



Science Dossier

Trichloroacetic acid in the environment

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Contents

Summary	2
1. Properties of trichloroacetic acid (TCA, $\text{CCl}_3\text{C}(\text{O})\text{OH}$)	5
2. Sources of fluxes into the environment - Primary	
2.1 Industrial production	5
2.2 Uses	5
2.3 Byproduct emissions	6
3. Sources of fluxes into the environment - Secondary	
3.1 Oxidation of perchloroethylene (PCE, perc, tetrachloroethene)	6
3.2 Oxidation of methyl chloroform (111tri, 1,1,1-trichloroethane)	8
3.3 Mass balance of TCA in the atmosphere	8
3.4 Soil processes	9
4. Observed occurrence of TCA in the environment	
4.1 Air	10
4.2 Environmental water	
4.2.1 Contemporary precipitation	
4.2.1 (a) Rain, snow and ice	10
4.2.1 (b) Throughfall	10
4.2.2 Contemporary surface water	
4.2.2 (a) Surface (other than rivers and lakes)	11
4.2.2 (b) Rivers	11
4.2.2 (c) Lakes	11
4.2.2 (d) Seawater	11
4.2.3 Treated waters	11
4.3 Historical environmental water	12
4.4 Soil	12
4.5 Biota	13
5. Removal processes	
5.1 Air	14
5.2 Soil	15
5.3 Large plants	15
5.4 Water	16
6. Environmental effects	16
7. Conclusions	18
8. Suggestions for the future	19
9. References	20
APPENDIX A. Measurements of environmental TCA concentrations	
A.1 Air	29
A.2 Water	29
A.3 Historical environmental water	34
A.4 Soil	35
A.5 Biota	37
APPENDIX B. Measurements of perchloroethylene and methyl chloroform in the atmosphere and in biota	
B.1 Perchloroethylene in the atmosphere	40
B.2 Methyl chloroform in the atmosphere	40
B.3 Perchloroethylene and methyl chloroform in industrial plumes	42
B.4 and B.5 Perchloroethylene and methyl chloroform in conifer needles	44

Summary

This *dossier* from Euro Chlor¹ and the European Chlorinated Solvent Association (ECSA) attempts to draw together information from the open literature and from reports commissioned by Euro Chlor on the occurrence and potential sources and sinks of environmental trichloroacetic acid (TCA, CAS 76-03-9). Where possible, original papers have been examined and cited. However, extensive use has been made of the excellent prior compendia of *Juuti* [1997] and *Schöler* [1998]. The environmental measurements are listed (where possible as disaggregated values) in the appendices to this report, which cover observations of TCA itself and of the potential precursors: perchloroethylene and 1,1,1-trichloroethane.

As a result of some sketchy experiments in the 1980s on the effect of chlorinated organic solvents on trees, TCA has been widely supposed to contribute to forest dieback. Environmental TCA was presumed to be formed exclusively from oxidation of chlorinated solvents.

The yields of TCA from chlorinated hydrocarbon solvents are small. Measurements show that, while the atmospheric oxidation of perchloroethylene and methyl chloroform may account for some of the TCA detected in precipitation, large additional sources are required in order to effect a global or regional mass balance.

Instead of the almost complete conversions originally proposed, it is estimated that approximately 5% of perchloroethylene (PCE) released into the atmosphere could be converted into trichloroacetic acid and the upper limit on the conversion of methyl chloroform is 1.3%. So that, on a global basis, the yields of TCA are: from PCE 13,600 tonnes yr⁻¹ and from methyl chloroform 4,300 tonnes yr⁻¹, at late 1990s rates.

TCA is also produced during oxidative water treatment and could amount to 55,000 tonnes yr⁻¹ (from pulp and paper manufacture, potable water and cooling water treatments). This flux would be introduced directly into the aqueous environment and, because TCA is so soluble and is fully dissociated in water, it should be expected to remain in that phase.

TCA is widely distributed in forest soils (where it was sometimes used as a herbicide). Calculations from environmental measurements indicate that a typical production rate for European forest soil would be in the region of 1,600 g ha⁻¹ yr⁻¹, with a range of 8 to 31,000 g ha⁻¹ yr⁻¹. This would suggest a soil flux of 160,000 tonnes yr⁻¹ in European forests.

There are many field measurements but few comprehensively chart concentrations in all local environmental compartments, so that there are no direct mass balances between precipitation, soil, biota and surface water. However, some general conclusions can be drawn.

¹ Compiled by A. McCulloch, Marbury Technical Consulting

TCA is ubiquitous in rainwater and snow. Its concentrations are highly variable and the variations cannot be connected with location or date. Washout of the highly soluble haloacetic acids during rain events has been demonstrated but there is no consistent anticorrelation between the quantity of rainfall and the TCA concentration (to be expected for a constant rate of input of TCA into the atmosphere), nor any significant difference globally between the concentrations in cloud, rain and snow (although local enhancement in fog water has been shown). A significant reduction the rainwater concentrations in rural SW Germany between 1988 and 1994 has been observed (far greater than the change in chlorinated solvent use in Europe over this period) but there is no clear trend in the global concentrations measured.

If the input of TCA were predominantly of anthropogenic origin, one would expect concentrations in the Northern hemisphere to be higher than in the Southern. This is not the case. There is no significant difference between the concentrations found in Chile and in eastern Canada (by the same analysts), or between Malawi and Western Canada, or between Antarctica and Switzerland.

TCA is present in old ice and firn. At the deepest levels, the firn was deposited early in the 19th century, well before the possibility of contamination by industrial production of reactive chlorine, implying a non-industrial background.

TCA is ubiquitous in soils. Concentrations are highly variable, but there are some indications that soils under coniferous trees (particularly *Pinus sylvestris*, Scots pine) contain higher amounts. The analyses do not indicate why the concentrations there should be higher. Interestingly, the Rothamstead archive showed concentrations well above the current global average in samples going back to 1865, supporting the measurements in old ice and firn.

The concentrations of TCA found in plant tissue are region-specific and may also be plant-specific, to the extent that conifers seem to contain more than other species, in general, and, in the same area, *Pinus sylvestris* (Scots pine) contained several times as much as *Picea abies* (Spruce). Among the lichens, *Usneaceae* contained more than *Hypogymnia physodes*, but the trees (*Picea abies*) on which they were growing all had similar concentrations of TCA in their needles (of unspecified age).

A background environmental level of TCA is supported by plume measurements from pulp mills in Finland where a local influence was shown in the TCA concentration up to 20 km downwind. Beyond that, the Scots pine needles harvested appeared to contain a constant 20 to 40 microg kg⁻¹.

TCA is removed from the environment naturally. There is abundant evidence that soil microorganisms dehalogenate TCA, and a soil lifetime of a few weeks would match the observations. The loss rate of TCA from within spruce needles is first order with a half-life of 10 days. There is also recent evidence of an abiotic aqueous decarboxylation mechanism with a half-life of 22 days.

The supposedly widespread effects of TCA in conifer needles are not shown in controlled experiments. At concentrations in the needles of Scots pine similar to those observed in needles in forest trees, changes consequent on TCA treatment of field laboratory specimens were almost all insignificant. The routine microscopic methods, which clearly show the effects of ozone and sulphur dioxide, do not allow diagnosis of effects from TCA.

If it is necessary to study the occurrence and environmental fate of TCA further, controlled field experiments would be required aimed at attempting to establish whether or not coniferous species, particularly *Pinus sylvestris*, generate (or otherwise interfere with) the local environmental burden and transport of TCA. Developments in the techniques of isotope analysis for ^2D , ^{13}C , ^{14}C , ^{35}Cl and ^{37}Cl in environmental samples of TCA and PCE may prove useful in identifying sources in the future.

1. Properties of trichloroacetic acid (TCA, CCl₃C(O)OH)

Attribute	Value	Source
Boiling point	198°C	Juuti [1997]
Vapour pressure	0.14 mmHg @ 25°C (equiv. to 19 Pa) 21 Pa @ 25°C	Stull [1947] Juuti [1997]
Water solubility	1306g/100g H ₂ O @ 25°C 1200g/l @ 20°C	Morris and Bost [1991] Juuti [1997]
Henry's constant	7.4 x 10 ⁴ mol kg ⁻¹ atm ⁻¹	Juuti [1997]
pK _a	0.2159 @ 25°C 0.26	Morris and Bost [1991] Juuti [1997]
logK _{ow}	<1 - 1.6	Juuti [1997]

Some key physical and chemical properties of TCA are presented in Table 1. TCA is highly soluble in water and, with a Henry's constant of 7.4 x 10⁴ mol kg⁻¹ atm⁻¹, the preferred environmental compartment where emissions will accumulate is the hydrosphere [Ballschmiter, 1992]. In aqueous solution TCA, with a pK_a of 0.22-0.26 is almost completely dissociated [Morris and Bost, 1991; Juuti, 1997].

2. Sources of Fluxes into the Environment - Primary

2.1 Industrial Production

Three processes were used to manufacture TCA: exhaustive chlorination of acetic acid, oxidation of chloral (CCl₃CHO) using H₂O₂ and hydrolytic oxidation of PCE. [Morris and Bost, 1991]. It has not been possible to estimate a global quantity of TCA manufactured but the estimated use in West Germany during the period "from the 1940s until 1990" was a total of about 30,000 tonnes [Schöler, 1998].

2.2 Uses

Apart from small quantities used as antiseptic, most of the manufactured material was used, in the form of sodium trichloroacetate, as a herbicide [Morris and Bost, 1991]. TCA was introduced in about 1950, principally to control wild grasses in brassicas and similar commercial crops planted in rows [Lockhart et al., 1990].

TCA is effective only in the control of monocotyledons, such as grasses. Potato, oil-seed rape, kale, turnip, spinach and flax are all highly resistant. Tomato, lettuce, alfalfa, clover, cotton, pea, sugar beet and bean plants may be grown after the ground has been treated with TCA [Crafts, 1961]. Application rates were 5-10lbs/acre for annual grasses up to 50-100lbs/acre for perennials [Crafts, 1961].

It was not recommended for control of weeds in forests, because it was not effective on forest weeds [Williamson and Mason, 1990].

2.3 Byproduct emissions

No significant byproduct sources from chemical production have been identified but aqueous chlorination and oxidation processes provide a continuing input of TCA into the environment. Table A.2.3 shows measurements that have been made in drinking water and treated effluent streams, with a record value of 7.6 mg l⁻¹ in an effluent stream from a Kraft pulp mill.

During water purification by chlorination, tri- and dichloroacetic acids can be as abundant products of fulvates in the water as chloroform. The humate content of water is not a source of TCA [Morris, 1986].

Fulvic acid is of shorter chain length than humic acid and contains more -(O)OH groups and so is water soluble. Expressed relative to the total dissolved organic carbon, fulvic acid accounts for approx 20% in seawater and groundwater, 25% in lake water, 60% in wetlands and 40% in streams and rivers. For humic acid, the equivalent values are 5-10%, 5%, 5-10%, 15% and 10%, respectively, or approximately 4 fulvic:1 humic in each case [Thurman, 1986].

Dichlorine is not essential to the formation of chlorinated oxidation products from these organic acids; chloroperoxidase gives chloroform and TCA from humic material (i.e. material that contains both humic and fulvic acids)[Hoekstra et al., 1995] and oxidation with ClO₂ gives chloroform in almost the same way as Cl₂ [Juuti et al., 1996a]. In the first case, the sources of chlorine are chlorine ions in solution or absorbed onto the humic substrate. So that the availability of chlorine does not determine the extent of chloroform and TCA formation.

As a first approximation, the upper limit for the by-product TCA flux is a quantity similar to the global total of chloroform from oxidative water treatment. This amounts to 55 Gg/yr (from pulp and paper manufacture, potable water and cooling water treatments) [Aucott et al., 1999]. This flux would be introduced directly into the aqueous environment and, because TCA is so soluble and is fully dissociated in water, it should be expected to remain in that phase. Speculatively, if environmental TCA were to be esterified, say to methyl trichloroacetate, then some could escape into the atmosphere.

3. Sources of fluxes into the environment - Secondary

3.1 Oxidation of perchloroethylene (PCE, perc, tetrachloroethene)

There is a presumption that, because elevated levels of PCE have been measured in the European polluted boundary layer (see Table B1 in Appendix B), it is a major source of the TCA detected in rainfall there. Conversions as high as 80% have been claimed [Frank, 1991] but it is now recognised that the real conversion is much lower than this.

It is generally accepted that the tropospheric oxidation of perchloroethylene commences with addition of a radical species such as hydroxyl ($\cdot\text{OH}$) or chlorine ($\cdot\text{Cl}$). This is the slowest part of the process, with a composite lifetime of 3.3 months at globally averaged abundances of $\cdot\text{OH}$ and $\cdot\text{Cl}$ [Franklin and Sidebottom, 1999]. As a consequence of this relatively slow rate determining step, the most important mechanism acting to reduce local concentrations of material

that is released into the atmosphere is dispersion by mixing along the boundary layer and up into the free troposphere [Wingenter et al., 1996]. Thus, while the rate of formation of trichloroacetic acid depends on the local concentration of perchloroethylene, the change in perchloroethylene concentration does not give a direct indication of the absolute quantities of reaction products that might be expected in that area.

Some 87% of perchloroethylene in the atmosphere reacts with $\cdot\text{OH}$ and the principal, if not the only, product of this reaction is phosgene (COCl_2) [Franklin, 1994; Franklin and Sidebottom, 1999] with little possibility of forming trichloroacetic acid or its precursors. On the other hand, reaction with chlorine gives (after further oxidation) the pentachloroethoxy radical ($\text{CCl}_3\text{CCl}_2\text{O}\cdot$) which, in turn, yields phosgene (15%) and trichloroacetyl chloride (85%). TCA would be formed from atmospheric trichloroacetyl chloride when it dissolves in cloud water and hydrolyses. Photolysis of trichloroacetyl chloride to yield phosgene is also an effective loss process in the troposphere, with a lifetime similar to that of dissolution in cloud water, and so the yield of TCA from trichloroacetyl chloride is calculated to be only 46%. Overall, it is estimated that, as a global average, approximately 5% of perchloroethylene released into the atmosphere could be converted into trichloroacetic acid [Franklin and Sidebottom, 1999].

However, the global value may not be indicative of local production rates or concentrations. The $\cdot\text{OH}$ radical field is relatively well parameterised in atmospheric models and the global average value (9.7×10^5 molecules cm^{-3} in Prinn et al. [1995]; 1.1×10^6 molecules cm^{-3} in Montzka et al. [2000]) gives good results for relatively long-lived compounds such as methyl chloroform.

Although the average value of 500 molecules cm^{-3} seems to be robust, the $\cdot\text{Cl}$ radical field is not documented at all [Rudolph et al., 1996; Aucott, 1997]. Local chlorine radical concentrations will depend on the local oxidising power of the atmosphere and on the local reactive chlorine² concentration, which is dominated by sea-salt aerosol [Keene et al., 1999]. It is therefore reasonable to expect the $\cdot\text{Cl}$ field to be strongly biased towards the marine boundary layer, consistent with the results of Wingenter *et al.* [1996] who showed the $\cdot\text{Cl}$ concentrations in the remote North Atlantic boundary layer to be an order of magnitude higher than the global average (at 3.3 to 6.5×10^4 molecules cm^{-3}), while the $\cdot\text{OH}$ concentration was near the global average (0.3 to 2.6×10^6 molecules cm^{-3}). Assuming that the relative differences from the global averages are open to interpretation, they indicate that the local reactive chlorine concentration has more influence on $\cdot\text{Cl}$ radical concentration than the local oxidising power. This view is reinforced by the results that the same group gained over the Southern Ocean in flights from Tasmania [Wingenter et al., 1999]. They estimated a chlorine atom concentration of 720 ± 100 molecules cm^{-3} with a hydroxyl radical concentration of $6.1 \pm 0.3 \times 10^5$ molecules cm^{-3} . It is possible that the $\cdot\text{Cl}$ radical concentration within a continental landmass is significantly lower than the global average. Keene *et al.* [1999] show the reactive chlorine flux within the mid-western USA to be less than $0.01 \text{ g Cl m}^{-2} \text{ yr}^{-1}$, over the North Atlantic Ocean about 0.1 - $0.2 \text{ g g Cl m}^{-2} \text{ yr}^{-1}$ and

² *Reactive chlorine*, as defined by Keene et al [1999] comprises those compounds containing chlorine that can be oxidised to release chlorine itself in the atmosphere.

Trichloroacetic acid in the environment

over large areas of Western Europe to be less than $0.1 \text{ g Cl m}^{-2} \text{ yr}^{-1}$. Within this area there are large variations, with Switzerland showing less than $0.01 \text{ g Cl m}^{-2} \text{ yr}^{-1}$ but with particularly high levels of $0.5 \text{ g Cl m}^{-2} \text{ yr}^{-1}$ over the North Sea.

It is possible that the production of TCA by atmospheric reaction of perchloroethylene over Europe is actually lower than calculations based on global averages would predict.

3.2 Oxidation of methyl chloroform (111tri, 1,1,1-trichloroethane)

Like PCE, atmospheric oxidation of methyl chloroform has also been considered to be a major source of TCA, with conversions of 100% claimed [Frank, 1991]. This is incorrect.

The principal product of tropospheric decomposition of methyl chloroform is chloral (CCl_3CHO); subsequent to H abstraction by $\cdot\text{OH}$, conversion of CCl_3CH_3 to CCl_3CHO by well known atmospheric oxidation processes has been shown to be virtually complete [Platz et al., 1995]. However, methyl chloroform is also photolysed in the stratosphere giving acetyl chloride, and hydrolysed in the oceans to acetic acid and 1,1-dichloroethene, so that only 84% of the total amount of methyl chloroform released into the atmosphere forms chloral [Kurylo and Rodríguez, 1999].

There are three possible sinks for tropospheric chloral: photolysis, which predominates with a lifetime of only a few hours and has a quantum yield close to unity [Starke et al., 1989; Barry et al., 1994; Rattigan et al., 1998; Franklin and Wenger, 2000]; reaction with OH, for which the lifetime is 5.4 days [Rattigan et al., 1998] and dissolution in cloud water. Despite its high solubility in water, the uptake of chloral in clouds is governed by atmospheric mixing and the lifetime of this process is a minimum of 10 days [Giorgi and Chameides, 1986; Kindler et al., 1995].

Only reaction in cloud water could possibly give TCA and the fraction of chloral that is absorbed in clouds is calculated to be 1.6% (on chloral) or 1.3% of the methyl chloroform released [Franklin and Sidebottom, 1999; Franklin and Wenger, 2000]. Subsequent oxidation of the dissolved chloral hydrate by dioxygen and $\cdot\text{OH}$ in the cloud to yield TCA is possible but has not been demonstrated. For the purposes of further calculations, it is assumed that the reaction does proceed and so an upper limit on the conversion of methyl chloroform is 1.3%. Folberth and colleagues concluded that "methyl chloroform can be ruled out as one of the major global TCA sources in the atmosphere" [Folberth et al., 1999].

3.3 Mass balance of TCA in the atmosphere

The quantities of TCA that may be formed by both of the anthropogenic potential precursors are very much smaller than had been supposed in the old literature and a mass balance between the sources and the observed concentrations is instructive. On a global basis, the yields of TCA are: from PCE 13,600 tonnes and from methyl chloroform 4,300 tonnes, at the atmospheric burdens and loss rates typical of the late 1990s.

Based on releases of PCE into the atmosphere [McCulloch et al., 1999], the atmospheric concentration of methyl chloroform [Kurylo and Rodríguez, 1999] and the conversions described in 3.1 and 3.2 above, Franklin and Sidebottom [1999] calculated the expected average concentrations of TCA that could be expected in precipitation in Europe, Antarctica and the Arctic. Their results are not adjusted for local variations in, for example, $\cdot\text{Cl}$ radical concentration and may be taken to be realistic concentrations arising from anthropogenic sources. The concentrations anticipated from both precursors were $0.11 \mu\text{g l}^{-1}$ for Europe (50°N), $0.04 \mu\text{g l}^{-1}$ in the Antarctic ($72\text{-}75^\circ\text{S}$) and $0.05 \mu\text{g l}^{-1}$ in the Arctic ($64\text{-}77^\circ\text{N}$).

Reference to Table A.2.1 shows that these are at the low end of the range of observations. In Europe, the lowest measured concentration was in Switzerland at less than $0.03 \mu\text{g l}^{-1}$ in rainwater; the highest was $20 \mu\text{g l}^{-1}$ in rain in urban Berlin and an unweighted average of the mean determinations would be $0.5 \mu\text{g l}^{-1}$ and, while the average weighted by rainfall could well be lower than this, it is not possible to quantify the difference. Similarly, observations exceed estimates in the Antarctic where, although there are fewer measurements, there is less spread; the minimum being $0.022 \mu\text{g l}^{-1}$ and the maximum $0.348 \mu\text{g l}^{-1}$ with $0.12 \mu\text{g l}^{-1}$ as the average of the means. There is somewhat better agreement in the Arctic, where the values ranged from not detected to a maximum of $0.035 \mu\text{g l}^{-1}$ with an average of $0.01 \mu\text{g l}^{-1}$. However, most of the measurements show that, while the oxidation of perchloroethylene and methyl chloroform makes a significant contribution to the atmospheric flux of trichloroacetic acid, other sources cannot be ruled out and may, themselves, be significant regionally [Thüner et al., 1999].

3.4 Soil Processes

Significant TCA production from acetic acid has been observed in laboratory experiments, even without enzymatic catalysis. Furthermore, in the presence of a catalyst - chloroperoxidase from *Caldariomyces fumago* - plus sodium chloride and hydrogen peroxide, the yield rose to $308 \mu\text{g g}^{-1}$ (of acetic acid). From a commercial sample of humic (including fulvic) acid the yield was $200 \mu\text{g g}^{-1}$ in the presence of chloroperoxidase and $150 \mu\text{g g}^{-1}$ without. [Haiber et al., 1996]

Hoekstra and de Leer [1993] showed both TCA and chloroform to be formed from humic material, hydrogen peroxide, chloride and chloroperoxidase and went on subsequently to demonstrate the production of TCA in real soil in forest environments, with the natural background of chloride ion as the source of soil chlorine [Hoekstra et al., 1999a and 1999b].

From these and other measurements Schöler [1998] calculated that a typical production rate for European forest soil would be in the region of $1600 \text{ g ha}^{-1} \text{ yr}^{-1}$. By contrast, the addition from rainwater would be 1000 times less, at $1.6 \text{ g ha}^{-1} \text{ yr}^{-1}$. Given the forested land area of Europe (102 million hectares [Eurostat, 2000]), the calculated flux of TCA from forest soil would be 160,000 tonnes yr^{-1} in Europe alone.

4. Observed Occurrence of TCA in the Environment

4.1 Air

The data are listed in Appendix A, Table A.1.

There are surprisingly few actual measurements of TCA in air but the data (which range from 0.006 to 0.7 ng m⁻³) are consistent between analysts and with observations in precipitation at the same time and place [*Peters, 2000*].

4.2 Environmental water

4.2.1 Contemporary precipitation

The data are listed in Appendix A, Tables A.2.1 (a) covering rain, snow and fresh ice and A.2.1 (b) covering throughfall.

The only safe conclusion from the data from open areas is that TCA is ubiquitous in rainwater and snow. It is clear that its concentrations are highly variable and that the variations cannot be connected with location or date. Although washout of the highly soluble haloacetic acids has been demonstrated by Berg *et al.* [2000], Clemens [1993] did not find a consistent anticorrelation between the quantity of rainfall and the TCA concentration (to be expected for a constant rate of generation of TCA in the atmosphere), nor is there any consistent difference between the concentrations in cloud, rain and snow. There is no clear trend in time in the global data set (the apparent trend is not significant and is heavily biased by two high results early in the time series). Furthermore, due to the wide variability between locations, any temporal trend analysis would require a long time series *at the same site*.

If the input of TCA were predominantly of anthropogenic origin, one might expect concentrations in the Northern hemisphere to be higher than in the Southern. This is not the case. There is no significant difference between the concentrations found in Chile and in Eastern Canada (by the same analysts), or between Malawi and Western Canada, or between Antarctica and Switzerland. This may be a consequence of different rainfall patterns.

As with rainfall sampled in open areas, the concentrations in throughfall are highly variable but, in general, the levels of TCA in rain below a tree canopy are significantly higher than those in the open in the same locality. *Schöler* [1998] adopted a factor of two, which seems reasonable. The only source of the additional TCA is the trees themselves but these analyses do not help to discriminate between TCA that has been sequestered from the atmosphere, or generated in and on the leaf and needle surface or that which was generated in the soil and carried through the tree by transpiration before being excreted at the foliage. This phenomenon of "guttation", transportation of soluble materials such as amino acids and sugars through the plant's xylem system with subsequent excretion in water droplets on the leaf surface is well known for mono- and dicotyledonous plants but has not yet been shown for conifers [*Von Scheffer et al., 1965; Goatley et al., 1966; Lütge, 1973; Guttridge et al., 1981; Dawson, 1993; Eschrich, 1995*].

4.2.2 Contemporary Surface Water

4.2.2 (a) Surface water (other than rivers and lakes)

Results are shown in Appendix A, Table A.2.2 (a). Given the high solubility of TCA, the fact that it is found in surface water is not surprising. Unfortunately the few results available do not show a significant difference from concentrations in precipitation, so no conclusions can be drawn from them regarding the source(s) of TCA.

4.2.2 (b) Rivers

The set of determinations in Appendix A, Table A.2.2 (b) does not cover a sufficiently wide geographical area for any global significance to be assessed. However, the concentrations in Germany and Switzerland are, in general, similar to or below the concentrations in contemporary rainfall in the same area. This would be expected from the work reported in 5.4 below. The high levels in the polluted rivers at Chemnitz, Germany, and Tokyo, Japan, are readily explained by the generation of TCA in oxidative water treatment processes which is well characterised (see 4.2.3).

4.2.2 (c) Lakes

These results (Appendix A, Table A.2.2 (c)) are interesting because they show a variation with depth in lakes in both Switzerland and Canada, that is not expected solely from riverborne input of a highly soluble material. However, while the high concentrations in deep waters indicate the presence of TCA there, they do not discriminate between TCA that is transported to that region absorbed onto, say insoluble humic substances, and TCA that is generated there.

4.2.2 (d) Seawater

Results for Tokyo Bay, showing a mean of 1.7 $\mu\text{g l}^{-1}$ which is significantly higher than the concentrations measured in lakes and rivers in Europe, are given in Appendix A, Table A.2.2 (d). Judging from contemporaneous measurements in rivers feeding Tokyo Bay, the source of this material would seem to be polluted drainage from the Tokyo metropolitan area.

4.2.3 Treated Waters

The results in Appendix A, Table A.2.3 amply demonstrate the production of TCA in aqueous treatments and the fact that it follows the aqueous effluent stream. In the work of *Benanou et al.* [1998], the background TCA in surface water was shown to be reduced to zero in the treatment process by filtration but subsequently TCA was reintroduced by oxidation, with either ozone or chlorine. Presumably the source of chlorine in the ozone oxidation was chloride ion, as in chloroperoxidase reactions.

According to *Juuti et al.* [1996a], TCA does not appear in the range of products determined in the volatile organics released from aqueous effluent from wood pulp bleaching. It is to be expected that TCA itself would not evaporate and would follow the water stream. Methyl dichloroacetate was detected in significant amounts in the volatiles before the effluent was treated but there is no record of methyl trichloroacetate.

4.3 Historical Environmental Water

Concentrations of TCA determined in old ice, firn and groundwater samples are recorded in Appendix A, Table A.3. Considerable care was taken to ensure that the old ice and firn samples were not contaminated by the present environment and, in the case of firn, it was shown that contamination through the years was highly unlikely due to the involatility of the trichloroacetate, present as salts, and very low ionic mobility in general in frozen firn at -51°C . At the deepest levels, the firn was deposited early in the 19th century, well before the possibility of contamination by industrial production of reactive chlorine.

4.4 Soil

The results, including those of a comprehensive survey of European soils, are shown in Appendix A, Table A.4 and plotted as a frequency distribution in Figure 1. Again, as in precipitation and run-off, TCA is shown to be ubiquitous, being below the limit of detection (generally $0.05 \mu\text{g kg}^{-1}$) in only 13% of the 114 determinations listed. Concentrations in soils are very variable and, while 60% of the determinations were less than $0.5 \mu\text{g kg}^{-1}$, the remainder spanned a wide range (up to $150 \mu\text{g kg}^{-1}$). There are some indications that soils

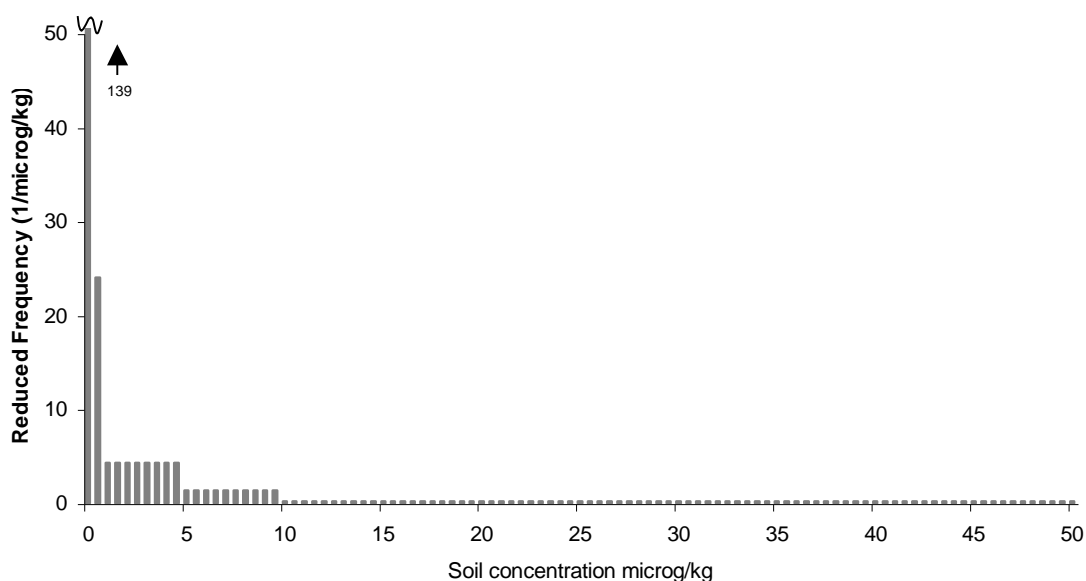


Figure 1. Frequency distribution of mean concentrations of TCA in soils, worldwide (Data in Appendix A, Table A.4).

under coniferous trees (particularly *Pinus sylvestris*, Scots pine) contain higher amounts. There are also indications, from Germany, Chile, Malawi and Canada, that concentrations are higher in the surface layer (down to 10cm) than in deeper layers, although the extensive work by Peters [2000] failed to show a correlation with depth of sample. Interestingly, the Rothamstead archive showed significant concentrations in historic samples. The high concentrations in the sample dating from 1865 may, however, be the result of contamination. The results from the Caucasus mountains show that altitude alone does not have a significant influence on TCA levels.

4.5 Biota

Plants

The concentrations of TCA found in plant tissue and recorded in Appendix A, Table A.5, are certainly region-specific and may also be plant-specific, to the extent that conifers seem to contain more than other species, in general, and, in the same area, *Pinus sylvestris* (Scots pine) contained several times as much as *Picea abies* (Spruce). Among the lichens, *Usneaceae* contained more than *Hypogymnia physodes*, but the trees (*Picea abies*) on which they were growing all had similar concentrations of TCA in their needles (of unspecified age). In the case of Norway spruce (*Picea abies*) the principal translocation path for TCA is uptake from soil into the root system, thence to the needles via the transpiration stream [Matucha et al., 2000].

Concentrations in the Caucasus were an order of magnitude lower than those in either Finland or Czechoslovakia, in fact generally lower than the background level evident in Finland (see below). The samples from the Caucasus enable the examination of regional variations over relatively short distances and show no variation either with height (at 1 standard deviation) or with season (April vs. July/August). There were significant differences (again 1) within the delta of the R. Volga and the shores of the Caspian Sea and on the steppe south of Volgograd.

The transects down and cross-wind of Kraft pulp mills that were performed by Juuti et al. [1995] present a unique view of the influence of a known anthropogenic source. TCA is known to be present in the aqueous effluent from these processes (see 4.2.3) and there is a clear and significant enhancement of TCA concentrations in the needles of *Pinus sylvestris* (3rd year growth) within 5 km of the plant.

In the downwind series from about 20 km onwards the differences between the measurements are not significant. Furthermore, the series of measurements on the parallel track at the same distance is statistically similar, leading to the conclusion that, although the pulp mills might have exerted an influence locally (within the first 20 km), this was additional to a background level of 20-40 microg kg⁻¹. The route by which TCA enters the atmosphere from a pulp mill is not obvious from these results. In the work described in 4.2.3, TCA has been identified only in aqueous effluent and, judged solely by the Henry's constant (7.4×10^4 mol kg⁻¹ atm⁻¹, see Section 1), it should remain in the aqueous phase. However, it is known to be carried through plant tissue from the root system [Sutinen et al., 1995] and to have higher loadings in precipitation beneath the forest canopy [Schöler, 1998].

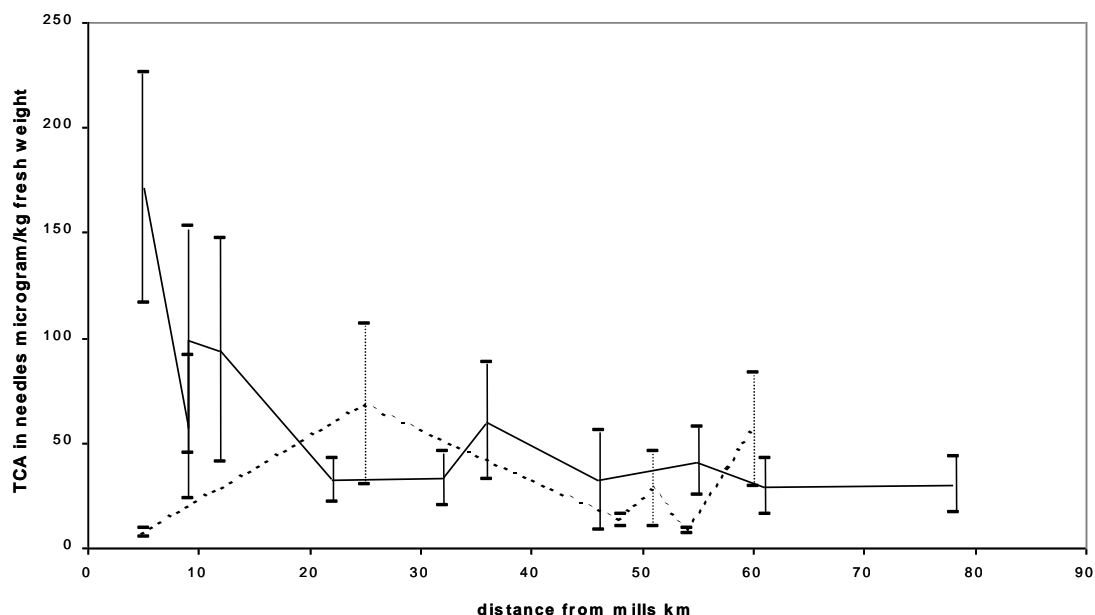


Figure 2: TCA in 3rd year growth Scots pine needles (*Pinus sylvestris*) and distance of the trees from two Kraft pulp mills. Solid line signifies *downwind*, dotted line signifies *across and downwind* (on a parallel track 48 km from the downwind series). Cross bars signify 1sigma uncertainties.

These processes alone could effect a migration of TCA into the forest local to the pulp mill and away from contaminated water courses. There is also the possibility that TCA would form comparatively volatile esters (such as methyl trichloroacetate) in the environment, although these were not observed in their atmospheric and aqueous effluents.

Animal Tissue

The clams (*Tapes japonica*) sampled from three Japanese rivers in 1995 and 1996 appeared to have concentrated TCA from water that was contaminated with municipal waste water and industrial effluent. Contemporary samples of the river sediment failed to show TCA and neither the clams nor the sediment contained significant amounts of chlorinated solvents. Furthermore, *in vitro* experiments failed to show metabolism of trichloroethylene or perchloroethylene by clam tissue.

5. Removal Processes

5.1 Air

The principal removal mechanism of airborne TCA is dissolution in cloud or rain-water. Because of its very high water solubility and Henry's constant (see section 1 - *Properties*) the lifetime of free trichloroacetic acid by this removal process (including uptake by the oceans) is governed by atmospheric mixing and is 10 days at most [Kindler et al., 1995; Kolb et al., 1995]. Salts of trichloroacetic acid (e.g. ammonium trichloroacetate) are similarly soluble and would have similar lifetimes but solubility data for esters of TCA (such as methyl trichloroacetate)

have not been found. Even if they were only sparingly soluble in water, their lifetimes would increase by a factor of only two or three (by analogy with substances such as phosgene) [Kindler et al., 1995]. The secondary removal process, reaction with hydroxyl radicals, has a lifetime of 84 days and has relatively little influence on atmospheric concentrations [Carr et al., 1996].

5.2 Soil

There is abundant evidence that soil microorganisms dehalogenate chlorinated aliphatic acid herbicides, particularly dalapon and TCA, and can use the carbon content as a sole source of energy. Eight active soil bacteria (from *Pseudomonas* sp., *Arthrobacter* sp. and *Pseudomonas dehalogens*), seven fungi (from *Trichoderma viride*, *Clorostachys* sp. and *Acrostalagmus* sp.) and two actinomycetes (from *Nocardia* sp.) have been identified [Foy, 1975].

Phytotoxic residues of TCA usually disappear from soil within 30-90 days [Foy, 1975]. The fastest degradation occurs on wet soil with high organic content and the slowest on dry, sandy soil [Foy, 1975]. In 12 weeks there was little degradation on sandy soil, most had disappeared on silt within 12 weeks and decomposition was "rapid" on a "muck" containing 82% organics [Crafts, 1961].

Based on full application rates (50-100 lbs/acre, equivalent to 55-110 kg ha⁻¹) and the most sensitive crop species (cereals), phytotoxicity of TCA persists in the soil for 3-6 months [Riley and Eagle, 1990]. However, more recent studies using [1,2-¹⁴C] TCA have shown that microamounts of TCA, such as those found environmentally, are rapidly degraded in soil [Forczek et al., 2000]. The same group also found that TCA was rendered less labile (and so less available) by absorption onto old wood, compost and similar carbonaceous components of the soil [Matucha et al., 2000].

5.3 Large plants

TCA sprayed onto spruce needles is slowly absorbed; 380 microg kg⁻¹ on the surface at the start of the laboratory experiment resulted in a maximum internal concentration at 15 days of about 20 microg kg⁻¹. Thereafter, the internal concentration decayed to about 15 microg kg⁻¹ in ten days [Frank, 1991].

The surface loss rate was first order in TCA, going from 380 to 100 microg kg⁻¹ in 25 days. Accumulation in the needle tissue was independent of the surface concentration and seemed to be first order in concentration in the needles, with an accumulation rate of 0.04 d⁻¹. This rather strange result would mean that the absolute flux of TCA into the needles increases with their internal TCA concentration (or perhaps with the duration of exposure to TCA - see 6. *Effects* below). Furthermore, for no apparent reason the accumulation switches to a loss process, again first order, with a time constant of 0.03 d⁻¹. Taken at their face value, and assuming that accumulation continued at the prior rate during the period when internal concentration was shown to fall (so that the observed value is the difference between the accumulation and loss rates), these results indicate a loss rate in spruce needles of 0.07 d⁻¹, presumed to be biological.

TCA has been shown to be cometabolised by microorganisms degrading ethanol under anaerobic conditions. The organisms appear to be dechlorinating TCA and will completely metabolise it at loadings up to 35 mg l⁻¹ [Kim et al., 2000].

5.4 Water

In a water course spiked with a pulse dose of TCA, none was detected after 48 hours and 14.5 km below the treatment site [Foy, 1975]. This may not be indicative of chemical or biological removal since absorption of TCA into sediments and the river bank could produce the same result.

Decarboxylation in the laboratory by conventional methods was shown to be rather slow, with a rate constant of $1.6 \times 10^{-5} \text{ s}^{-1}$ at 70°C [Hine et al., 1957] ($4 \times 10^{-5} \text{ s}^{-1}$ at 76°C in Fairclough [1938]). In the presence of water in solution in dimethyl sulphoxide and using 1,3,5-trinitrobenzene to trap the CCl₃⁺ carbocations formed, TCA was shown to decarboxylate at 25°C with a rate constant of $6 \times 10^{-3} \text{ s}^{-1}$ [Atkins et al., 1984].

Recently, however, TCA has been shown to decompose abiotically in water to give low (0.4 to 2.6 % conversion over 3 hours) yields of chloroform and perchloroethylene in the molar ratio 2:1. A decarboxylation mechanism in which the CCl₃⁺ carbocation reacts with either H⁺ or forms dichlorocarbene (:CCl₂) would fit the observations. In addition, TCA has been shown to form esters with substances such as dimethoxyphenol (a model for humic acid) which subsequently decompose giving chloroform, perchloroethylene and 2-chloro-3,5-dimethoxyphenyltrichloroacetate [Müller, 1996]. The apparent differences in these results may be a consequence of photo-oxidation reactions of the sort described by Spangenberg et al. [1996].

Recent environmental measurements have given rise to a wide range of estimates for the residence time of TCA in lake and river waters. The shortest was 8 days, for the disappearance of TCA during infiltration of river water into ground water in Switzerland [Berg et al., 2000] but this may have been influenced by the same factors as in Foy [1975]. Ellis *et al.* [2000], working in field aquatic microcosms showed removal over 40 days (including an induction period). Other rates were much slower, with Hashimoto et al. [1998] finding no loss in river water after 30 days (but 20% loss in seawater over 9 days), and Müller et al. [1996] deducing a half-life of more than 230 days from measurements in a Swiss lake.

6. Environmental Effects

TCA was introduced as a weedkiller that preferentially attacked monocotyledons; it could be used with relative impunity at application rates very much higher than the environmental loadings discussed here (see section 2.2 *Uses*). Although TCA is ubiquitous in the environment, it is particularly connected with conifers and there is a presumption that TCA is responsible for a significant part of forest die-back. The evidence for this is largely circumstantial (for example Frank et al., [1990]), and not borne out by its action on pine seedlings, which has been studied comprehensively and directly at real environmental loadings.

TCA is absorbed into scots pine (*Pinus sylvestris*) via both the roots and the needle surfaces [Sutinen et al., 1995]. It passes through the roots with the transpiration stream and there is some evidence for metabolism in this stream, up to a threshold (unspecified). Concentrations in needles up to 750 microg kg⁻¹ were achieved by sequential dosing but, with this route into the plant, there was no statistically significant change (at 1) in the mean area of the chloroplasts of the mesophyll cells (10.5±0.6 microm² for the control and 10.3±1.5 microm² with a needle loading of 750 microg kg⁻¹). By contrast, when applied to the needles, TCA solutions at 50 mg l⁻¹ gave concentrations up to 283 microg kg⁻¹ in the needles and reduced the mean area of the chloroplasts from 12.2±2.4 to 7.8±1.3 microm².

Physiologically, application of TCA to the needles disintegrated the structure of the epicuticular waxes and that of the stomatal cells. The extent of the effect was concentration and time dependent. A large fraction of the TCA (80%) remains on the needle surface and continues to cause disintegration of the stomatal cells and deterioration of the epistomatal waxes. This may account for the behaviour observed by Frank [1991], described in 5.3 above. However, the dosing concentrations used were 1 and 50 mg l⁻¹ (roughly 1,000 times environmental concentrations and corresponding to pH in the range 3.5 to 5.2). It is possible that the needle effects were simply a response to acid attack.

Solutions of lower acidity were used in subsequent experiments (Sutinen et al. reported in Juuti [1997]). In this case the exposure (via both roots and needles) was to 0.5 mg l⁻¹ and 1 mg l⁻¹ solutions (pH 5.5 to 5.2). The results showed that TCA was reversibly absorbed. The needle concentration of 16 microg kg⁻¹ before the first dosage rose to 250 microg kg⁻¹ at the higher dose rate and 60 microg kg⁻¹ at the lower within three weeks. However, when dosing stopped, the concentrations fell, ending at 35 microg kg⁻¹ in the needles of the seedlings treated with 0.5 mg l⁻¹ TCA and 60 microg kg⁻¹ at the higher dosage concentration. The higher dose rate gave a small but significant *increase* in chlorophyll concentration. Chlorophyll a/b ratio and net photosynthesis were not significantly different from the control and the small drop in transpiration rate seen with both TCA treatments was not significant. Changes in ultrastructure (chloroplast area and number, and starch grain area) were not significant in these tests, neither was the small reduction in dry weight after TCA treatment.

The concentrations observed in the needles were within those observed in needles in the field and the changes consequent on TCA treatment were almost all insignificant. The routine microscopic methods, which clearly show the effects of ozone and sulphur dioxide, do not allow diagnosis of effects from TCA.

In the same dose regime, changes were observed in oxidative metabolism (peroxidase, POX) and conjugation (glutathione S-transferase, GST) [Schröder et al., 1997]. Although none of the treated plants showed visible stress symptoms, induction of these enzymes of xenobiotic metabolism may be a stress response to TCA. It was speculated that the enhancement of enzyme activities might suggest a possible involvement of glutathione dependent detoxification but more work would be needed to substantiate the hypothesis.

Very little ill effect, if any, was observed in these controlled experiments, in contrast to some of the very early work where extensive chlorophyll bleaching was imputed to aerial incorporation of chlorinated solvents into spruce (*Picea omorica*) needles and subsequent degradation to halogenated acids by UV light (for example *Frank and Frank*, 1985; 1986]. These are not considered further here because the experimental controls were such that confounding effects of parameters (such as the use of UVC to simulate environmental UV) could not be ruled out.

7. Conclusions

The yields of TCA from chlorinated hydrocarbon solvents are small; measurements show that, while the atmospheric oxidation of perchloroethylene and methyl chloroform may account for some of the TCA detected in precipitation, large additional sources are required in order to effect a global or regional mass balance. Instead of the almost complete conversions originally proposed, it is estimated that approximately 5% of perchloroethylene released into the atmosphere could be converted into trichloroacetic acid and the upper limit on the conversion of methyl chloroform is 1.3%. So that, on a global basis, the yields of TCA are: from PCE 13,600 tonnes yr⁻¹ and from methyl chloroform 4,300 tonnes yr⁻¹, at late 1990s rates.

TCA is also produced during oxidative water treatment and could amount to 55,000 tonnes yr⁻¹ (from pulp and paper manufacture, potable water and cooling water treatments). This flux would be introduced directly into the aqueous environment and, because TCA is so soluble and is fully dissociated in water, it should be expected to remain in that phase.

TCA is widely distributed in forest soils (where it was rarely used as an herbicide). Calculations from environmental measurements indicate that a typical production rate for European forest soil would be in the region of 1600 g ha⁻¹ yr⁻¹ (range 8 to 31,000 g ha⁻¹ yr⁻¹) and the flux from the 102 million hectares of forest soils in Europe could be in the region of 160,000 tonnes yr⁻¹.

TCA is ubiquitous in rainwater and snow. Its concentrations are highly variable and the variations cannot be connected with location or date. Nor is there an anticorrelation between the quantity of rainfall and the TCA concentration (to be expected for a constant rate of generation of TCA in the atmosphere), nor any significant difference between the concentrations in cloud, rain and snow. There is no clear trend in time.

If the input of TCA were predominantly of anthropogenic origin, one would expect concentrations in the Northern hemisphere to be much higher than in the Southern. This is not the case. There is no significant difference between the concentrations found in Chile and in Eastern Canada (by the same analysts), or between Malawi and Western Canada, or between Antarctica and Switzerland.

TCA is present in old ice and firn. At the deepest levels, the firn was deposited early in the 19th century, well before the possibility of contamination by industrial production of reactive chlorine, implying a non-industrial background.

TCA is ubiquitous in soils. Concentrations are very variable but there are some indications that soils under coniferous trees (particularly *Pinus sylvestris*, Scots pine) contain higher amounts. Interestingly, the Rothamstead soil archive showed significant concentrations, supporting the measurements in old ice and firn. The highest concentration in the oldest sample studied (1865) may be the result of contamination and is still under investigation.

The concentrations of TCA found in plant tissue are region-specific and may also be plant-specific, to the extent that conifers seem to contain more than other species, in general. In the same area, *Pinus sylvestris* (Scots pine) contained several times as much as *Picea abies* (Spruce). Among the lichens, *Usneaceae* contained more than *Hypogymnia physodes*, but the trees (*Picea abies*) on which they were growing all had similar concentrations of TCA in their needles (of unspecified age).

The likelihood of a background environmental level of TCA is supported by plume measurements from pulp mills in Finland where a local influence was shown in the TCA concentration up to 20 km downwind. Beyond that, the Scots pine needles harvested appeared to contain a constant 20 to 40 microg kg⁻¹.

TCA is removed from the environment naturally. There is abundant evidence that soil microorganisms dehalogenate TCA, and a soil lifetime of a few weeks would match the observations. The loss rate of TCA from within spruce needles is first order with a constant of 0.07 d⁻¹. There is also recent evidence of an aqueous decarboxylation mechanism with a half-life of 22 days.

The supposed highly adverse botanical effects of TCA are not shown in controlled experiments. At concentrations in the needles of Scots pine similar to those observed in needles in forest trees, changes consequent on TCA treatment of field laboratory specimens were almost all insignificant. The routine microscopic methods, which clearly show the effects of ozone and sulphur dioxide, do not allow diagnosis of effects from TCA.

8. Suggestions for the Future

The greatest single difficulty with interpreting these results is that many of the data are disparate and intercomparisons are difficult, perhaps impossible in some cases. The underlying reason is that most of the studies were carried out to investigate a subset of the environmental fate of TCA so that not all relevant data were collected. Thus, for example, concentrations in rainfall and pine needles were measured but not in air or soil in the same area. The most pressing need is that, in all future studies, the TCA concentrations are measured in all environmental compartments that would be important to a field experiment. Similarly, in much of the work to date there have been presumptions, about the source of TCA or the route by which it enters plant species, that serve to confound the results, especially if not all of the relevant information is gathered.

Developments in the techniques of isotope analysis for ²D, ¹³C, ¹⁴C, ³⁵Cl and ³⁷Cl in environmental samples of TCA and PCE may prove useful in helping to

determine the sources of the TCA that has been observed in precipitation and soil. Some of these techniques may be applied now but full implementation awaits determination of the base data that will enable rigorous interpretation of results from field samples. The current status of these techniques was the subject of a workshop held on 29 January 2001 and is discussed separately in proceedings that will be published shortly.

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APPENDIX A. Measurements of environmental TCA concentrations

A.1 Measurements of TCA in air

Date	Location	ng m ⁻³		n	ng m ⁻³		Source
		mean	SD		min	max	
				21	0.03	0.3	(1) reported in (2)
					0.006	0.5	(3) reported in (4)
1999	Speulderbos, Apeldoorn, NL	0.7					(5)
1999	Bleiswijk, Rotterdam, NL	<0.5					(5)

Sources: (1) Frank et al. [1995]; (2) Juuti [1997]; (3) Klein [1997]; (4) Jordan & Frank [1999]; (5) Peters [2000]

A.2 Measurements of TCA in water

A.2.1 Contemporary precipitation

A.2.1 (a) Rain, snow and ice

Date	Location	Rain or snow	microg l ⁻¹			microg l ⁻¹		Comment	Source
			mean	SD	n	min	max		
1988-89	SW Germany, open land	R	0.44	median	34	0.119	3.3	8 sites*	(1) reported in (2)
1988-91	Canada (Mt Tremblanc Q)	Cloud				n.d.	2.5		(3)
1990-91	Berlin (urban)(D) (all)	R				0.1	20		(4) reported in (2)
1990-91	Berlin (urban)(D) (open field)	R	2.1						(4) reported in (2)
1990-91	Bonn (environ.) (D)	R	0.8	0.25	median		7.5		(5) reported in (2)
Aug-91	Spitzbergen	S	n.d.		3				(6)
Dec-91	Grossenbach (s.rural)(Siegen) (D)	R	0.57	annual average		<0.1			(6)
1989-91	open field (rural D)	R	0.44	median	34	0.02	3.27		(7) reported in (2)
Feb-92	Oberjoch (Alps)	S	0.4	0.05	2				(6)
Jun-92	Grossenbach (s.rural)(Siegen) (D)	R					2		(6)
Dec91-Nov92	Hau (rural) (D)	R				0.08	0.21		(6)
Jan/Oct 92	Hau (rural) (D)	R	0.15	0.12	median	0.08	0.3		(8) reported in (2)
1991-93	Bleche (rural) (D)	R	0.16	median		0.05	9.7		(9) reported in (2)
1991-93	Bleche (rural) (D)	S	0.09	median		0.03	0.4		(9) reported in (2)
1991-93	Austria				85	0.01	0.3		(10) reported in (2)
1993	Switzerland		0.3			<0.03	0.9		(11) reported in (2)
1993	Switzerland	R	0.3			0.044	0.71		(12) reported in (2)
1993-94	open field (rural D)	R	0.12	median	29	0.055	0.46		(7) reported in (2)
1993-94	N. Sweden/Norway	S	0.019	0.01	16	<0.005	0.037		(13)
1993-94	Antarctica, Dronning Maud	S	0.053	0.038	6	0.022	0.118		(13)
Jun/Jul-94	Russia (tundra)	S	0.009	n.s.s.	5	<0.005	0.035		(13)
Nov-94	Canada (BC)	S	0.026	0.018	4	0.006	0.043		(13)
1994-95	Kuopio (urban Finland)	R&S	0.1		18	0.02	0.21		(14)
1994-95	Kuopio (urban Finland)	R	0.12					Difference between R&S not statistically significant	(14)
1994-95	Kuopio (urban Finland)	S	0.8						(14)
1995	Switzerland	R	0.13					no difference: Zurich & Alpthal	(12)
1993-94	SW Germany, open land	R	0.124	median	115	<0.03	0.8	11 sites ⁺	(15)
1993-94	SW Germany, open land	R	0.118	median	29	0.021	0.56	11 sites*	(15)
1996-97	Antarctica, Filchner-Ronne	S	0.195	0.12	6	0.058	0.348		(16)

A.2.1 (a) Rain, snow and ice (con.)

Date	Location	Rain or Snow	microg l ⁻¹			microg l ⁻¹		Comment	Source
			mean	SD	n	min	max		

Trichloroacetic acid in the environment

1997	Canada 94W to 123W		<0.006		28			4 sites	(17)
1997	Canada (Algoma 84W)		0.033		11				(17)
1997	Canada (Chapais 74W)		0.039		11				(17)
1997	Canada (Kejimikujik 65W)		0.144		11	<0.006	0.87		(17)
1996-97	Switzerland	R&S	0.24		73			6 sites	(18)
1998	S. Scotland (forest)	R					0.09	1	(19)
1986-98	Canada (Mt Sutton Q)	cloud					n.d.	2.3	(3)
Mar/May-99	Canada (Chapais, Ont.)	R&S	0.04	0.026	6				(20)
Mar/May-99	Canada (Algoma, Ont.)	R&S	0.26	0.33	4				(20)
	Canada (Kedji, NS)	R					n.d.	1.58	(21)
Feb/Mar-99	Malawi (Senga Bay)	R	0.026	0.024	14				(20)
May/Jul-99	Chile (urban; Concepcion)	R	0.42	0.325	35				(20)
May/Sep-99	Chile (rural)	R	0.24	0.25	35				(20)
Nov-99	Speulderbos, Apeldoorn, NL	R	0.16						(22)
Nov-99	Bleiswijk, Rotterdam, NL	R	0.15						(22)

Notes: n.d. signifies *not determined*; n.s.s. signifies *not statistically significant*

* determinations carried out by the same technique, in the same location and showing a difference in time

Sources: (1) Schleyer et al. [1991]; (2) Schöler [1998]; (3) Scott et al. [1999a]; (4) Plümacher [1995]; (5) Schöler et al. [1991]; (6) Haiber et al. [1996]; (7) Schleyer et al. [1996]; (8) Fillibeck et al. [1995]; (9) Clemens [1993]; (10) Lorbeer et al. [1994]; (11) Müller et al. [1996]; (12) Reimann et al. [1996]; (13) von Sydow et al. [1999]; (14) Juuti [1997]; (15) Schleyer [1996]; (16) von Sydow et al. [2000]; (17) Scott et al. [2000a]; (18) Berg et al. [2000]; (19) Reeves et al. [1999]; (20) Scott et al. [2000b]; (21) Scott et al. [1998]; (22) Peters [2000].

A.2.1 (b) Throughfall

Date	Location	microg l ⁻¹			microg l ⁻¹		Comment	Source
		mean	SD	n	min	max		
1989-91	Rural Germany	2.68	median	35	0.69	6.85		(1) reported in (2)
	Spruce Forest	0.7	0.1	29	n.d.	2.2		(3) reported in (4)
	Beech Forest	0.3	0.02	23	n.d.	0.69		(3) reported in (4)
1990-91	Berlin (urban)(D)	0.1						(5) reported in (2)
1989-95	Spruce Forest	0.7	median	46	<0.03	2.3	4 sites	(6)
1989-95	Beech Forest	0.16	median	34	<0.03	1.03	3 sites	(6)
1989-95	Mixed Woodland	0.19	median	21	<0.03	0.94	2 sites	(6)
1993-94	Rural Germany	0.63	median	30	0.55	2.33		(1) reported in (2)

Sources: (1) Schleyer et al. [1996]; (2) Schöler [1998]; (3) Fillibeck et al. [1995]; (4) Hoekstra [1999]; (5) Plümacher [1995]; (6) Schleyer [1996].

A.2 Contemporary surface water

A.2.2 (a) Surface (other than rivers and lakes)

Date	Location		microg l ⁻¹			microg l ⁻¹		Comment	Source
			mean	SD	n	min	max		
Oct-93	Osterzgebirge (D)	bog	0.53	0.08	3				(1)
Jul-95	SW Germany	pond	0.33	0.05	3				(1)
Jul-95	Odenwald (D)	bog	0.33	0.07	3				(1)
Jul-95	Black Forest (D)	bog	1	0.12	3				(1)
	Spruce forest	soil pore	0.6	0.3	8	0.36	1.3		(2) reported in
	Agricultural land	soil pore	1	2	8	0.14	5		(4)
1989-95	SW Germany spruce forest	soil pore			25	n.d.	0.46	4 sites	(5)
1989-95	SW Germany beech forest	soil pore			16	n.d.	0.08	3 sites	(5)
1989-95	SW Germany mixed woodland	soil pore			20	n.d.	0.16	2 sites	(5)
1989-95	SW Germany open land	soil pore			28	n.d.	0.7	7 sites	(5)
1996-97	Schanghau, Switzerland	moor	0.015			0.007	0.03		(6)

Notes: n.d. signifies *not detected (limit not specified)*

Sources: (1) *Haiber et al. [1996]*; (2) *Renner & Mülhausen [1989]*; (3) *Hoekstra [1999]*; (4) *Renner et al. [1990]*; (5) *Schleyer [1996]*; *Berg et al. [2000]*.

A.2.2 (b) Rivers

Date	Location	River/location	microg l ⁻¹		microg l ⁻¹		Source
			mean	n	min	max (all reported in (2))	
1992-93	Switzerland (10 rivers)		0.14	27	<0.03	0.34	(1)
1992-93	Switzerland (alpine rivers)				<0.03		(1)
1992-93	Switzerland	Aare	0.32				(1)
1995	Germany (4 rivers)			9	0.12	0.6	(3)
1995	Germany	Neckar		4	0.15	0.51	(4)
1995-96	Germany	Heidelberg		2	0.08	0.33	(4)
1995	Germany	Rhein		3	0.1	0.16	(4)
1995	Germany	Sieg		2	0.05	0.21	(4)
1996	Germany	Schönau		2	0.09	0.09	(4)
1995	Germany	Saar	0.2	1			(4)
1995	Germany	Luek	<0.03	1			(4)
1995	Germany	Mosel	0.22	1			(4)
1995	Germany	Wupper	0.11	1			(4)
1995	Germany	Naab	0.06	1			(4)
1995	Germany	Donau	0.05	1			(4)
1995	Germany	Regen	<0.03	1			(4)
1995	Germany	Elsenz	0.16	1			(4)
1996	Germany	Chemnitz	1.88	1			(4)
1996	Japan	Sen			2.5	4.6	(5)
1996	Japan	Kurome	4.1				(5)
1996	Japan	Yagami			2.6	5.8	(5)
1996	Japan, Tokyo region	Rivers	4.55	38	0.07	22.0	(6)
1996	Japan, Tokyo region	Canals	5.93	22	0.07	20.3	(6)
1996-97	Switzerland	various rivers	0.114	80	0.014	0.7	(7)

Sources: (1) *Müller et al. [1996]*; (2) *Schöler [1998]*; (3) *Frank et al. [1995]*; (4) *Bertram [1996]* (see (2)); (5) *Hashimoto and Otsuki [1998]*; (6) *Hashimoto et al. [1998]*; *Berg et al. [2000]*.

Trichloroacetic acid in the environment

A.2.2 (c) Lakes

Date	Location	Depth or position	microg l ⁻¹		Comment	Source
			mean	n		
1992-93	Switzerland (Greifensee)	Hypolimnion	0.06			(1) reported in (2)
1992-93	Switzerland (Greifensee)	Epilimnion	0.13		other lakes less than 0.1	(1) reported in (2)
	Canada (Great Slave Lake)		0.004	1	2 other lakes n.d.	(3)
	Canada (Lake Winnipeg)		0.037	1	also n.d in Huron, Erie &	(3)
	Canada (Lake Superior) spring		n.d.	3	Ontario	(3)
	Canada (Lake Superior) summer	Lakehead	0.003	4	2 other stations n.d.	(3)
1996	Canada (L. Simcoe, Ont.)		0.14			(4)
1996-97	Switzerland	Alt. <500m	0.058	20	3 eutrophic mid-alt. lakes	(5)
1996-97	Switzerland	alt. >2330m	0.46	8	4 shallow glacial lakes	(5)
1997	Sweden (L. Groevelsjoen, Dalarna)		0.017			(4)
1997-98	Canada (Lake Superior)	60m	0.35			(6)
1997-98	Canada (Lake Superior)	90m	0.25			(6)
1997-98	Canada (Lake Superior)	120m	0.13			(6)
1997-98	Canada (Lake Superior)	150m	0.23			(6)
1997-98	Canada (Lake Superior)	180m	n.d.			(6)
1997-98	Canada (Lake Superior)	210m	0.22			(6)
1997-98	Canada (Lake Superior)	270m	n.d.			(6)
1997-98	Canada (Lake Erie)	Surface	0.13			(6)
1997-98	Canada (Lake Erie)	10m	0.15			(6)
1997-98	Canada (Lake Erie)	28m	0.18			(6)
1997-98	Canada (Lake Erie)	34m	0.2			(6)
1997-98	Canada (Lake Erie)	40m	0.4			(6)
1997-98	Canada (Lake Erie)	50m	0.53			(6)
1997-98	Canada (Lake Erie)	60m	0.24			(6)

Sources: (1) Müller et al. [1996]; (2) Schöler [1998]; (3) Scott et al. [1998]; (4) von Sydow [1998]; (5) Berg et al. [2000]; (6) Scott et al. [1999b].

A.2.2 (d) Seawater

Date	Location	Microg l ⁻¹		n	microg l ⁻¹		Source
		Mean	SD		min	max	
1996	Tokyo Bay, Japan				0.98	1.55	1
1996-97	Tokyo Bay, Japan	1.7		62	<0.07	14.9	2

Sources: (1) Hashimoto and Otsuki [1998]; (2) Hashimoto et al. [1998].

Trichloroacetic acid in the environment

A.2.3 Treated waters

Date	Location	microg l ⁻¹			Microg l ⁻¹		Source
		mean	SD	n	Min	max	
A.2.3 (a) Drinking water							
	Netherlands				0	1.4	(1) reported in (2)
	Netherlands				0.02	0.9	(1) reported in (3)
	Canada (Hamilton, Ont.)	8.4	3.3	3			(4)
	Canada (Burlington)	2.9					(4)
	Switzerland, non-chlorinated				n.d.	0.04	(5) reported in (6)
	Switzerland, non-chlorinated	0.083		6	n.d.	0.225	(7)
	Switzerland, chlorinated				n.d.	0.8	(5) reported in (6)
	USA				4	54	(8) reported in (2)
	USA				30	160	(9) reported in (2)
	France (20 sources)	4.3		20	<0.1	11.6	(10)
A.2.3 (b) Sewerage treatment plant							
1993	Switzerland, 5 plants	1.4			0.27	3.6	(11) reported in (3)
		0.43			0.04	1.1	(11) reported in (3)
		0.3		1			(12) reported in (3)
		1		1			(12) reported in (3)
	Municipal	3		1			(5) reported in (6)
1996	Tokyo, Japan				2.9	7.4	(13)
1996-97	Switzerland	0.002		17	0.0001	0.03	(7)
A.2.3 (c) Industrial							
	Kraft bleaching plant	7600					(14) reported in (2)
	Pulp mill waste	295		1			(5) reported in (6)
	Pulp mill waste	104		1			(5) reported in (6)
	"Industrial waste water", Switzerland	0.122		5	0.001	0.54	(7)
A.2.3 (d) Swimming pools							
	Germany			4	6	112	(5) reported in (6)
	Switzerland	0.045		4	0.017	0.095	(7)

Sources: (1) *Peters et al.* [1991]; (2) *Sinkkonen et al.* [1998]; (3) *Schöler* [1998]; (4) *Scott et al.* [1998]; (5) *Reimann* [1996]; (6) *Hoekstra* [1999]; (7) *Berg et al.* [2000]; (8) *Norwood et al.* [1986]; (9) *Uden & Miller* [1983]; (10) *Benanou et al.* [1998]; (11) *Müller et al.* [1996]; (12) *Bertram* [1996] (see (3)); (13) *Hashimoto & Otsuki* [1998]; (14) *Yu & Welander* [1994].

A.3 Historical environmental water

Date	Location		microg l ⁻¹			microg l ⁻¹		Comment	Source
			mean	SD	n	min	max		
A.3 (a) Old Ice									
ca 1900	Alps - Monte Rosa	Ice	0.1	0.04	3				(1)
	Storglaciaren (SE)	Ice	<0.005						(2)
	Marmaglaciaren (SE)	Ice	0.013						(2)
	Antarctica, Filchner-Ronne	Firn	0.007				36m below surface		(2)
	Antarctica, Filchner-Ronne	Firn	0.01				42m below surface		(2)
19th century	Antarctica, Filchner-Ronne	Firn	0.009				46m below surface		(2)
	Antarctica, Dronning Maud	Firn				0.014	0.0380-5m below surface		(3)
	Antarctica, Dronning Maud	Firn				0.004	0.0125-10m below surface		(3)
	Antarctica, Dronning Maud	firn				0.005	0.01710-15m below surface		(3)
19th century	Antarctica, Dronning Maud	firn				0.003	0.0415-20m below surface		(3)
A.3 (b) Groundwater									
	SW Germany, 9 wells		0.034		183	n.d.	0.21	At least one non-zero value in each well	(4)
	Germany				110	0.02	0.9		(5) reported in (6) (7) reported in (6)
1996	SW Germany, 5 wells				7	<0.03	0.09		(8) reported in (9)
	Switzerland, old groundwater		n.d.		3			15000±1800 yrs. B.P.	(10)

Sources: (1) Haiber et al. [1996]; (2) von Sydow et al. [1999]; (3) von Sydow et al. [2000]; (4) Schleyer [1996]; (5) Renner et al. [1990]; (6) Juuti [1997]; (7) Müller et al. [1996]; (8) Bertram [1996] (see (9)); (9) Schöler [1998]; Berg et al. [2000].

A.4 Soil

Date	Location	Depth cm/or horizon	microg kg ⁻¹			microg kg ⁻¹		Comment min max(predominant vegetation)	Source
			mean	SD	n	min	max		
1865/81, 1944/56	Rothamstead archive (UK)	0-10	30		4	<1	110	vegetation not known, earliest sample possibly contaminated	(1)
1986	Freudenstadt, Germany		100	200	5	20	380	Coniferous forest	(2)
Nov-91 - Jul-92	Fochteloo NL		1.6	0.9	3	1	2.7	Peat moor	(3)
Nov-91 - Jul-92	De Wieden NL		3.4	0.9	4	2.6	4.6	Peat bog	(3)
Nov-91 - Jul-92	Speulderbos, Apeldoorn, NL		0.4	0.4	3	0.2	0.9	Beech	(3)
Nov-91 - Jul-92	Speulderbos, Apeldoorn, NL		0.5	0.5	4	0.2	1.3	Douglas fir	(3)
	Berlin (D)	O	40	40				Pine	(5) reported in (4)
	Berlin (D)	A	7	4				Pine	(5) reported in (4)
	Berlin (D)	B	3	4				Pine	(5) reported in (4)
	Berlin (D)	O	8	2				Agricultural	(5) reported in (4)
	Berlin (D)	A	0.92	0.05				Agricultural	(5) reported in (4)
	Berlin (D)	B	0.08	0.004				Agricultural	(5) reported in (4)
	Hessian Odenwald (D)		3.8					R. sediment (Rotwasser)	(6)
Apr-97	Caucasus 2200m asl		0.04					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Caucasus 2200m asl		0.09					<i>Pinus Sylvestris</i>	(7)
Apr-97	Caucasus 300m asl		0.22					<i>Pinus Sylvestris</i>	(7)
Apr-97	Caucasus 800m asl		0.31					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Caucasus 800m asl		0.21					<i>Pinus Sylvestris</i>	(7)
Apr-97	Caucasus (height not spec.)		0.24					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Caucasus (height not spec.)		0.35					<i>Pinus Sylvestris</i>	(7)
Apr-97	Caucasus 2000m asl		0.46					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Caucasus 2000m asl		0.39					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Caspian Sea (Volga delta)		0.32					<i>Pinus Sylvestris</i>	(7)
Apr-97	Caspian Sea (Volga delta)		1.09					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Caspian Sea (Volga delta)		1.06					<i>Pinus Sylvestris</i>	(7)
Apr-97	Steppe S of Volgograd		0.34					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Steppe S of Volgograd		0.22					<i>Pinus Sylvestris</i>	(7)
Apr-97	Steppe S of Volgograd		0.08					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	Steppe S of Volgograd		0.22					<i>Pinus Sylvestris</i>	(7)
Apr-97	40km W of Moscow		0.1					<i>Pinus Sylvestris</i>	(7)
Jul/Aug-97	40km W of Moscow		n.d.					<i>Pinus Sylvestris</i>	(7)
Jul-99	Chile (11 sites)	0-10	22			0.3	152	<i>Pinus radiata</i>	(1)
Jul-99	Chile (11 sites)	10-20	5.4			0.3	21	<i>Pinus radiata</i>	(1)
Jul-99	of which, 4 sites	0-20	<1					<i>Pinus radiata</i>	(1)
Jul-99	4 sites	0-10	<1					<i>Pinus radiata</i>	(1)
Jul-99	2 sites	10-20	<1					<i>Pinus radiata</i>	(1)
Jul-99	Chungara	0-10	62					<i>Pinus radiata</i>	(1)
Jul-99	Cotacotani	10-20	4					<i>Pinus radiata</i>	(1)
Jul-99	Masi (site (a))	0-10	152					<i>Pinus radiata</i>	(1)
Jul-99	Masi (site (b))	10-20	13					<i>Pinus radiata</i>	(1)
Jul-99	Polcura	10-20	14					<i>Pinus radiata</i>	(1)
Jul-99	Risopatron	10-20	130					<i>Pinus radiata</i>	(1)
Jul-99	Venus	0-10	20					<i>Pinus radiata</i>	(1)

Trichloroacetic acid in the environment

4.4 Soil (con.)

Date	Location	Depth cm/or horizon	microg kg ⁻¹			microg kg ⁻¹		Comment max(predominant vegetation)	Source
			mean	SD	n	min	max		
Jul-99	Venus (Chile)	10-20	24				<i>Pinus radiata</i>	(1)	
13 Oct 99	Speulderbos, Apeldoorn, NL	10	0.44				Spruce, humic soil	(8)	
13 Oct 99	Speulderbos, Apeldoorn, NL	30	0.18				Spruce, humic soil	(8)	
13 Oct 99	Speulderbos, Apeldoorn, NL	100	0.21				Spruce, sandy soil	(8)	
13 Oct 99	Speulderbos, Apeldoorn, NL	10	0.26				non agricult., sandy soil	(8)	
13 Oct 99	Speulderbos, Apeldoorn, NL	30	0.34				non agricult., sandy soil	(8)	
13 Oct 99	Speulderbos, Apeldoorn, NL	100	0.44				non agricult., sandy soil	(8)	
13 Oct 99	Bleiswijk, Rotterdam, NL	10	<0.05				deciduous, sandy soil	(8)	
13 Oct 99	Bleiswijk, Rotterdam, NL	30	<0.05				deciduous, sandy soil	(8)	
13 Oct 99	Bleiswijk, Rotterdam, NL	100	0.14				deciduous, sandy soil	(8)	
13 Oct 99	Bleiswijk, Rotterdam, NL	10	<0.05				non agricult., clay soil	(8)	
13 Oct 99	Bleiswijk, Rotterdam, NL	30	<0.05				non agricult., clay soil	(8)	
13 Oct 99	Bleiswijk, Rotterdam, NL	80	0.13				non agricult., clay soil	(8)	
20 Oct 99	Freudenstadt, Germany	10	2.1				Spruce, humic soil	(8)	
20 Oct 99	Freudenstadt, Germany	30	5.4				Spruce, humic soil	(8)	
20 Oct 99	Freudenstadt, Germany	60	12				Spruce, humic soil	(8)	
20 Oct 99	Freudenstadt, Germany	10	1.3				non agricult., sandy soil	(8)	
20 Oct 99	Freudenstadt, Germany	30	1.9				non agricult., sandy soil	(8)	
20 Oct 99	Freudenstadt, Germany	90	0.63				non agricult., sandy soil	(8)	
23 Oct 99	Kiel, Germany	10	0.81				Spruce, humic soil	(8)	
23 Oct 99	Kiel, Germany	30	1.4				Spruce, humic soil	(8)	
23 Oct 99	Kiel, Germany	80	0.33				Spruce, sandy soil	(8)	
23 Oct 99	Kiel, Germany	30	0.18				non agricult., sandy soil	(8)	
23 Oct 99	Kiel, Germany	100	0.29				non agricult., sandy soil	(8)	
26 Oct 99	Mölndal, Göteborg, Sweden	10	0.29				Spruce, humic soil	(8)	
26 Oct 99	Mölndal, Göteborg, Sweden	30	<0.05				Spruce, humic soil	(8)	
26 Oct 99	Mölndal, Göteborg, Sweden	70	0.63				Spruce, sandy soil	(8)	
26 Oct 99	Mölndal, Göteborg, Sweden	10	<0.05				non agricult., sandy soil	(8)	
26 Oct 99	Mölndal, Göteborg, Sweden	30	0.22				non agricult., sandy soil	(8)	
26 Oct 99	Mölndal, Göteborg, Sweden	80	0.30				non agricult., sandy soil	(8)	
15 Nov 99	Sherwood Forest, Notts., UK	10	1.26				Spruce, humic soil	(8)	
15 Nov 99	Sherwood Forest, Notts., UK	30	0.19				Spruce, sandy soil	(8)	
15 Nov 99	Sherwood Forest, Notts., UK	70	0.18				Spruce, sandy soil	(8)	
15 Nov 99	Sherwood Forest, Notts., UK	10	0.11				non agricult., sandy soil	(8)	
15 Nov 99	Sherwood Forest, Notts., UK	30	0.23				non agricult., clay soil	(8)	
15 Nov 99	Sherwood Forest, Notts., UK	80	0.27				non agricult., clay soil	(8)	
16 Nov 99	Aberfoyle, Scotland, UK	10	<0.05				Spruce, humic soil	(8)	
16 Nov 99	Aberfoyle, Scotland, UK	30	0.20				Spruce, humic soil	(8)	
16 Nov 99	Aberfoyle, Scotland, UK	60	0.18				Spruce, sandy soil	(8)	
16 Nov 99	Aberfoyle, Scotland, UK	10	<0.05				non agricult., sandy soil	(8)	
16 Nov 99	Aberfoyle, Scotland, UK	30	0.23				non agricult., sandy soil	(8)	
16 Nov 99	Aberfoyle, Scotland, UK	80	0.15				non agricult., sandy soil	(8)	
18 Nov 99	Fosso, near Venice, Italy	10	0.63				Spruce, humic soil	(8)	
18 Nov 99	Fosso, near Venice, Italy	30	0.16				Spruce, humic/sandy soil	(8)	
18 Nov 99	Fosso, near Venice, Italy	80	0.14				Spruce, sandy soil	(8)	
18 Nov 99	Fosso, near Venice, Italy	10	0.17				non agricult., sandy soil	(8)	

Trichloroacetic acid in the environment

4.4 Soil (con.)

Date	Location	Depth cm/or horizon	microg kg ⁻¹			microg kg ⁻¹		Comment max(predominant vegetation)	Source
			mean	SD	n	min	max		
18 Nov 99	Fosso, near Venice, Italy	30	0.10					non agricult., sandy soil	(8)
18 Nov 99	Fosso, near Venice, Italy	80	0.11					non agricult., sandy soil	(8)
19 Nov 99	Nami, near Rome, Italy	10	0.37					Spruce, humic soil	(8)
19 Nov 99	Nami, near Rome, Italy	30	0.09					Spruce, humic soil	(8)
19 Nov 99	Nami, near Rome, Italy	100	<0.05					Spruce, sandy soil	(8)
19 Nov 99	Nami, near Rome, Italy	10	<0.05					non agricult., sandy soil	(8)
19 Nov 99	Nami, near Rome, Italy	30	0.11					non agricult., sandy soil	(8)
19 Nov 99	Nami, near Rome, Italy	80	<0.05					non agricult., sandy soil	(8)
25 Nov 99	Jessheim, Oslo, Norway	10	0.23					Spruce, humic soil	(8)
25 Nov 99	Jessheim, Oslo, Norway	30	0.46					Spruce, humic soil	(8)
25 Nov 99	Jessheim, Oslo, Norway	60	<0.05					Spruce, sandy soil	(8)
25 Nov 99	Jessheim, Oslo, Norway	10	<0.05					non agricult., sandy soil	(8)
25 Nov 99	Jessheim, Oslo, Norway	30	0.08					non agricult., sandy soil	(8)
25 Nov 99	Jessheim, Oslo, Norway	80	<0.05					non agricult., sandy soil	(8)
Dec-99	Lancaster (rural) UK	0-10	8.5		5		<1	29non agricultural field	(1)
1999	Malawi (3 sites)	0-10	2.6				<1	9Conifer (unspecified)	(1)
1999	Malawi (3 sites)	10-20	<1				<1	3Conifer (unspecified)	(1)
Feb-00	Canada (2 sites)	0-10	5.4				<1	19Conifer (unspecified)	(1)
Feb-00	Canada (2 sites)	10-20	4				<1	10Conifer (unspecified)	(1)
Feb-00	of which, Guelph W	0-10	1					Conifer (unspecified)	(1)
Feb-00	Guelph E	0-10	5					Conifer (unspecified)	(1)
Feb-00	Burlington	0-10	0.5					Conifer (unspecified)	(1)
Feb-00	Burlington	10-20	0.5					Conifer (unspecified)	(1)

Notes: n.d. signifies *not detected (limit not specified)*

Sources: (1) *Scott et al.* [2000]; (2) *Frank* [1988]; (3) *Hoekstra and de Leer* [1993]; (4) *Hoekstra* [1999]; (5) *Plümacher* [1995]; (6) *Bertram* [1996] (see *Schöler* [1998]); (7) *Weissflog et al.* [1999]; (8) *Peters* [2000].

A.5 Biota

Date	Location	Needle Age yrs	microg kg ⁻¹			microg kg ⁻¹		Comment	Source
			fr. wt. mean	SD	n	fr. wt. min	max		
Plants									
1989-90	Bernstein, N. Black Forest (D)	1			15		4	67Spruce needles	(1)
1989-90	680-750 m asl	2			15		8	96Spruce needles	(1)
1989-90	Schönbuch, S. of Stuttgart (D)	1			11		3	25Spruce needles	(1)
1989-90	360m asl	2			12		10	50Spruce needles	(1)
1989-90	Black Forest (D)	1	11		1			Fir needles	(2)
1989-90	Black Forest (D)	2	16		1			Fir needles	(2)
1990s	Ore Mts. Czech Rep.	1			2		28	106 <i>Picea abies</i> needles	(3)
1990s	Ore Mts. Czech Rep.	2			2		90	126 <i>Picea abies</i> needles	(3)
1990s	Ore Mts. Czech Rep.	3	47	38	10		11	126 <i>Picea abies</i> needles	(3)
					29		0.2	6Vegetables, fruit, grains	(4) reported in (6)
					9		<1	44Deciduous forest leaves	(5)
	Various European				1600		0.6	178conifer needles	(6)

4.5 Biota (con.)

Date	Location	Age yrs	microg kg ⁻¹ fr. wt.			microg kg ⁻¹ fr. wt.		Comment	Source
			mean	SD	n	min	max		
Autumn	Pallastunturi (SF)	3	29		89	6	160	<i>Pinus sylvestris</i> needles	(6) & (7)
winter	Sodankyla (SF)	3	22		10	16	69	<i>Picea abies</i> needles	(6) & (7)
autumn	Rovaniemi (SF)	3	23		57	6	64	<i>Pinus sylvestris</i> needles	(6) & (7)
winter	Taivalkoski (SF)	3	24		13	18	36	<i>Picea abies</i> needles	(6) & (7)
autumn	Joensuu (SF)	3	12		10	6	39	<i>Picea abies</i> needles	(6) & (7)
summer	Ilomantsi (SF)	3	74		10	33	180	<i>Pinus sylvestris</i> needles	(6) & (7)
summer	Jamijarvi (SF)	3	45		10	20	73	<i>Pinus sylvestris</i> needles	(6) & (7)
autumn	Janakkala (SF)	3	18		10	13	49	<i>Pinus sylvestris</i> needles	(6) & (7)
autumn	Janakkala (SF) (2nd site)	3	6		9	1	16	<i>Pinus sylvestris</i> needles	(6) & (7)
	Sodankyla (lichen)		90	median		75	128	<i>Usneaceae</i>	(7)
	Sodankyla (needles)		28	median		25	42	on <i>Picea abies</i>	(7)
	Taivalkoski (lichen)		138	median		110	193	<i>Usneaceae</i>	(7)
	Taivalkoski (needles)		25	median		23	33	on <i>Picea abies</i>	(7)
	Joensuu (lichen)		15	median		10	16	<i>Hypogymnia physodes</i>	(7)
	Joensuu (needles)		13	median		12	23	on <i>Picea abies</i>	(7)
	Riihimaki (lichen)		6	median		5	9	<i>Hypogymnia physodes</i>	(7)
	Riihimaki (needles)		12	median		8	24	on <i>Picea abies</i>	(7)
1993	Various German forests	1	4.4	median	12	0.9	19.3	conifer needles, species	(8)
		2	5.3	median	8	0.7	30.7	not known	(8)
1993-94	Finland downwind of kraft pulp mill - 5km, 20m asl	3	171	55	14	92	276	<i>Pinus sylvestris</i> needles	(9)
	9km, 35m asl	3	57	34	17	11	116	<i>Pinus sylvestris</i> needles	(9)
	9km, 40m asl	3	99	54	6	16	171	<i>Pinus sylvestris</i> needles	(9)
	12km, 70m asl	3	94	53	12	28	202	<i>Pinus sylvestris</i> needles	(9)
	22km, 80m asl	3	32	10	6	18	45	<i>Pinus sylvestris</i> needles	(9)
	32km, 90m asl	3	33	13	10	15	53	<i>Pinus sylvestris</i> needles	(9)
	36km, 115m asl	3	60	28	12	16	116	<i>Pinus sylvestris</i> needles	(9)
	46km, 145m asl	3	32	24	6	6	71	<i>Pinus sylvestris</i> needles	(9)
	55km, 145m asl	3	41	16	6	28	64	<i>Pinus sylvestris</i> needles	(9)
	61km, 145m asl	3	29	13	5	11	45	<i>Pinus sylvestris</i> needles	(9)
	78km, 140m asl	3	30	13	6	6	43	<i>Pinus sylvestris</i> needles	(9)
Feb-94	Finland crosswind from kraft pulp mill - 5km, 5m asl	3	7	2	6	5	11	<i>Pinus sylvestris</i> needles	(9)
	25km, 10m asl	3	68	38	5	29	111	<i>Pinus sylvestris</i> needles	(9)
	48km, 10m asl	3	13	3	5	10	18	<i>Pinus sylvestris</i> needles	(9)
	51km, 45m asl	3	28	18	5	11	54	<i>Pinus sylvestris</i> needles	(9)
	54km, 80m asl	3	8	1	4	6	9	<i>Pinus sylvestris</i> needles	(9)
	60km, 100m asl	3	56	27	5	15	83	<i>Pinus sylvestris</i> needles	(9)
1996	Various German forests	1	2.7		21	0.8	16.7	Conifer needles,	(8)
		2	3.6		10	1.9	10.5	species not known	(8)
		3	4.7		10	2	7.6		(8)
Apr-97	Caucasus 2200m asl	2	3.18	0.95				<i>Pinus sylvestris</i> needles	(10)
Jul/Aug-97	Caucasus 2200m asl	2	3.54	1.5				<i>Pinus sylvestris</i> needles	(10)
Apr-97	Caucasus 300m asl	2	4.99	2.79				<i>Pinus sylvestris</i> needles	(10)
Apr-97	Caucasus 800m asl	2	4	1.12				<i>Pinus sylvestris</i> needles	(10)
Jul/Aug-97	Caucasus 800m asl	2	5.2	1.82				<i>Pinus sylvestris</i> needles	(10)
Apr-97	Caucasus (height not spec.)	2	3.91	0.88				<i>Pinus sylvestris</i> needles	(10)
Jul/Aug-97	Caucasus (height not spec.)	2	5.15	1.4				<i>Pinus sylvestris</i> needles	(10)
Apr-97	Caucasus 2000m asl	2	7.25	3.94				<i>Pinus sylvestris</i> needles	(10)

4.5 Biota (con.)

Date	Location	Age yrs	microg kg ⁻¹ fr. wt.			microg kg ⁻¹ fr. wt.		Comment	Source
			mean	SD	n	min	max		
Jul/Aug-97	Caucasus 2000m asl	2	5.28	2.1				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	Caucasus 1500m asl	2	4.29	0.16				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	Caspian Sea (W shore)	2	8.69	1.61				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	Caspian Sea (Volga delta)	2	3.15	1.39				<i>Pinus sylvestris</i> needles (10)	
Apr-97	Caspian Sea (Volga delta)	2	20.73	5.8				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	Caspian Sea (Volga delta)	2	27.4	9.99				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	R. Volga valley	2	10.37	17.12				<i>Pinus sylvestris</i> needles (10)	
Apr-97	Steppe S of Volgograd	2	6.85	2.71				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	Steppe S of Volgograd	2	10.07	2.73				<i>Pinus sylvestris</i> needles (10)	
Apr-97	Steppe S of Volgograd	2	28.43	9.44				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	Steppe S of Volgograd	2	68.91	37.97				<i>Pinus sylvestris</i> needles (10)	
Apr-97	40km W of Moscow	2	5.28	0.79				<i>Pinus sylvestris</i> needles (10)	
Jul/Aug-97	40km W of Moscow	2	n.d.					<i>Pinus sylvestris</i> needles (10)	
Jul-99	Chile (8 sites)	1	<1					<2 <i>Pinus Radiata</i> needles (11)	
Mar-98	Canada (Banff Nat. Park, 15 sites)	1	<1					<1 <i>Picea glauca</i> , <i>Abies lasiocarpa</i> needles (11)	
1999	Netherlands							25 Kale exposed to PCE @ NOEC (2000 µg m ⁻³) (12)	
1999	Netherlands							7 Bean exposed to PCE @ NOEC (46 µg m ⁻³) (12)	
1999	Netherlands							3 Bean exposed to PCE @ NOEC (2000 µg m ⁻³) (12)	
Oct-99	Speulderbos, Apeldoorn, NL		6.4					Spruce needles (13)	
Oct-99	Bleiswijk, Rotterdam, NL		7.7					deciduous leaves (13)	
Oct-99	Freudenstadt, Germany		6.8					Spruce needles (13)	
Oct-99	Kiel, Germany		17					Spruce needles (13)	
Nov-99	Mölnädal, Göteborg, Sweden		5.5					Spruce needles (13)	
Nov-99	Sherwood Forest, Notts., UK		12					Spruce needles (13)	
Nov-99	Aberfoyle, Scotland, UK		9.8					Spruce needles (13)	
Nov-99	Fosso, near Venice, Italy		5.4					Spruce needles (13)	
Nov-99	Nami, near Rome, Italy		5.1					Spruce needles (13)	
Nov-99	Jessheim, Oslo, Norway		4.7					Spruce needles (13)	
Feb-00	Canada (Guelph, Ont.)	1	2					Pine needles (11)	
	Malawi	1	3					Conifer needles (11)	
	Lancaster UK	1	87					Conifer needles (11)	
Animal Tissue									
1995	Ariho R., Yamaguchi, Japan		21	2	5				Clam <i>Tapes japonica</i> (13)
1995	Koe R., Yamaguchi, Japan		50	6	5				Clam <i>Tapes japonica</i> (13)
1995	Okita R., Yamaguchi, Japan		< 1						Clam <i>Tapes japonica</i> (13)
1996	Ariho R., Yamaguchi, Japan		27	3					Clam <i>Tapes japonica</i> (13)
1996	Koe R., Yamaguchi, Japan		69	4					Clam <i>Tapes japonica</i> (12)

Notes; n.d. signifies *not detected (limit unspecified)*, asl signifies *above sea level*, * signifies that the results are awaited.

Sources: (1) Frank [1991]; (2) Frank et al. [1990]; (3) Matucha et al. [1999]; (4) Reimann et al. [1996]; (5) Frank [1988]; (6) Juuti [1997]; (7) Juuti et al. [1996b]; (8) Frank et al., [1998]; (9) Juuti et al. [1995]; (10) Weissflog et al. [1999]; (11) Scott et al. [2000]; (12) van der Eerden et al. [2000]; (13) Gotoh et al. [1998].

APPENDIX B. Measurements of perchloroethylene and methyl chloroform in the atmosphere and in biota

Measurements of the environmental concentrations of the man-made potential precursors to trichloroacetic acid are listed in the following tables.

Table B.1. Perchloroethylene in the atmosphere

Date	Location		microg		SD	n	min	max	Source
			m ⁻³	ppt					
			mean	mean					
Aug-Sep-86	Mauzenberg, B.F.(D) 740m asl		0.89		0.42	13			(1)
	Bernstein, B.F.(D) 600m asl		0.78		0.54	13			(1)
	Sulzbach, B.F.(D) 320m asl		0.63		0.22	13			(1)
	Schönbuch, B.F.(D) 460m asl		0.69		0.38	13			(1)
1986-87	Cities (unspecified)		6.7						(2) reported in (3)
	Black Forest (B.F.)(D)		1.2	median			0.2	25	(3)
Sep-87	Mauzenberg, B.F.(D) 740m asl		1.9	air	1.8	6			(4)
			3	soil	0.6	6			(4)
	Bernstein, B.F.(D) 600m asl		2.5	air	1.8	4			(4)
			3.8	soil	0.5	4			(4)
	Schönbuch, B.F.(D) 460m asl		0.9	air	0.5	6			(4)
1986-1988	SW Germany (B.F., 4 sites)		3.4	soil	0.7	6			(4)
Nov-88	SW Germany		0.9			32	0.2	20	(5) repeated in (6)
	S of Lisbon (P)					31	0.2	8.3	(6) repeated in (7)
Nov-88 - Mar-89	Madeira					3	0.1	2	(6) repeated in (7)
	Centre of Tübingen (D)		2				0.1	0.1	(6) repeated in (7)
	Rastatt Northern B.F. (D)		1				1	120	(7)
	S of Lisbon (P)		0.3				0.2	9	(7)
1989	Remote Atlantic NH	ppt					0.02	0.5	(7)
		microg m ⁻³	0.10	13	6				(8)
1989	Remote Atlantic SH	ppt		2.7	4				(8)
		microg m ⁻³	0.02		0.03				calculated from (8)
Sep 1991	North Sea	ppt				10	14	(9) reported in (13)	
Sep-Oct-91	W. Pacific lats >25N	ppt	2.2	7.2		149	2.1	231	(9) reported in (13)
		microg m ⁻³	0.05				0.02	1.71	calculated from (10)
Jun-92	Madeira/Azores	ppt		16	7		0.01	35	calculated from (10)
		microg m ⁻³	0.12		0.05		0.01	0.26	calculated from (11)
Sep-Oct-92	Brazil (Tocantins)	ppt		2.4			1.8	2.8	(12)
		microg m ⁻³	0.02				0.01	0.02	calculated from (12)
Feb-Mar-94	W. Pacific lats >25N	ppt		21		134	16	370	(10)
		microg m ⁻³	0.16				0.12	2.74	calculated from (10)
		ppt		7.5		178	1.9	24	(10)
Sep 1994	W. Pacific lats 4N-43N	ppt		7	17.4		0.01	0.18	calculated from (10)
		microg m ⁻³	0.05		0.13				(13)
Nov 1995	Southern Ocean off Hobart Tas.	ppt		1.47	0.03				calculated from (14)
		microg m ⁻³	0.01		0.0002				calculated from (14)
		ppt		1.09	0.02				(14)
Mar 1996*	Bilbao, Spain	ppt	0.01		0.0002				calculated from (14)
		microg m ⁻³	3	400	800			10900	(15)
Oct 1996	Southern Pacific	ppt		1.8	0.8				calculated from (15)
		microg m ⁻³	0.01		0.006				(16)
Oct 1996	Remote Atlantic NH	ppt		1.0	0.2	11 locations			calculated from (16)
		microg m ⁻³	0.01		0.002				(17)
Oct-Nov 1996	Remote Atlantic SH	ppt		0.3	0.06	11 locations			calculated from (17)
		microg m ⁻³	0.002		0.0005				(17)
July-Aug 1997	Ny-Ålesund, Spitzbergen	ppt		2.72	0.17	303	2.39	3.52	calculated from (18)
		microg m ⁻³	0.021		0.001				calculated from (18)
1997	Global - 8 Sites in CMDL network	ppt					1	8	(19)

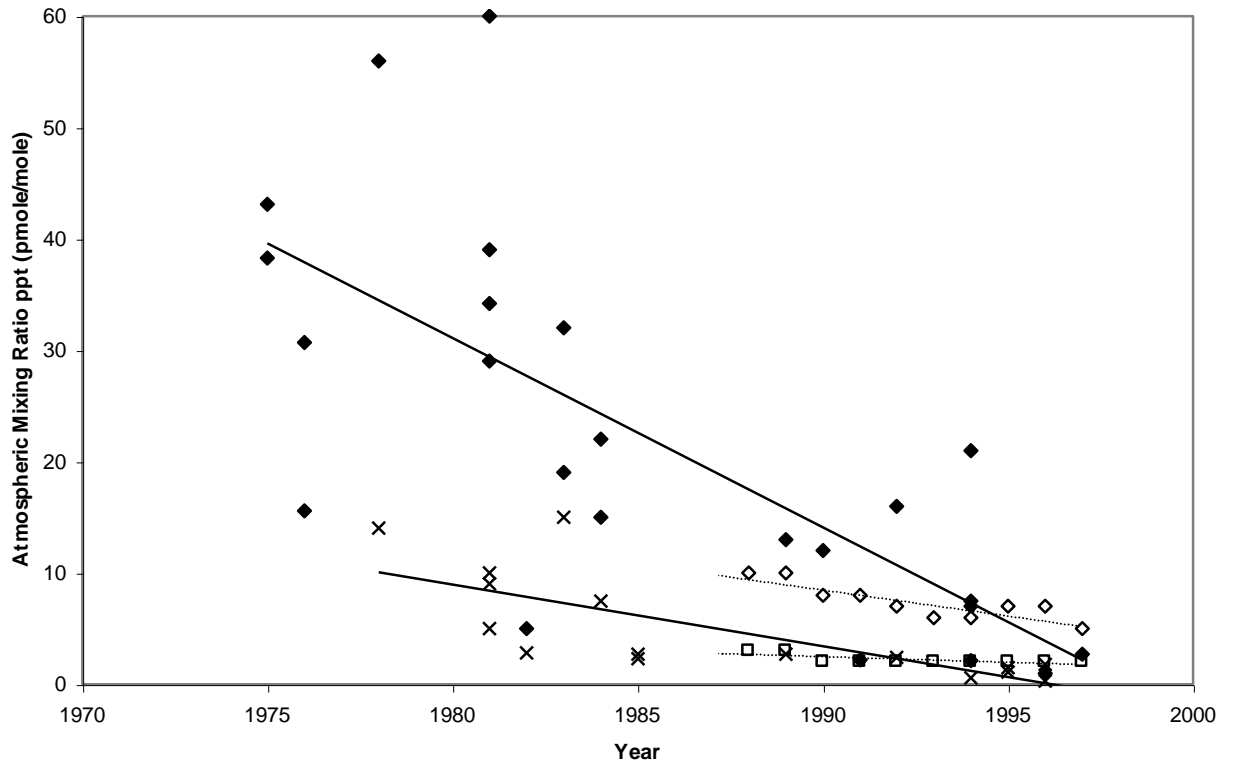


Figure B-1. Atmospheric concentration of perchloroethylene above the remote ocean.

Filled diamonds: measured northern hemispherical concentrations from Table B-1 and Fischer et al. [2000], together with the trend line.

Open diamonds: calculated northern hemispherical concentrations and trend from Dimmer et al. [2001].

Crosses: measured southern hemispherical concentrations from Table B-1 and Fischer et al. [2000], together with the trend line.

Open squares: calculated southern hemispherical concentrations and trend from Dimmer et al. [2001].

Notes to Table B-1: * these results seem wholly at odds with the rest and may not be reliable.

"B.F." signifies Black Forest.

Sources: (1) Frank & Frank [1988a]; (2) Neumayr [1981]; (3) Frank & Frank [1988b]; (4) Frank et al. [1989]; (5) Frank & Frank [1990]; (6) Frank [1991]; (7) Frank et al. [1991]; (8) Koppmann et al. [1993]; (9) Quack [1994]; (10) Blake et al [1997]; (11) Blake et al. [1996b]; (12) Blake et al. [1996c]; (13) Quack & Suess [1999]; (14) Blake et al. [1999]; (15) Alonso et al. [1999]; (16) Wingenter et al. [1999]; (17) Fischer et al. [2000]; (18) Dimmer et al. [2001]; (19) CMDL [1998].

Table B.2. Methyl chloroform in the atmosphere

Date	Location	microg		SD	n	min	max	Source
		m ⁻³ mean	ppt mean					
Aug-Sep 86	Mauzenberg, B.F.(D) 740m asl	1.4		0.48	13			(1)
Aug-Sep 86	Bernstein, B.F.(D) 600m asl	1.25		0.56	13			(1)
Aug-Sep 86	Sulzbach, B.F.(D) 320m asl	1.18		0.43	13			(1)
Aug-Sep 86	Schönbuch, B.F.(D) 460m asl	1.29		0.46	13			(1)
	Cities (unspecified)	2.2						(2) reported in (3)
1986-87	Northern Black Forest (D)	1.2	median			0.6	5.7	(3)
Sep-87	Mauzenberg, B.F.(D) 740m asl	1.3	air	0.3	6	1	1.9	(4)
		2.3	soil	0.4	6	1.7	2.7	(4)
	Bernstein, B.F.(D) 600m asl	1.4	air	0.3	4	0.9	1.6	(4)
		2.1	soil	0.3	4	1.7	2.3	(4)
	Schönbuch, B.F.(D) 460m asl	1.2	air	0.3	6	0.8	1.5	(4)
		2.6	soil	0.8	6	1.9	2.8	(4)
1986-1988	SW Germany (B.F., 4 sites)	1.25				0.5	5	(5) repeated in (8)
1986	Mace Hd. IRL (background air)	0.74	125					(6), (7)
Nov-88 - Mar-89	Centre of Tübingen (D)	2				1	20	(8)
	Rastatt Northern B.F. (D)	1.5				0.4	4	(8)
	S of Lisbon (P)	0.6				0.4	1.5	(8)
	Madeira	0.6				0.4	1	(8)
1989	Mace Hd. IRL (background air)	0.83	140					(6), (7)
Sep-Oct-91	W. Pacific lats >25N	ppt	137		149	114	695	(9)
		Microg m ⁻³	0.82			0.68	4.14	calculated from (9)
	W. Pacific lats <25N	ppt	124		172	102	194	(9)
		Microg m ⁻³	0.74			0.61	1.16	calculated from (9)
Jun-92	Madeira/Azores	ppt	156	12		139	194	(9)
		Microg m ⁻³	0.93	0.07		0.83	1.16	calculated from (9)
1992	Mace Hd. IRL (background air)	0.89	150					(6), (7)
Feb-Mar-94	W. Pacific lats >25N	ppt	133		134	128	550	(9)
		Microg m ⁻³	0.79			0.76	3.28	calculated from (9)
	W. Pacific lats <25N	ppt	127		178	117	189	(9)
		Microg m ⁻³	0.76			0.70	1.13	calculated from (9)
1995	Mace Hd. IRL (background air)	0.69	115					(6), (7)
1997	Global - 8 sites in CMDL network		77					(10)
1998	Mace Hd. IRL (background air)	0.42	70					(6), (7)

Note: "B.F." signifies Black Forest.

Sources: (1) Frank & Frank [1988a]; (2) Neumayr [1981]; (3) Frank & Frank [1988b]; (4) Frank et al. [1989]; (5) Frank & Frank [1990]; (6) Prinn et al. [1995]; (7) Prinn et al. [1998]; (8) Frank et al. [1991]; (9) Blake et al [1997]; CMDL [1998].

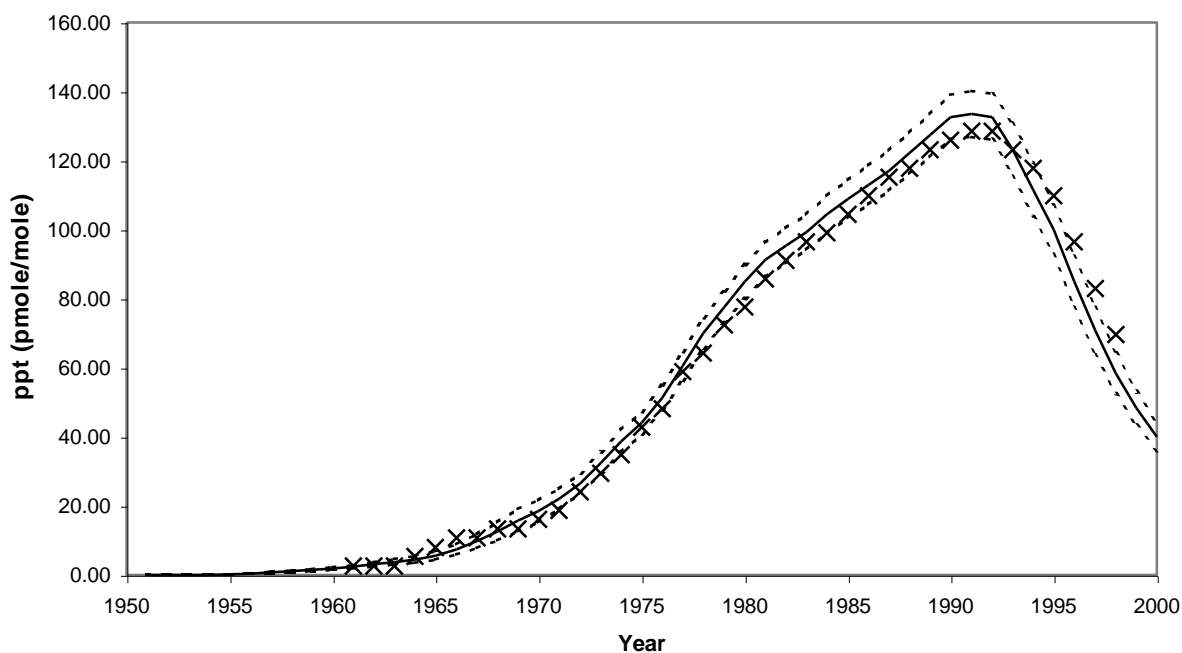


Figure B-2. Time history of globally averaged methyl chloroform concentration.

(x): globally averaged concentrations calculated from measurements [*Prinn et al., 2000*].

(-): concentrations calculated from emissions using an atmospheric lifetime of 4.8 years and, dotted lines (...), their two uncertainties [*McCulloch and Midgley, 2001*].

Table B.3. Perchloroethylene and methyl chloroform in industrial plumes over the Western Pacific Ocean in 1992

Source	Methyl chloroform		Perchloroethylene	
	Measured	Representative background	Measured	Representative background
	ppt	ppt	ppt	ppt
Source fingerprints (measured = urban)				
Tokyo	524	158	84	8
Hong Kong	195	137	35	5
San Jose	305	162	84	13
Plume fingerprints (measured = average in plume)				
S. Taiwan	121	121	3	3
S. Korea	159	117	16	5
E. China	139	123	11	3
S. Japan	146	122	11	4

Source: *Blake et al. [1996a]*

The relative urban enhancement of the concentration of perchloroethylene is markedly greater than the similar enhancement of methyl chloroform

concentrations. It appears that this reflects the shorter lifetime of perchloroethylene and the smaller influence of the background concentration in an urban atmosphere near emission sources. This is also illustrated in the plume results of *Blake et al.* [1996a] shown in Table A3 above.

Both perchloroethylene and methyl chloroform concentrations are enhanced in soil pores compared to the prevailing atmosphere. No significance has been attached to this.

Within the limits of the uncertainty of atmospheric lifetime, Figure B-2 shows that the methyl chloroform measured in the atmosphere can be ascribed to anthropogenic emissions. The case is not nearly as clear for perchloroethylene, shown in Figure B-1. While there has been a marked downward trend in the concentrations measured in remote marine locations, the rate of decline is significantly greater, in both northern and southern hemispheres, than the decline in concentration calculated from emissions. These differences argue for release to the atmosphere of perchloroethylene from sources additional to its manufacture and use as a solvent. The sources may well be man-made.

Perchloroethylene and methyl chloroform in sea water

During several cruises in the North Sea in the years 1988-1991, perchloroethylene was found in 781 surface water samples at an arithmetic mean concentration of 1.34 ng l⁻¹ and a range of 0.09 to 21.4 ng l⁻¹ [*Nightingale*, 1991]. The lower measurements agree with those of *Singh et al.* [1983] (0.1 to 2.8 ng l⁻¹) in the Eastern Pacific Ocean. The spatial distribution of the North Sea measurements was consistent with riverborne anthropogenic input and solubility controlled by water temperature. The values reported in *de Rooij et al.* [1998] of up to 470 ng l⁻¹ for the Rhine estuary and 820, 870 and 590 for the Elbe, Scheldt and Tees, respectively, support this.

Although there were fewer determinations, methyl chloroform presented a similar spatial distribution controlled by riverborne input and loss to the atmosphere by volatilisation. The mean concentration in the North Sea was 4.73 ng l⁻¹ [*Nightingale*, 1991] and estuaries of the major feed rivers carried up to 90 ng l⁻¹ [*Euro Chlor* , 1999].

Table B.4. **Perchloroethylene in conifer needles**

Date	Location	microg kg ⁻¹		microg kg ⁻¹		Comments	Source
		mean	SD	min	max		
1993-94	Crathes Forest Grampian Sc.	26	3.5dry wt.			<i>Pinus sylvestris</i>	(1)
	Devilla Forest, Fife, Sc.	11.3	3.5dry wt.			<i>Pinus sylvestris</i>	(1)
	Ponsonby Tarn, Cumbria UK.	12	3.9dry wt.			<i>Pinus sylvestris</i>	(1)
	same results - Crathes	11	fresh wt.			<i>Pinus sylvestris</i>	(1)
	same results - Devilla	4.9	fresh wt.			<i>Pinus sylvestris</i>	(1)
	same results – Ponsonby	4.6	fresh wt.			<i>Pinus sylvestris</i>	(1)
unspecified	Berlin (D)	0.5 - 6	fresh wt.	0.06	35	<i>Pinus sylvestris</i>	(2) reported in (
	Unspecified industrial	5.5	fresh wt.			Norway spruce	(3) reported in (
	Tübingen (D)	2.2 - 4	ng cm ⁻³			Norway spruce	(4) reported in (
	S. Finland	130-350	dry wt.	0	490	<i>Pinus sylvestris</i>	(5) reported in (
	Ghent city centre	222	dry wt.			Douglas fir	reported in (1)
	Ghent city centre	107	dry wt.			Lawson cypress	reported in (1)
	Ghent city centre	28	dry wt.			Noble fir	reported in (1)
	Achenkirch (Austria) 970-1420m asl		fresh wt.	0.8	2.3	Norway spruce	(6) reported in (
	Black Forest (D)	0.2 - 2	ng cm ⁻³			Norway spruce	(4) reported in (

Hohe Mark (D)	<3.0	fresh wt.	Norway spruce	(3) reported in (
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Sources: (1) Brown et al. [1999]; (2) Plümacher & Renner [1993]; (3) Diezel et al. [1988]; (4) Frank & Frank [1989]; (5) Dewulf et al. [1996]; (6) Plümacher & Schröder [1994].

Table B.5. Methyl chloroform in conifer needles

Date	Location	Microg kg ⁻¹		microg kg ⁻¹		Comments	Source
		Mean	SD	min	max		
1993-94	Crathes Forest, Grampian Sc.	15	3.2	dry wt.		<i>Pinus sylvestris</i>	(1)
	Devilla Forest, Fife, Sc.	7.2	6.6	dry wt.		<i>Pinus sylvestris</i>	(1)
	Ponsonby Tarn, Cumbria, UK	12	4.7	dry wt.		<i>Pinus sylvestris</i>	(1)
unspecified	Berlin (D)	0.1 - 0.6		fresh wt.	0.03	1 <i>Pinus sylvestris</i>	(2) reported in (
	Unspecified industrial	3.5 - 5.5		fresh wt.		Norway spruce	(3) reported in (
	Achenkirch (Austria) 970-1420m asl			fresh wt.	0.1	0.05 Norway spruce	(2) reported in (
	Hohe Mark (D)	<3.0		fresh wt.		Norway spruce	(3) reported in (

Sources: (1) Brown et al. [1999]; (2) Plümacher & Renner [1993]; (3) Diezel et al. [1988].

Both perchloroethylene and methyl chloroform appear to be widespread in conifer needles at concentrations that are highly variable both between sites and within the same site. There are not enough data to establish geographical trends or differences between species. It is not even clear that trees in urban environments accumulate a different loading from those in remote rural environments.

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