usage and emission calculated to be 0.040 Tg . Similarly, for tetrachloroethene, 0.01025 Tg out of 0.117 were reported, and for dichloromethane, the values were 0.04563 out of 0.145 . The higher reportage of trichloroethene reflects the higher proportion of large-scale industrial processes that use this material.

These geographically differentiated releases to atmosphere were assigned directly to the appropriate grid squares. The total for each compound that could be so allocated was then subtracted from the calculated national emission to give a value for the releases that had to be assigned across all of the country using a surrogate distribution parameter.

7. Population as a Distribution Parameter

The materials in this study are used in relatively labour intensive industries such as metal working and dry cleaning; thus for the remainder of the national releases, that are not included in the mapped industrial emissions from significant point sources, population is a reasonable distribution parameter.

The population distribution for 1990 was taken from the work described by Li [1996] in which the global population was assigned to 1° latitude \times 1° longitude grid squares. As described by Li *et al.*

Table 2. Calculated National Emissions of Chlorinated Hydrocarbon Solvents During 1990

Country	Trichloroethene,	Tetrachloroethene,	Dichloromethane
	Mg as C ₂ HCl ₃	Mg as C ₂ Cl ₄	Mg as CH ₂ Cl ₂
Algeria	268	604	1,139
Angola	9	13	52
Argentina	331	517	2,041
Armenia	22	49	93
Australia	712	1,113	4,394
Austria	2,004	2,385	3,592
Azerbaijan	79	177	334
Bahrain	5	10	19
Bangladesh	204	418	769
Belarus	367	827	1,560
Belgium	2,550	3,036	4,571
Brazil	1,148	1,795	7,087
Brunei Darussalam	2	4	7
Cameroon	98	201	370
Canada	3,341	9,824	12,156
Chile	51	80	317
China	5,403	4,119	9,028
Colombia	363	742	1,368
Costa Rica	23	46	85
Cote d'Ivoire	84	172	318
Cuba	172	352	648
Denmark	1,549	1,844	2,776
Dominican Republic	37	75	138
Ecuador	9	14	56
Egypt	398	815	1,502
El Salvador	17	35	64
Estonia	2	5	10
Ethiopia	26	53	97
Finland	1,673	1,992	3,000
France	18,559	22,094	33,269
Gabon	10	20	38
Georgia	102	230	435
Germany	23,430	27,893	42,001
Ghana	28	57	105
Greece	539	642	966
Guatemala	42	85	158
Honduras	25	50	93
Hong Kong	674	1,378	2,539
India	2,952	6,037	11,125
Indonesia	1,018	2,083	3,838
Iran	3,978	8,972	16,918
Iraq	452	1,019	1,922
Ireland	162	193	290
Israel	325	733	1,382
Italy	16,998	20,237	30,472
Jamaica	7	15	28
Japan	51,715	39,425	86,419
Kazakhstan	438	988	1,864
Kenya	4	7	27
Korea (S)	3,137	2,391	5,242
Kuwait	232	474	874
Kyrgyzstan	7	16	30
Latvia	53	121	227
Libya	368	752	1,386
Lithuania	86	193	365
Malaysia	387	792	1,459
Martinique	2	3	6
Mexico	2,369	4,844	8,927
Moldova	56	126	237
Morocco	108	243	459
Myanmar	199	408	752
Netherlands	4,011	4,775	7,190
New Zealand	91	142	560
Nigeria	286	584	1,077

Table 2. (continued)

Country	Trichloroethene,	Tetrachloroethene,	Dichloromethane
	Mg as C ₂ HCl ₃	Mg as C ₂ Cl ₄	Mg as CH ₂ Cl ₂
Oman	70	144	265
Pakistan	430	880	1,621
Panama	16	33	60
Peru	75	118	464
Philippines	400	818	1,508
Poland	447	549	827
Portugal	427	508	765
Qatar	39	80	147
Romania	70	86	130
Russian Federation	7,018	15,826	29,844
Saudi Arabia	783	1,602	2,953
Senegal	21	43	79
Singapore	312	639	1,177
South Africa	234	366	1,446
Spain	7,344	8,744	13,166
Sri Lanka	45	91	168
Sudan	127	259	478
Sweden	3,120	3,714	5,593
Switzerland	3,090	3,679	5,593
Syria	92	208	393
Taiwan	1,472	1,123	2,460
Thailand	806	1,649	3,038
Trinidad and Tobago	17	35	64
Tunisia	6	13	24
Turkey	1,900	2,262	3,406
Ukraine	1,782	4,018	7,577
United Arab Emirates	299	612	1,127
United Kingdom	15,147	18,033	27,153
United States of America	39,954	117,485	145,374
Uruguay	3	5	20
Uzbekistan	279	630	1,188
Venezuela	445	910	1,677
Viet Nam	54	110	204
Yemen	30	61	112
Yugoslavia	115	141	212
Total	241,429	366,200	582,668

[1996], these grid squares were also assigned to individual countries, so enabling the estimates of national emissions to be distributed according to the national population distribution using the formula

$$E_{ij} = E_j \times (P_{ij} / \sum_i P_{ij}) \quad (3)$$

where E_{ij} is the emission from the i th grid square of the j th country, P_{ij} is the population in the i th grid square of the j th country, and E_j is the national emission of the j th country, as recorded in Table 2.

Plates 1 to 3 show the gridded global distributions of trichloroethene, tetrachloroethene, and dichloromethane estimated by this method. Consistent with the other inventories in this activity, these distributions are expressed in terms of the mass chlorine content of the release per square meter of terrestrial area per year.

8. Uncertainty

The regional totals of the industrial emissions of each material were derived from audited data with an uncertainty of $\pm 5.5\%$, as described by McCulloch and Midgley [1996]. Translation into national emissions using equation (2) introduces a further uncertainty for all three halocarbons combined of $\pm 4\%$ relative to the top of the range of emissions. While the uncertainty in the emissions of each

individual compound cannot be determined accurately by the procedures used here, uncertainty in the combined emissions has a profound effect at the lower end of the distribution scale where the cutoff point, at which a country is deemed to have too little economic activity to show emissions of these solvents, can vary by 60% (specifically 0.0224 ± 0.0125). However, the fluxes per unit area there are 10 million times less than the largest fluxes; so low that the effect of the relative uncertainty on the global distribution of emissions is insignificant.

9. Change in the Distributions With Time

Within the regions in which most of these materials are consumed and emitted, the population distribution is relatively fixed and is unlikely to change markedly in the short term; over periods of the order of 10 years. On the other hand, the quantities of the chlorinated hydrocarbon solvents that are used have been shown to change from year to year and for two of the materials to be subject to longer-term trends. McCulloch and Midgley [1996] showed the emissions between 1988 and 1992;

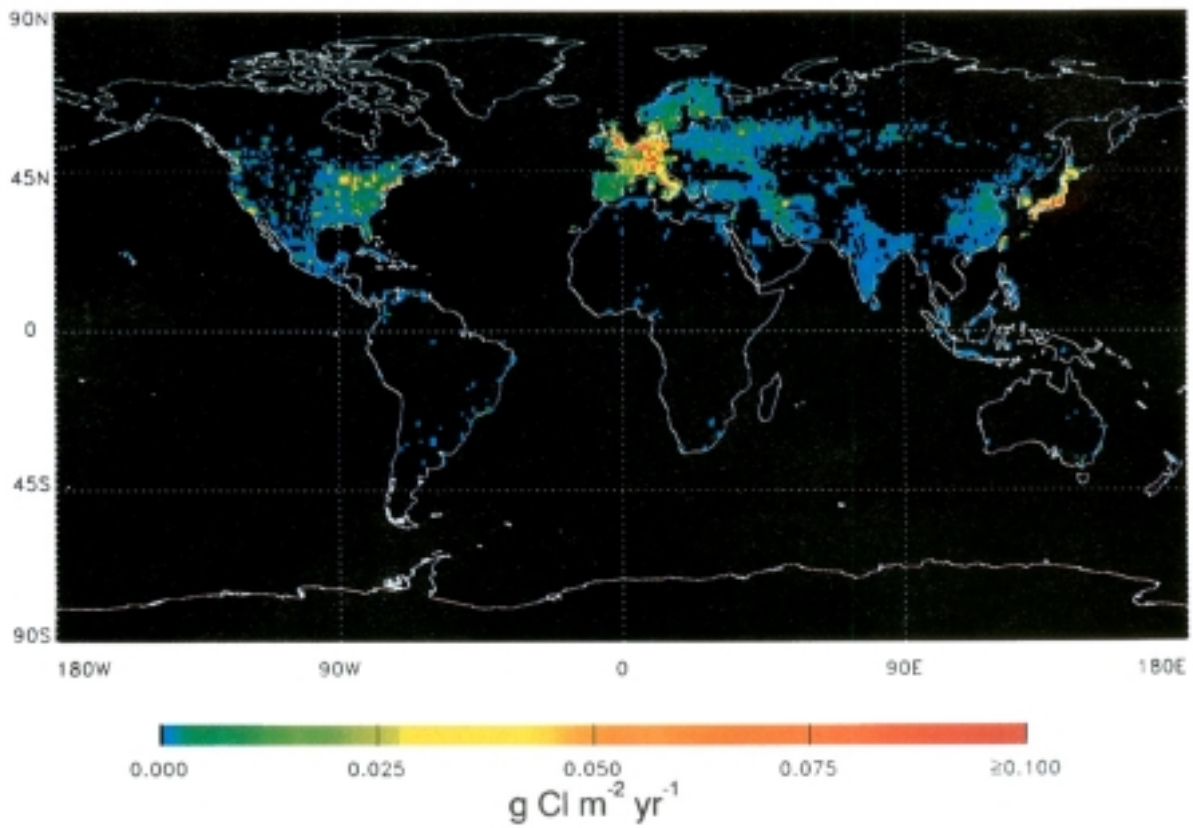


Plate 1. Global distribution of trichloroethene emissions in 1990, expressed as equivalent chlorine emission per square meter.

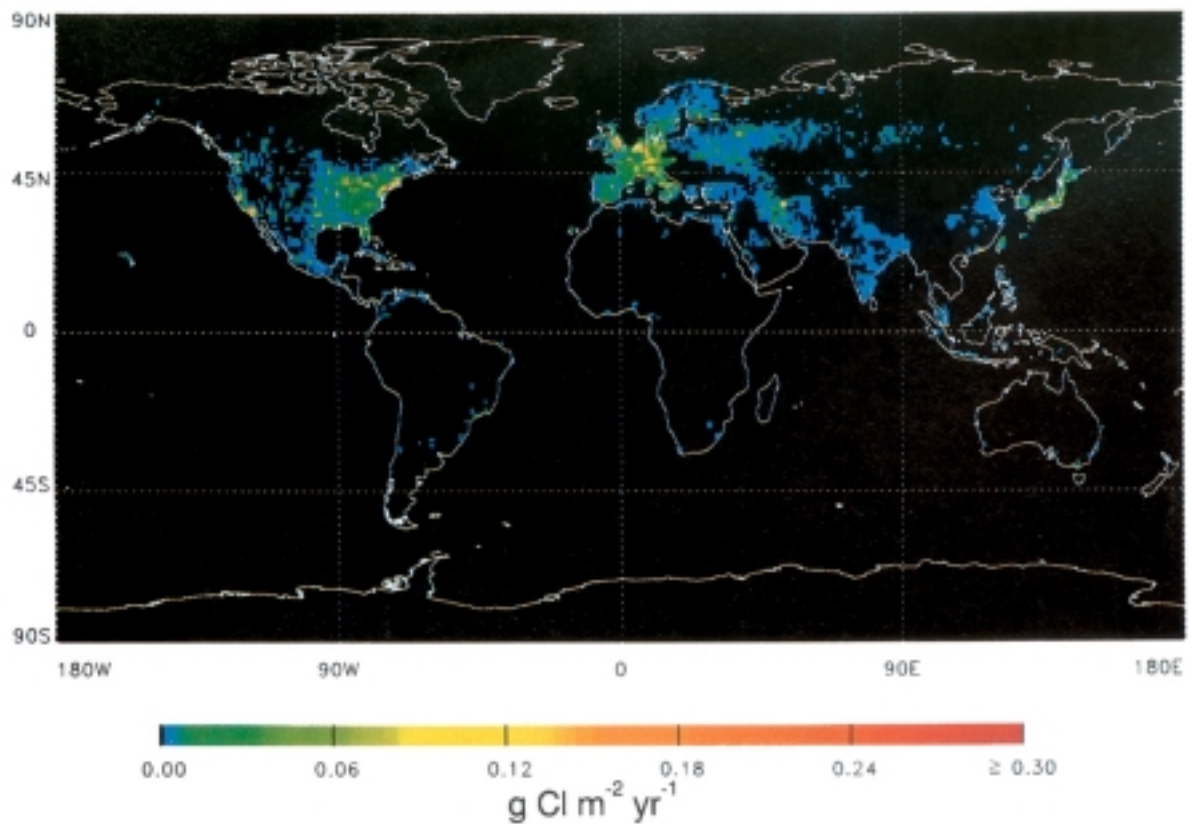


Plate 2. Global distribution of tetrachloroethene emissions in 1990, expressed as equivalent chlorine emission per square meter.

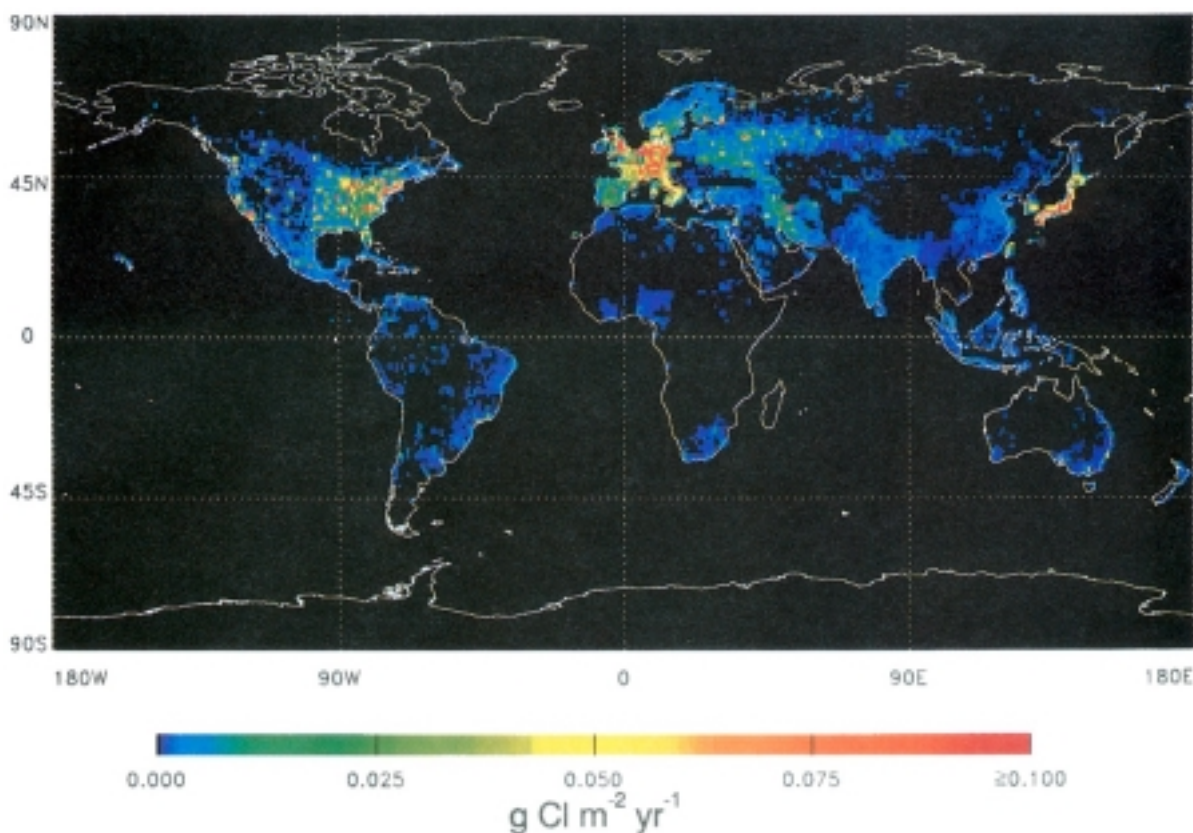


Plate 3. Global distribution of dichloromethane emissions in 1990, expressed as equivalent chlorine emission per square meter.

subsequently, more data have become available from the producers [European Chlorinated Solvent Association (ECSA), 1997] enabling the trends to be brought more up to date. Figure 2 shows the emissions calculated from the audited sales data, together with the trends with time. For trichloroethene, emissions are neither rising nor falling, and the average release is about 0.240 Tg yr^{-1} . Emissions of both the other solvents show clear reductions in time; dichloromethane emissions are declining at the rate of $0.012 \pm 0.009 \text{ Tg yr}^{-2}$ and tetrachloroethene emissions are falling at $0.023 \pm 0.010 \text{ Tg yr}^{-2}$. Both linear trends are significant at the 95% level. The apparent shorter-term fluctuations about this trend are most likely due to economic activity: previously in this paper, usage was shown to be heavily influenced by GDP, and the minima occur in the years 1992 to 1993, when manufacturing industry globally was in recession.

Having postulated that the distribution of these emissions is unlikely to change markedly over a few years, then absolute emissions in individual grid squares for a year other than 1990 could be scaled linearly using the total global emissions in 1990 and the target year. The factor by which the 1990 value should be multiplied to give trichloroethene emissions in 1995 is 1.02; the similar factor for tetrachloroethene is 0.76 and for dichloromethane it is 0.89.

10. Results and Discussion

It is clear that the industrial emissions of all three materials span a wide range of flux, with the lowest estimated rate of emission per unit area being 10 million times less than the highest. Equally clearly, the highest emissions of tetrachloroethene and dichloromethane are from industrial regions of the northern hemisphere: North America, Europe, and Japan. There are also significant estimated fluxes from the developing nations of Asia. Emissions of trichloroethene are even

more concentrated in industrial regions, reflecting a relatively higher use of this solvent in large-scale manufacturing processes.

In addition to the industrial emissions recorded here, there would appear to be other substantial emission sources of the title compounds. For example, Singh *et al.* [1996] have indicated that an oceanic source of about 0.18 Tg yr^{-1} of dichloromethane is necessary to reconcile the difference between the observed concentration in the southern hemisphere and the concentration predicted on the basis of the balance between anthropogenic emissions alone and environmental loss processes (principally oxidation by atmospheric OH), an observation echoed by Villenave *et al.* [1997] but without quantification. The estimate of the oceanic flux by Khalil *et al.* [1999] at 0.16 Tg yr^{-1} as reactive chlorine (0.19 Tg yr^{-1} as CH_2Cl_2) is in remarkably good agreement with the calculations of Singh *et al.* [1996]. On this basis, the total flux of dichloromethane would amount to some 0.68 Tg yr^{-1} ; somewhat less than, but consistent with, the $0.75 \pm 0.08 \text{ Tg yr}^{-1}$ suggested by Koppmann *et al.* [1993], based on their measurements of 36 pmol mol^{-1} of dichloromethane above the middle of the North Atlantic Ocean and 18 pmol mol^{-1} above the South Atlantic.

An additional flux of tetrachloroethene of approximately 0.1 Tg yr^{-1} was inferred by Aucott [1997] based on a comparison of modeled and reported atmospheric concentrations. On the other hand, Singh *et al.* [1996] reported that an oceanic flux of 0.03 Tg yr^{-1} of tetrachloroethene would be sufficient to match observed oceanic concentrations, consistent with the global oceanic flux of 0.04 Tg yr^{-1} (0.034 Tg yr^{-1} as Cl) calculated by Khalil *et al.* [1999]. Tetrachloroethene has been determined in the atmosphere in a number of campaigns. Within the polluted boundary layer, its concentration can rise to hundreds of pmol mol^{-1} [Blake *et al.*, 1996a, 1997]. However, with an atmospheric lifetime, toward removal by reaction with OH radicals, of 0.4 years [Prather *et al.*, 1991], it is sufficiently

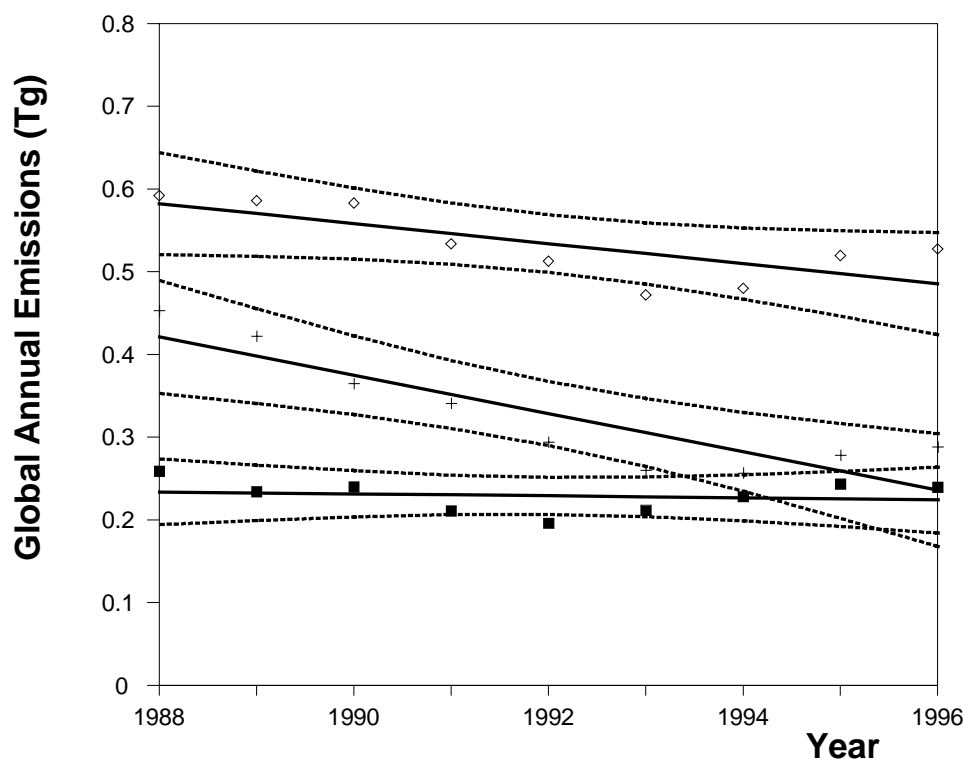


Figure 2. Trends in annual emissions: open diamonds, dichloromethane; crosses, tetrachloroethene; solid squares, trichloroethene. Solid lines represent the least squares trends fitted, and dotted lines denote the 95% confidence limits of each.

reactive to show vertical and horizontal concentration gradients in the atmosphere. The reduction in concentration with altitude is particularly sharp in the first 2 km, concentrations above this being much more uniform, particularly in the southern hemisphere [Blake *et al.*, 1996a, b, c, 1997; Wingenter *et al.*, 1996]. Blake *et al.* [1996b] also show that, in remote regions of the troposphere, at times when atmospheric circulation does not advect polluted air from industrial regions, the concentration in the boundary layer is similar to that in the free troposphere, due to mixing between the layers occurring on a timescale that is fast compared with the reactivity of tetrachloroethene. The remote marine boundary layer concentrations measured at 13 ± 6 pmol mol⁻¹ in the northern hemisphere and 2.7 ± 0.4 in the southern hemisphere were taken by Koppmann *et al.* [1993] to be representative of hemispherical concentrations in 1989. The values are similar to other measurements reported by Wiedmann *et al.* [1994] (21 ± 5 pmol mol⁻¹ from 30° to 90°N, 7 ± 3 from 0° to 30°N, and 2.2 ± 0.5 in the southern hemisphere), by Wang *et al.* [1995] (7 to 26 pmol mol⁻¹ in NH and 1 to 5 in SH), by Rudolph *et al.* [1996] ($14.3 + 4.7/-3.3$ pmol mol⁻¹ in NH, $2.5 + 0.8/-0.5$ in SH), and by Blake *et al.* [1996b] (16 ± 7 pmol mol⁻¹ over the North Atlantic). Koppmann *et al.* [1993] calculated the global flux of tetrachloroethene to be 0.58 ± 0.24 Tg yr⁻¹, based on their results, so that about 0.19 Tg yr⁻¹ of tetrachloroethene (0.16 Tg yr⁻¹ as chlorine) in addition to the industrial source would be necessary to balance its atmospheric budget. The somewhat smaller difference of 0.09 Tg yr⁻¹ calculated by Keene *et al.* [1999] is a result of a smaller calculated flux but, given the errors, is consistent with this value.

Trichloroethene measurements seem even less matched to known industrial emissions in both northern and southern hemispheres. There are fewer measurements, but those made in 1989 averaged 3 ± 1 pmol mol⁻¹ in the northern hemisphere boundary layer and 0.6 ± 0.1 pmol mol⁻¹ in the southern [Koppmann *et al.*, 1993]. The values were

judged to be representative of the background tropospheric concentrations in August/September in each hemisphere. Yokouchi *et al.* [1996] report measurements for 1992 to 1994 from Alert, Canada, that show strong seasonal variation from 0.01 pmol mol⁻¹ in summer (May to September) to up to 8 pmol mol⁻¹ in winter (January/February). The variation is ascribed to the short (7 day) lifetime of trichloroethene with respect to oxidation by OH radicals, the concentrations of which are highest in summer. Transport of trichloroethene from lower latitudes takes several weeks, sufficient time to allow almost complete removal of trichloroethene during summer. Similarly, trichloroethene may be expected to react during the few days while it is transported upward from the boundary layer, so that its concentration is lower in the free troposphere than at the surface. There are few measurements of trichloroethene itself in the free troposphere, but a comprehensive survey of hydrocarbons over the North Atlantic by Penkett *et al.* [1993] showed that substances that were oxidized by OH and NO₃ radicals, and have atmospheric lifetimes similar to that of trichloroethene, were less abundant above the boundary layer. The ratios between free tropospheric and boundary layer concentrations ranged from 0.8 in the case of ethane to 0.45 for toluene. Applied to trichloroethene, this reduction is consistent with the model result quoted by Ko *et al.* [1997], who suggested a factor of 2 between boundary layer and free troposphere. Other work suggests a much higher differential, approaching 6 (M. Aucott, unpublished calculation, 1998). Assuming such a higher differential, the global burden of trichloroethene represented by the observed concentrations is calculated [Keene *et al.*, 1999] to be 0.0065 Tg (0.0053 Tg as Cl). This corresponds to a calculated flux of 0.43 Tg yr⁻¹ of trichloroethene (0.35 Tg yr⁻¹ as Cl). The industrial flux reported here at 0.195 Tg yr⁻¹ as Cl, together with the flux from gasoline combustion of 0.003 Tg yr⁻¹ and the oceanic flux of 0.024 Tg yr⁻¹ [Khalil *et al.*, 1999], are not sufficient to effect a balance.

Even on this most conservative estimate of the sink, there would appear to be another source of trichloroethene as large as the industrial flux. Furthermore, if the difference does indeed represent a missing source, or sources, the bulk of the emissions would need to be in the northern hemisphere, based on the observed interhemispherical concentration gradient. This would not be consistent with the source being in the open ocean, but sources associated with shallow waters of the continental shelves might account for the northern bias [Abrahamsson *et al.*, 1995; Pedersén *et al.*, 1996]. Although Rudolph *et al.* [1995] found that emissions of trichloroethene from biomass burning in West Africa were very small (they calculated an upper limit of 0.017 Tg yr⁻¹ global contribution), the northern bias is also consistent with the distribution of chlorine from biomass burning that is 70% in the northern hemisphere [Lobert *et al.*, 1999].

The uncertainties could be resolved substantially with a comprehensive and reliable set of measurements of trichloroethene concentrations and its vertical profiles at midlatitudes.

The gridded inventories represent the best estimates of the distribution of the known anthropogenic fluxes of these simple chlorinated hydrocarbons. They are consistent in format with other inventories of the Global Emissions Inventory Activity described by Pacyna and Graedel [1995] and should be valuable adjuncts to the modeling of atmospheric processes.

11. Access to Data

The inventory grids generated in this work are available online from the GEIA website at <http://groundhog.sprl.umich.edu/geia/rcei>. It is planned to update these inventories as new information becomes available.

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