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Trichloroacetic acid in the vegetation of polluted and remote areas of both hemispheres—Part I. Its formation, uptake and geographical distribution

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Abstract

Trichloroacetic acid (TCA; CCl_3COOH) is a phytotoxic chemical. Although TCA salts and derivatives were once deployed as herbicides against perennial grasses and weeds, their use has since been banned because of their indiscriminate herbicidal effects on woody plant species. However, TCA can also be formed in the atmosphere. For instance, high-volatile C_2-chlorohydrocarbons tetrachloroethene (TECE, C_2Cl_4) and 1,1,1-trichloroethane (TCE, CCl_3CH_3) can react to TCA and other substances under oxidative conditions here. Owing to further industrialisation of Southeast Asia, South Africa and South America, a rise can be expected in the use of TECE as solvents in the metal and textile industries of these regions in the southern hemisphere (SH). The increasing emissions of this substance—together with the rise in the atmospheric oxidation potential caused by urban activities, slash and burn agriculture and forest fires in the SH—will result in the increased input/formation of TCA in the vegetation located on the lee side of these emission sources. By means of biomonitoring studies, inputs/formation of TCA related to the climatic conditions were detected at various locations in South America, Africa, and Europe.

Keywords: C_2-chlorohydrocarbons; Trichloroacetic acid; Transport; Formation; Interactions

1. Introduction

High-volatile chemicals such as C_2-chlorohydrocarbons are subject to increasingly ubiquitous spread owing to their long-distance transport in the atmosphere. When transported through the air, these compounds are exposed to oxidative, photolytic and hydrolytic processes, which can alter their original structure and thus their chemical and physical properties, as well as their potential phytotoxicity. According to Fischer et al. (1982) and Pearson (1982), 90–100% of the TECE produced escapes into the environment. Additional

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amounts of these substances come from other sources, such as combustion processes. Rudolph et al. (2000, 1995) published global emission rates of TCE from biomass burning of 4–30 Gg yr^{-1}. Garcia et al. (1992) reported about emissions of TECE and TCE from coal-fired power stations. Hoekstra (1999) and Midgley and McCulloch (1999) published the following data (Table 1) on the worldwide emission of chlorinated solvents. Folberth et al. (2001), Sidebottom and Franklin (1996), and Franklin (1994) reported one important tropospheric chemical reaction path for TECE and TCE in the planetary boundary layer to be the oxidation of these two substances by Cl-, OH- and O_2H-radicals, respectively, OH- and O_2H-radicals to form TCA. Franklin (1994) quotes an average TECE lifetime in the atmosphere of 84 days. As analytically measuring atmospheric TCA concentrations in open land throughout the required periods of time would currently necessitate huge amounts of time and resources, we have to rely (as in other similar cases of detecting pollutant emissions over large areas) on biomonitoring by mainly using suitable indicator plants (Weissflog et al., 1999a, b). Frank et al. (1994, 1992), Plümacher and Schröder (1994), Juuti et al. (1996, 1995, 1994, 1993) and Norokorpi and Frank (1995) reported TCA levels in needles of various conifer species, used as indicator plants for the atmospheric concentrations of this substance in Europe (Table 2). Barrens and Hummer (1951), Zöttl (1953), Foy (1969) and Matolcsy et al. (1988), Frank (1989) have published extensive findings on the phytotoxic properties of TCA. The impact on the growth of agricultural crops by low TCA concentrations is also well known, namely growth acceleration and shoot deformation. In the 1950s, TCA was used in agriculture at an application level of 15–30 kg TCA–sodium ha^{-1} as a herbicide against monocotyledonous grasses (Brian, 1976). Only little is known about the physiological and biochemical basis of its damaging effects on vegetation. Field experiments showed that a single application of 6.0 g TCA–sodium m^{-2} of soil surface harms 8-yr-old Scots pine trees and 6-yr-old birch trees (Weissflog et al., 2000). For example, a concentration of 6.0 g TCA–sodium m^{-2} of soil surface caused the total loss of the 2-yr-old Scots pine needles and chlorosis in the 1-yr-old Scots pine needles within 4 months following the application of the substance at the beginning of spring. Many leaves of birch trees showed strong yellow discolouration after a single application of 3.0 g TCA–sodium m^{-2} of soil surface in the same experimental period.

Table 1
Worldwide emission of chlorinated solvents (Gg yr^{-1}) in 1988–1997 (Midgley and McCulloch, 1999)

Solvent	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997
$CCl_2=CCl_2$	454	423	366	342	295	261	258	278	289	
CH_3-CCl_3	666	691	718	635	593	380	283	234	65	10

Table 2
Contents of TCA (μg kg^{-1} fw needles) in 2-yr-old needles of various conifers in Europe

Authors	Research area	Sampling time	Conifer species	Concentration
Frank et al. (1994, 1992)	Schwarzwald (Germany)	1990–1991	*Pinus sylv.* L.	3.0–89.8
	Southwestern Erzgebirge (Germany)	1990–1991	*Picea abies* L.	11.0–26.8
	Erzgebirge (Germany)	1990–1991	*Picea abies* L.	8.1–24.4
	Northern Finland	1991–1992	*Picea abies* L.	9.7–130.4
Plümacher and Schröder (1994)	Berlin (Germany)	1990–1991	*Pinus sylv.* L.	0.7–175.0
Weissflog et al. (1999b)	Southern Russia	1997	*Pinus sylv.* L.	3.5–68.9
Juuti et al. (1996)	Finland	1995	*Pinus sylv.* L.	33.0–180.0
			Third-year needles	
			Picea abies L.	16.0–69.0
Juuti et al. (1995)	Northwestern Finland	1994	*Pinus sylv.* L.	16.0–276.0
Juuti et al. (1994)	Northern Finland	1993	*Pinus sylv.* L.	6.0–276.0
Juuti et al. (1993)	Uimaharju (Eastern Finland)	1992	*Pinus sylv.* L. Third-year needles	5.0–135.0
Norokorpi and Frank (1995)	Rovaniemi (Northern Finland)	1992	*Pinus sylv.* L.	8.0–65.0

Further field investigations of the phytotoxic activities of chloroacetic acids, especially TCA concerning the consequences resulting from the destabilisation of the vegetation due to global warming are of great scientific importance. In this paper, we report on biomonitoring studies carried out to measure the inputs of TCA in the environment of various continents, the formation of TCA in plants, and thus the ecotoxicological relevance of TCA for the vegetation of different climatic zones.

2. Materials and methods

In order to perform these biomonitoring studies, 2-yr-old needles of five examplars of 7–12-yr-old trees were collected in 1996–1999 at 42 collecting sites in different continents (collecting time was June/July in the northern hemisphere, respectively, and December/February in the southern hemisphere; all needles were taken from the sun side of the trees). The needles were packed air-tight, transported at $+5^{\circ}C$ by air to Germany, and stored at $-65^{\circ}C$ until the TCA determination. The method for determining the TCA in unrinsed pine needles is described in detail in Weissflog et al. (1999a). It is based on the thermic decarboxylation of TCA using the headspace technique to form trichloromethane ($CHCl_3$) and its subsequent measurement by gas chromatography. The content of tertrachloroethene (C_2Cl_4) in the needles is measured also by gas chromatography using headspace technique. The detection limit for $CHCl_3$ is $0.02\,ng\,kg^{-1}$ pine needles (fresh weight, fw) and for C_2Cl_4 $0.01\,ng\ kg^{-1}$ pine needles (fw.). Each $CHCl_3$-, C_2Cl_4- and TCA value presented is based on the average of two analytical determinations.

3. Results

The studies performed for the assessment of TCA emission situation clearly indicate the varying pollution of the air by this substance at the various collecting locations. Areas with low background levels (Table 3), less polluted regions with average TCA levels (Table 4) and polluted locations (Table 5) could be identified in South America, Africa, and in Europe. From Table 3, it can be seen that even at locations which are far removed from known anthropogenic TCA emission sources, the concentration of TCA in the pine needles can be explained only by the input of atmospherically formed TCA into the vegetation, by the contribution of natural formation of TCA in soils (Hoekstra, 1999) and by the direct formation of TCA by plants due to the ubiquitous spread of TECE and TCE. The concentration range of TCA found in the pine needles at these locations is between 1.6 and $8.2\,\mu g\,kg^{-1}$ fw. These amounts can be regarded as reference values for the background situation in the NH and SH. The collecting sites of Cape of Good Hope (South Africa) and Ushuaia/near Cape Horn (Argentina) in the SH with the lowest amounts of TCA in the needles (1.6 and $5.0\,\mu g$ TCA kg^{-1} fw needles, respectively) are characterised by the influence of the only slightly polluted air masses of the global west wind system of the SH. The Russian collecting sites Kluchor pass, Ahty and North Karelia in the NH with the lowest amounts of TCA in the needles (3.5, 4.3 and $5.2\,\mu g$ TCA

Table 3
TCA concentrations in 2-yr-old needles of pine trees ($n = 5$) at background locations with very low pollution in South America, Africa, and Europe in 1996–1999. Concentration data ($\mu g\,kg^{-1}$ fw needles)

Location	Vegetation zone, plant species	TCA
Ushuaia, Tierra del Fuego (Argentina), near Cape Horn; 150 m a.s.l.	Mountain forest, *Pinus ponderosa* Lawson	5.0
Concepción, Pacific coast (Chile); 50 m a.s.l.	Coastal forest, *Pinus sylvestris* L.	6.1
Potrerillos, eastern side of the Andes (Argentina); 1500 m a.s.l.	Mountain forest, *Pinus sylvestris* L.	8.0
Cape of Good Hope (South Africa); 150 m a.s.l.	Coastal forest, *Pinus sylvestris* L.	1.6
Graskop (South Africa); 800 m a.s.l	Mountain forest, *Pinus radiata*	8.1
North Karelia/Kola Peninsula (Russia); 10 km southwest of Mončegorsk, MS5; 400 m a.s.l.	Boreal coniferous forest, *Pinus sylvestris* L.	5.2
North Karelia/Kola Peninsula (Russia); 8 km southwest of Mončegorsk, MS6; 420 m a.s.l.	Boreal coniferous forest, *Pinus sylvestris* L.	6.9
Zvenigorod, 40 km west of Moscow (Russia); 150 m a.s.l.	East European Mischwald, *Pinus sylvestris* L.	5.3
Kluchor pass, western Caucasus (Russia); 2200 m a.s.l.	Mountain forest, *Pinus sylvestris* L.	3.5
Ahty, eastern Caucasus (Russia); 1500 m a.s.l.	Mountain forest, *Pinus sylvestris* L.	4.3
Elbrus Massif, Central Caucasus (Russia); 2000 m a.s.l.	Mountain forest, *Pinus sylvestris* L.	5.3
El Portillo/Tenerife, Canary Islands (Spain); 2020 m a.s.l.	Mountain forest, *Pinus canariensis*	8.2

Table 4
TCA concentrations in 2-yr-old needles of pine trees ($n = 5$) at locations with low pollution in South America, Africa, and Europe in 1996–1999. Concentration data ($\mu g\,kg^{-1}$ fw needles)

Location	Vegetation zone, plant species	TCA
Concepción, industrial zone (Chile); ca. 150 m a.s.l.	Semi-desert, *Pinus canariensis*	14.3
Kruisfontein, Highveld (South Africa), ca 1100 m a.s.l.	Highveld vegetation, *Pinus radiata*	12.4
Palmerstone, Highveld (South Africa), 1000 m a.s.l.	Highveld vegetation, *Pinus radiata*	17.5
Lovozero/Kola Peninsula (Russia); 170 km north of the Arctic Circle; 380 m a.s.l.	Boreal coniferous forest, *Pinus sylvestris* L.	11.8
Kola Peninsula (Russia), MS4; 31 km southwest of Monˇegorsk; 420 m a.s.l.	Boreal coniferous forest, *Pinus sylvestris* L.	19.6
Cërnyje Yar, 180 km north of Astrakhan (Russia); 110 m a.s.l.	Semi-desert, *Pinus sylvestris* L.	10.4
Elista (Russia); 180 m a.s.l.	Black Sea steppe, *Pinus sylvestris* L.	10.1
Garafia/Las Palmas, Canary Islands (Spain), 875 m a.s.l.	Mountain forest, *Pinus canariensis*	18.5
Mercedes-wood/Tenerife, Canary Islands (Spain); 900 m a.s.l.	Mountain forest, *Pinus canariensis*	15.4
Gernrode/Harz, Saxony-Anhalt (Central Germany); 290 m a.s.l.	Mixed deciduous and coniferous forest, *Pinus sylvestris* L.	19.1

Table 5
TCA concentrations in 2-yr-old needles of pine trees ($n = 5$) at highly polluted locations in South America, Africa, and Europe in 1996–1999. Concentration data ($\mu g\,kg^{-1}$ fw needles)

Location	Vegetation zone, plant species	TCA
Puente del Inca, eastern side of the Upper Andes (Argentina); 2800 m a.s.l.	Mountainous steppe, *Pinus ponderosa* Lawson	43.1
Elandsfontein, Highveld (South Africa), 1100 m a.s.l.	Highveld vegetation	43.9
George (South Africa), 400 m a.s.l.	Mountain forest, *Pinus radiata*	29.5
North Karelia/Kola Peninsula (Russia), MS3; 48 km southwest of Monˇegorsk; 420 m a.s.l.	Boreal coniferous forest, *Pinus sylvestris* L.	28.6
North Karelia/Kola Peninsula (Russia), MS2; > 110 km southwest of Monˇegorsk, near the Russian–Finnish border; 435 m a.s.l.	Boreal coniferous forest, *Pinus sylvestris* L.	37.9
Astrakhan-Načalovo (Russia); 50 m a.s.l.	Semi-desert, *Pinus sylvestris* L.	27.4
Godshur, ca. 120 km south of Volgograd (Russia); 200 m a.s.l.	Black Sea steppe, *Pinus sylvestris* L.	68.9
Lagos (Portugal); 30 m a.s.l.	Coastal forest, *Pinus sylvestris* L.	47.8
Southern tip of Las Palmas/Canary Islands (Spain); 510 m a.s.l.	Mountain forest, *Pinus canariensis*	70.6
El Fayal/Las Palmas, Canary Islands (Spain); 520 m a.s.l.	Mountain forest, *Pinus canariensis*	71.0
Cumbre Nueva/Las Palmas, Canary Islands (Spain); 1450 m a.s.l.	Mountain forest, *Pinus canariensis*	39.4
Northwest of St. Cruz de Las Palmas/Las Palmas, Canary Islands (Spain); 780 m a.s.l.	Mountain forest, *Pinus canariensis*	118.9
Ringsdorf, Brandenburg, (Central Germany); 42 m a.s.l.	Mixed deciduous and coniferous forest, *Pinus sylvestris* L.	36.6
Jessen/Elster, Brandenburg (Central Germany); 75 m a.s.l.	Pine forest, *Pinus sylvestris* L.	41.4
Emden, Saxony-Anhalt (Central Germany); 140 m a.s.l.	Pine forest, *Pinus sylvestris* L.	37.1
Dübener Heide, Saxony-Anhalt (Central Germany); 174 m a.s.l.	Pine forest, *Pinus sylvestris* L.	27.3
Hettstedt, Saxony-Anhalt (Central Germany); 180 m a.s.l.	Mixed pine and deciduous forest, *Pinus sylvestris* L.	90.8
Serrahn/Müritz National Park, Mecklenburg–Western Pomerania (Northern Germany); 131 m a.s.l.	Mixed pine and deciduous forest, *Pinus sylvestris* L.	25.4
Cape Arkona/Rügen, Mecklenburg–Western Pomerania (Northern Germany); 45 m a.s.l.	Mixed pine and deciduous forest, *Pinus sylvestris* L.	30.7

kg^{-1} fw needles, respectively) are influenced by slightly polluted air masses.

The locations listed in Table 4 are all subject to relatively low pollution, even though their distances from industrial plants and urban areas emitting C_2-chlorohydrocarbons vary. One possibility is that the collecting sites are near emitters but in a stable windward position in relation to them. The range of TCA concentrations in the pine needles is between 10.1 and 19.1 $\mu g\,kg^{-1}$ fw at these collecting sites.

By contrast, the TCA levels in the pine needles at collecting sites near emission sources are between 25.4 and 118.9 $\mu g\,kg^{-1}$ fw (Table 5). The candidates for the localised emission sources of C_2-chlorohydrocarbons mainly include certain industrial emission sources at a distance between 0 km and approximately 500 km (e.g. insufficiently sealed industrial hazardous waste dumps, technologically obsolete or poorly managed recycling operations in smelting works and waste incineration plants, as well as pulp mills with pulp bleaching by Cl_2 and ClO_2). Large urban centres with a high industrial density (e.g. the metal-working industries and textile-cleaning facilities) can all be regarded as area sources of C_2-chlorohydrocarbons. Franklin (1994) states that any C_2Cl_4 which is initially discharged to surface waters tends to be rapidly transferred to the ambient air. Weissflog et al. (1999b) published that surface waters, which are heavily polluted by C_2Cl_4, are sources of this substance in the atmosphere. The seasonal dynamic of TCA concentrations in 2-yr-old pine needles, which were measured at a polluted location in Central Germany, is presented in Table 6. Single applications of TCA–sodium lead to TCA levels in the pine needles as shown in Table 7. TCA levels in the leaves and needles of various plant species at a polluted location are listed in Table 8. The effect of sunshine intensity on the TCA and TECE levels in needles from different pine species is given in Table 9.

Table 6
Dynamic development of TCA levels ($\mu g\,kg^{-1}$ fm needles) in 2-yr-old needles of five pine trees (*Pinus sylvestris* L.) at the lowland location of Golssen/Brandenburg (Germany) in the period April 1998 to March 1999

Sampling date	TCA concentration
01.04.1998	16.5
21.04.1998	62.6
25.05.1998	72.9
24.06.1998	85.9
15.07.1998	90.4
25.08.1998	81.9
25.09.1998	48.5
26.10.1998	64.3
25.11.1998	23.6
16.12.1998	45.2
13.01.1999	58.0
17.02.1999	38.1
17.03.1999	63.1

4. Discussion

A global comparison and interpretation of the TCA content in vegetation reported in the literature to date is contradictory and cannot explain our existing data

Table 7
Dynamic development of TCA concentrations in 1-yr-old needles of 7-yr-old pines (*Pinus sylv.* L.) following the single application of different amounts of TCA–sodium dissolved in 10 l water via the circular bed surrounding the tree. After an initial sampling on 18 March 1999, the TCA–sodium solution was always applied to an area measuring 1 m^2 around the trunk

Amount of TCA–Na applied (g)	Start and sampling data	TCA concentration ($\mu g\,kg^{-1}$ fw needles)
1.6 (18.03.1999)	18.03.1999	28
	21.04.1999	4114
	16.06.1999	6360
	20.07.1999	21745
	07.09.1999	17578
	09.11.1999	11683
0.8 (18.03.1999)	18.03.1999	11
	21.04.1999	4670
	16.06.1999	4548
	20.07.1999	13572
	07.09.1999	2960
	09.11.1999	313
0.4 (18.03.1999)	18.03.1999	13
	21.04.1999	349
	16.06.1999	474
	20.07.1999	394
	07.09.1999	204
	09.11.1999	14
0.2 (18.03.1999)	18.03.1999	39
	21.04.1999	254
	16.06.1999	268
	20.07.1999	127
	07.09.1999	89
	09.11.1999	12
0.1 (18.03.1999)	18.03.1999	19
	21.04.1999	19
	16.06.1999	90
	20.07.1999	50
	07.09.1999	26
	09.11.1999	9
0.0 (18.03.1999)	18.03.1999	46
	21.04.1999	6
	16.06.1999	23
	20.07.1999	31
	07.09.1999	29
	09.11.1999	10

adequately. Particularly, large discrepancies occur when simultaneously considering the atmospheric lifetimes of TECE and TCE, their resulting possible fate and the average local wind speeds and levels of TCA measured. Franklin (1994) reported that the atmospheric lifetime of TECE is 84 days. WMO (1995) claims the atmospheric lifetime of TCE to be 5.4 yr. These discrepancies are especially apparent in the example of TCA levels in pine needles at various measuring locations on the Finnish–Russian transect "Northern Karelia" and the South African transect "Highveld", as well as the TCA levels in pine needles from various locations of Las Palmas/Canary Islands (Spain) (Table 10). Hence, the seasonal dynamics of TCA concentrations in 2-yr-old pine needles measured at a polluted location in Central Germany cannot be explained by the input of atmospherically formed TCA (Table 6). Frank et al. (1990a, b) calculated the following values for the course of the annual dynamics of TCA concentrations in spruce needles in a low-mountain region (Table 11). The annual dynamic developments of the TCA contents in pine needles and in spruce needles shown in Tables 6 and 11 are very similar. The TCA levels in the pine needles in Golssen/Brandenburg (Germany) (Table 6) reach a maximum in July, whereas in the spruce needles in Bernstein/northern Black Forest (Germany) (Table 11) the concentrations reach a maximum in October. This is attributed to a number of factors, including species-related differences in the formation and breakdown of TCA in pine and spruce needles, as well as climatically and meteorologically caused ecological differences between the two locations. As the annual precipitation at the two sites differs, and precipitation also takes place at different times, input by the hydrophilic TCA with rainwater must also be different. This not only holds for deposition on the needles but also for inputs into each site's soil. It is, however, certain that inputs of atmospherically formed TCA take place into these soils, and are taken up by local vegetation via the *soil/root* pathway. For example, single applications of TCA–sodium lead to TCA levels in the pine needles as shown in Table 7. These observations concerning the possibility of TCA being taken up via the *soil/root* pathway have been made by, among others, Sutinen et al. (1995) and Frank (1991), and Franich and Wells (1980). Frank (1991) reported that when an aqueous solution of TCA–sodium is directly applied to pine needles the majority remains physically adsorbed on the surface and can simply be rinsed off with water. Small quantities of airborne TCA can of course be directly taken up via the needle surface. The diffusion of TCA through epicuticular layers, plasmodesmata and cell membranes is slow due to its total dissociation at neutral pH. The concentrations in the leaves and needles of different plant species from a polluted location in Germany listed in Table 8 argue against the majority of the TCA detected in the needles and leaves of various plant species being taken up via the *soil/root* pathway. The difference between the data of the TCA-concentration in needles of *Scots pine* and *Black pine* is not significant. As the leaves of *Betula pendula*, for example, have a higher stomatal and cuticular transpiration rate than the needles of *Picea abies* and *Scots pine*, their greater sap flow ought to result in larger quantities of TCA reaching the plant via the *soil/root* pathway and accumulating in the leaf organs of the birch. However, as can be seen, this is not the case. This provides further evidence countering the previous assumption that the *soil/root* pathway does not play the main role in the uptake of TCA at sites in the open countryside (Weissflog et al., 1999b). The biomonitoring studies carried out over a

Table 8
TCA levels ($\mu g\,kg^{-1}$ fw) in the leaves and needles of trees ($n = 5$) of various plant species at a polluted location (Golssen/Brandenburg, Germany)

Plant species	TCA concentration
Oak (*Quercus robur* L.)	3.4
Bird cherry (*Prunus avium* L.)	4.7
Birch (*Betula pendula* ROTH)	7.0
Acacia (*Robinia pseudo-acacia* L.)	9.6
Red fire spruce (*Picea abies* L.)	23.5
Scots pine (*Pinus sylvestris* L.)	39.2
European black pine (*Pinus nigra* ARNOLD)	43.7

Table 9
Effect of sunshine on the TCA and TECE levels in needles from different pine species ($\mu g\,kg^{-1}$ fw needles)

Location and collection time	Pine species	Needle age (yr)	Shade side		Sun side	
			TCA	TECE	TCA	TECE
Ushuaia,Tierra del Fuego (Argentina), December 1996	*Pinus ponderosa* L.	2	6.7	0.1	8.6	0.1
		3	14.4	0.2	17.8	0.2
		4	16.2	0.1	20.5	0.1
Godshur (Russia), June 1997	*Pinus sylvestris* L.	2	7.8	0.3	30.5	1.1

Table 10
Geographical position of selected transects and their collecting locations, the main emission sources of the TCA precursors TECE and TCE, and the TCA levels detected at the collecting locations in 2-yr-old needles of pine trees ($n = 5$) of various species

Geographical arrangement of collecting sites	Geographical position of collecting sites	Main wind direction	Probable main emission sources of TECE and TCE	Collecting sites and their distance from the probable emission sources (km)	TCA levels in pine needles ($\mu g\,kg^{-1}$ fm needles)
Northern hemisphere					
Transect North Karelia (Finland, Russia)	From southwest to northeast	*Winter*: Cyclonal air masses from the southwest *Summer*: From the south; moderate wind force From the north; low wind strength	Pulp and paper mills in Kemijärvi, Kemi and Oulu (Finland)	Distance from Kemi:	
				*MS1, 5 km	200.0[a]
				*MS2, 320 km	37.9
				*MS3, 380 km	28.6
				*MS4, 400 km	19.6
				*MS5, 420 km	5.2
				*MS6, 422 km	6.5
Las Palmas measuring network, Canary Islands (Spain)	Measuring network	Atlantic northeast trade winds	(1) Obsolete waste incineration plants	Distance from and position in relation to the island's tallest mountain,	
			(2) Industrial plants	Roque de los Muchachos, 2426 m a.s.l.	
				*Northwest of St. Cruz de Las Palmas (780 m a.s.l.), 9.5 km; 112°	118.9
				*southern tip of Las Palmas (510 m a.s.l.), 23 km; 174°	70.6
				*El Fayal (520 m a.s.l.) 6.7 km; 282°	71.0
				*Cumbre Nueva (1450 m a.s.l.) 11.6 km; 155°	39.4
Southern hemisphere					
Transect South African Highveld (South Africa)	From west–southwest to east–northeast	From west–southwest	(1) Industrial region of Johannesburg/South Africa	Distance from Johannesburg:	
			(2) Coal-fired super power stations (mineral coal) in the Highveld	*Elandsfontein, 165 km;	43.9
				*Palmerstone, 285 km;	17.5
				*Kruisfontein, 300 km;	12.4
				*Graskop, 425 km	8.1

[a] Juuti et al. (1994).

large area at the collecting transects listed in Table 10 indicate that the levels of TCA detected in pine needles at the respective collecting locations of such a transect can best be explained by the dilution during long-distance transport of the TECE and TCE, their adsorption on/absorption in cuticular wax layers of plants, and their subsequent oxidation by OH radicals, superoxide and $^1O_2$ in the chloroplasts of the plant cell.

Table 11
Dynamics of the development of TCA levels ($\mu g\,kg^{-1}$ fw needles) in 2-yr-old spruce needles *(Picea abies* L.*)* at Bernstein/northern Schwarzwald (Germany) in the period of June 1989 to June 1999 (Frank et al., 1990a, b)

Sampling date	TCA concentration
05.06.1989	31
26.06.1989	18
17.07.1989	45
08.08.1989	76
30.08.1989	77
28.09.1989	85
19.10.1989	98
08.11.1989	80
12.12.1989	48
02.01.1990	25
05.02.1990	35
30.04.1990	10
06.06.1990	15
11.07.1990	30
06.08.1990	38

Special meteorological situations such as strong global radiation and low air temperatures at the site lead to "oxidative stress situations" in plants. In this phase, higher concentrations of active forms of oxygen can be detected in the chloroplasts of plants (Mohr and Schopfer, 1995). Normally, the plants can detoxify themselves of these toxic compounds. In the presence of TECE and TCE, which reach the chloroplasts by the *atmosphere/wax layer/plant cell* way, these two substances may be oxidised by these active forms of oxygen and Cl radicals to form TCA in a similar way as in the atmosphere. These oxidation processes, thus, may lead to an increase in the TCA content of needles/leaves of plants and to acute and chronic disturbances of photosynthesis and eventually to the alteration of the cell metabolism. We argue that the plants are poisoned by the internal oxidation processes of TECE and TCE to form phytotoxic TCA. We believe that the absorption of the TECE and TCE via the cuticular wax layer of the needles of *Pinus sylv*. L. is similar to that observed by Figge (1990) on spruce needles (*Picea abies* L.). According to this author, the absorption behaviour of TECE in air having concentrations of 10–189 $\mu g\,l^{-1}$ air on spruce needles can be excellently described using the following equation:

$$c_n = 0.103 c_g \quad (1)$$

(c_n is the TECE concentration in the "fumigated" needles; c_g is the TECE equilibrium concentration in air). Equilibrium between the two compartments sets in after just one hour. The data in Table 12 for the partition coefficients between various types of wax and

Table 12
Partition coefficients of tetrachloromethane, trichloroethene and tetrachlorethene between lipid and air; temperature 22°C (Frank and Frank, 1986)

Compartment	CCl_4	C_2HCl_3	C_2Cl_4
	Concentration *x*-fold greater as in the polluted air		
Beeswax	140	270	740
Total lipid and wax[a]	400	1000	2200
Spruce needles	17	44	95

[a]The total lipid and wax content of needles of *Picea abies*, extracted with cyclohexane and chloroform/methanol (2 : 1, v/v), was 4.5% of the fresh weight.

airborne chlorohydrocarbons were published by Frank and Frank (1986). In comparison with the corresponding TCE data, and taking into account the global concentrations of TCE and TECE in the atmosphere, the partition coefficient of TECE between the compartments air/total lipid and wax of needles and the faster oxidation of TECE by Cl-, OH- and O_2H-radicals indicates that atmospheric TECE concentrations up to about 500 km away from the emission source are especially important for the formation of TCA levels in plants (Table 10 and Fig. 1). By contrast, more attention must be paid to atmospheric TCE levels concerning the formation of TCA fractions at greater distances away from emitters. As TCA ought mainly to be adsorbed on aerosols due to its hydrophobic properties in the atmosphere, and Stahl et al. (1998) did not notice any particular effect at the edge of the forest in the formation of TCA levels in spruce needles, it proves that the necessarily existing interactions involve inputs of gaseous C_2-chlorohydrocarbons into the vegetation. The influence of direct sunshine on the oxidation of TECE in the chloroplasts and the resulting TCA level from various locations is evident from the data in Table 9. Although the needles of the trees exposed to sunshine at Ushuaia (Argentina) were only slightly yellowed, at Godshur (Russia) they had a clear yellowish-brown discolouration, indicating the greater effect exerted on a whole range of photosynthetic processes. This in turn can partly be attributed to the reduced synthesis of new chlorophyll as a result of the impact of TCA and the OH radicals, superoxide and $^1O_2$ increasingly formed in the needles. In contrast, the needles in the shade at these two locations were green. This phenomenon indicates that exact but nonetheless very complex dose/effect relations exist between the substances TECE, TCE and TCA in the various cell compartments, and that various stages of damage occur in the needles/leaves. In the needles in the shade, the detoxification capacity of the plant cell

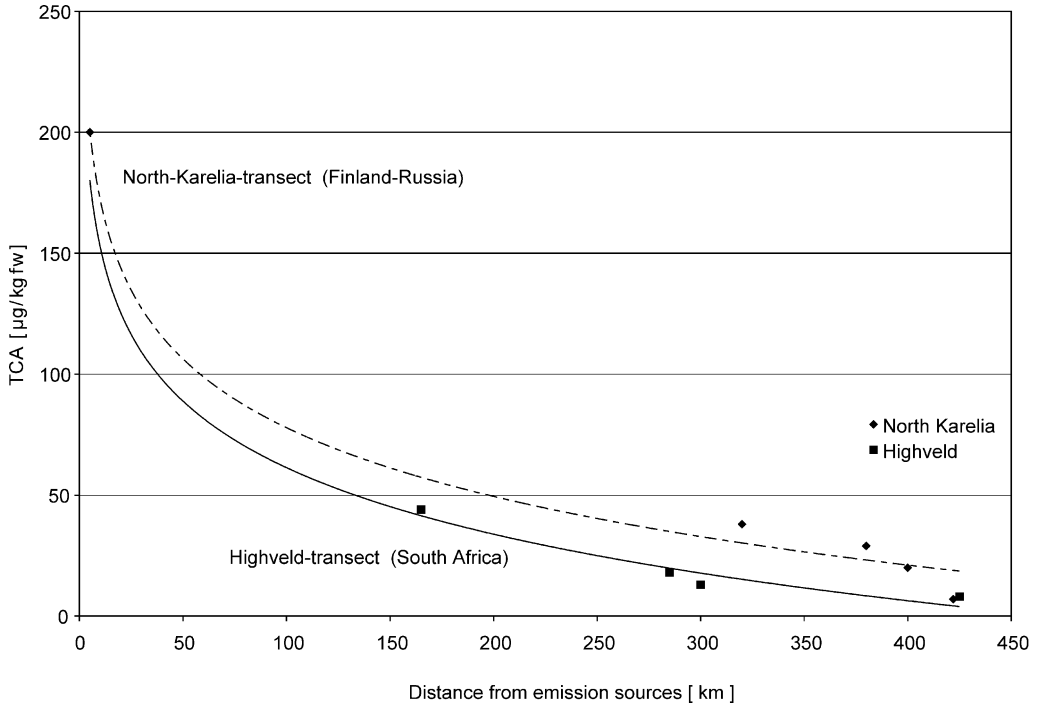

Fig. 1. TCA concentrations in 2-yr-old pine needles (*Pinus sylvestris* L.) as a function of the distance to TECE emission sources.

for active oxygen forms is still sufficient despite the formation of phytotoxic TCA and the consequent cell damage. In the case of the higher chronic load of the plant cell by TECE, however, premature cell senescence takes place, which is associated with the greater discolouration of the needles. The difference in TECE levels in the cuticular waxes of needles exposed to the light and the shade following, respectively, the chronic effect of this substance, indicates the altered composition of these natural wax surfaces and consequently changed TECE adsorption/absorption. Changes in the biosynthesis of epicuticular wax caused by TCA were also observed by Franich and Wells (1980). Frank (1991) published a half-lifetime of TCA in spruce needles of mobilisation or metabolism of about 10 days. The observation reported by Figge (1990) that after 24 h TECE fumigation followed by 99 h desorption, a TECE 3.4% fraction which was heavy and could no longer be desorbed persisted in the needles (irrespective of the initial TECE concentration in the differently polluted spruce needles), should be reinterpreted following the investigations described here. As this fraction determined in the needles significantly increases as gassing is prolonged, the fraction is not, as Figge (1990) holds, TECE which can no longer be desorbed, but rather newly formed TCA. This interpretation could not be made by the author cited owing to the analysis technique used. Although links between the uptake of C_2-chlorohydrocarbons and their interaction with plant cell systems were also identified by Frank and Frank (1986), they did not associate this with the formation of TCA from TECE and TCE in chloroplasts as a result of the direct oxidative effect of OH-, O_2H-, and Cl-radicals on these two substances. The findings presented here also contradict the observations made by Plümacher (1995) and Plümacher and Dombrowsky (1998), who reported that TCA is probably not formed in needles from TECE or TCE since no positive correlations were observed between the concentrations of those compounds and those of TCA in needles. As the levels of TECE and TCE in the pine needles they studied were in "brief equilibrium" with the ambient air, but the TCA levels detected are subject to different mobilisation and metabolic processes, in no case can "temporally" correct positive correlations exist between the TECE, TCE and TCA levels in pine needles.

5. Conclusions

By means of biomonitoring studies, different inputs and formation of TCA in vegetation were detected at various locations in South America, in Africa, and in

Europe. Areas with low background levels of TCA (1.6 and 8.2 μg kg^{-1} fw pine needles), less polluted regions with average TCA levels (10.1 and 19.1 μg kg^{-1} fw pine needles), and polluted locations (25.4–118.9 μg kg^{-1} pine needles and 276.0* μg kg^{-1} pine needles (*Juuti et al., 1995) can be identified in Africa and South America, and in Europe.

Areas with the highest inputs are to be found in South America (Puente del Inca/Andes mountains; 43.1 μg TCA kg^{-1} fw pine needles), South Africa (Elandsfontein; 43.9 μg TCA kg^{-1} fw pine needles), Central Germany (Hettstedt; 90.8 μg TCA kg^{-1} fw pine needles), in the Russian measuring sites Kalmykian steppe (Godshur; 68.9 μg TCA kg^{-1} fw pine needles) and North Karelia (37.9 μg TCA kg^{-1} fw pine needles), and at a few collecting sites in the Canary Islands (e.g. northwest of St. Cruz de La Palma; 118.9 μg TCA kg^{-1} fw pine needles).

Aspecially in areas with a high solar radiation intensity and simultaneous low air temperature, oxidative stress in plants leads to an increase in the concentrations of active forms of oxygen, for example also to the increase in OH and O_2H radicals in the chloroplasts of plants. In normal cases, the plants can detoxify these toxic compounds. TECE and TCE, which reach the chloroplasts by the *atmosphere/wax layer/plant cell* pathway, can be oxidised by OH-, O_2H- and Cl-radicals to form TCA in a similar way as in the atmosphere. These oxidation processes lead to an increase in the TCA contents of vegetation and to disturbances of the processes of photosynthesis. We argue that the plant is poisoned additionally by its internal oxidation processes of TECE and TCE to form TCA.

TCA in plants is a potential global risk for sensitive ecosystems, such as grassy steppes, savannas, mountain pastures and woods/forests on all continents.

6. Uncited References

ECDIN, 1996; Linak et al., 1992; NAS, 1976.

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