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Airborne trichloroacetic acid and its deposition in the catchment area of the Caspian Sea

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Abstract

The main sources of pollution discharge into the Caspian Sea are metal and oil processing plants in the catchment areas of the Ural and Volga rivers, as well as the coastal and offshore oil industry in the countries bordering the sea. The high evaporation from the surface of this largest inland sea introduces highly volatile C_2-chlorohydrocarbons into the atmosphere. Subsequent reactions with OH radicals and other oxidants results in the formation of secondary pollutants, such as phytotoxic trichloroacetic acid (TCA), which are then delivered by the air or rain into the neighbouring ecosystems of various vegetation zones. Biomonitoring investigations in the catchment area of the Caspian Sea have revealed that differences in pollution levels in the southern Russian area between the Black Sea and the Caspian Sea, resulting from TCA originating in the atmosphere, are attributable to climatic conditions and the geographical position of the measuring sites. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In order to assess the ecotoxicological threat of pollutants to the stability of terrestrial ecosystems in the area of the Caspian Sea, information about the regional emissions situation is of vital importance. Whereas non-volatile and low-volatile pollutants such as heavy metals and various high-boiling organic compounds are subject to short-range transport and deposition at local to regional sinks, high-volatile organic substances may undergo supraregional to global spreading through the air (Fabian, 1986; Wiedmann et al., 1994). During air transportation, these substances are exposed to various oxidative, photolytic and hydrolytic processes, which lead to modifications of the chemical structure and associated toxicity of the compounds (Fabian, 1986; Parlar and Angerhöfer, 1991). As a consequence, secondary pollutants with lower or higher phytotoxicity, may be formed (Barrons and Hummer, 1951; Zöttl, 1953; Peters, 1963; Foy, 1969; Pearson, 1982; Quick, 1983; Schroeder et al., 1997). The direction and rate of the chemical processes occurring in the atmosphere are affected by altitude and climatic factors such as the intensity of various types of UV radiation, and the concentrations of water, particulate matter, ozone and hydroxyl radicals in the troposphere (Prinn et al., 1987; Matolcsy et al., 1988; Zabel, 1994). Moreover, geographical and meteorological conditions play a crucial role in the spread of pollutants in the biosphere.

The area under investigation (Fig. 1) is bounded by the Caucasus Mountains to the south, the Kalmykian steppe to the west and north, and the Caspian depression to the east. It has an area of around 350,000 km^2 and was characterized as one of the world's most severely endangered ecosystems (Gabunshina, 1997). The region has an arid–continental to semiarid–continental climate with an annual precipitation of 0–250 mm in the north and east and up to 1,000 mm in the mountainous regions in the south and west. The average temperatures in winter are between 0 and −10°C and in summer around 25–30°C (Diercke, 1994). At the centre of this area is the Caspian Sea. Some 423,000 km^2 in size

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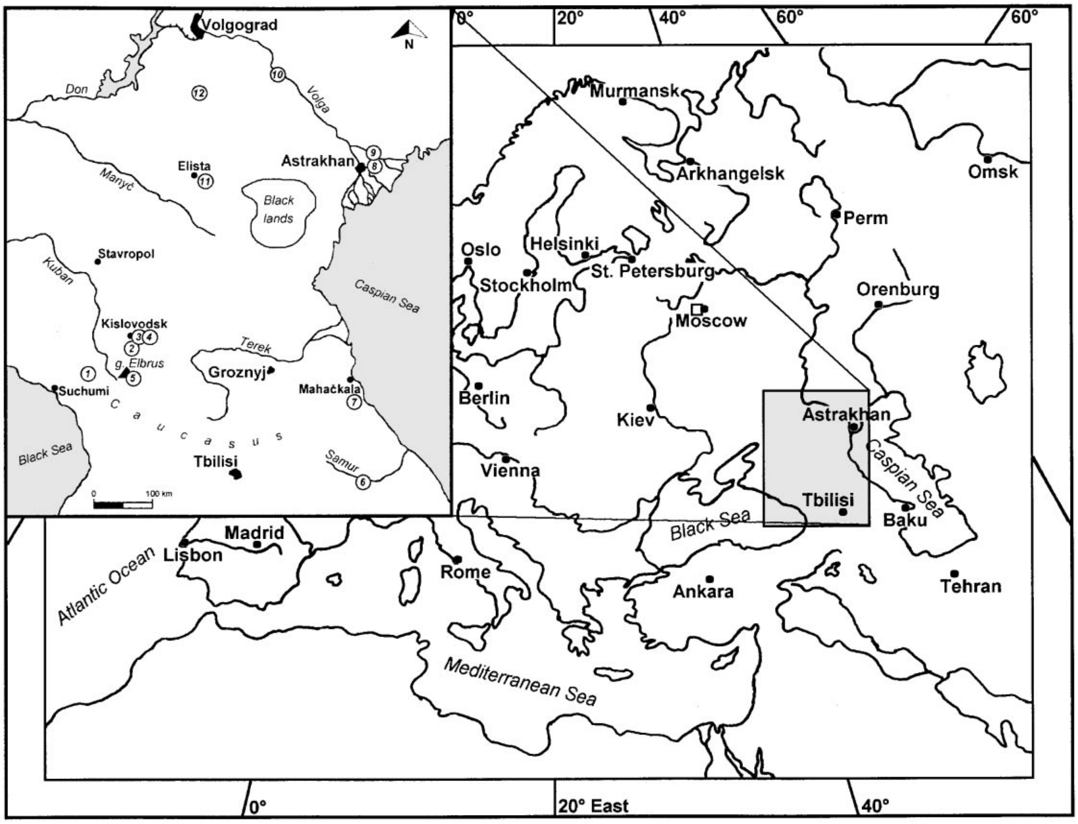

Fig. 1. Measuring sites in the investigation area.

and with a large inflow (the Volga alone accounts for 268 million m^3 of water every year) but no outflow, the salty Caspian Sea nevertheless maintains a more or less constant level owing to high evaporation due to regional climatic factors; in fact its level actually fell slightly from the late 1920s to the late 1970s. The inland nature of the Caspian Sea and the continuing high influx of pollutants from rivers such as the Volga and the Ural, and from offshore oil-drilling and oil-processing in the coastal region, result in particularly high pollution (Bucharizin, 1996). The area we investigated (Fig. 1) is bounded by the units of geographical structure listed in Table 1, which in turn contains the specifically selected measuring sites.

Evaporation of the volatile compound fraction leads to an accumulation of low-volatile and non-volatile pollutants entering the Caspian Sea. The high-volatile pollutants escape into the atmosphere in parts of south-eastern Europe and Central Asia.

The climatic boundary conditions can be characterized as follows. In the north-eastern part of the area investigated, hot easterly to south-easterly winds from the deserts of Central Asia which cross the northern part of the Caspian Sea are to be observed in summer, along with north-westerly air mass flows. By contrast, eastern to north-easterly winds predominate in winter. In view of this situation, the fate of the group of technically significant high-volatile C_2-chlorohydrocarbons, tetrachloroethene (TCEE), trichloroethane (TCE), and the phytotoxic trichloroacetic acid (TCA) they create in the atmosphere, is of particular ecotoxicological importance. The atmospheric penetration of the environment by these substances and their spatial distribution—and hence their ecotoxicological significance for the vegetation in the investigation area—were measured by initial biomonitoring investigations. In order to perform an initial ecotoxicological assessment of these primary and secondary airborne pollutants, their concentrations in conifer needles were analyzed.

2. Materials and methods

At each of the 13 measuring sites listed in Table 1, samples were taken from five pine trees of the species *Pinus sylvestris* L. aged 7–12 years. Two-year-old needles were packed in airtight containers for air transport to Germany and stored at $-20°C$ until the TCA was analyzed. Samples were also taken of the topsoil in the immediate vicinity of the indicator trees at the measuring locations. Five equivalent sub-samples were blended to form a mixed sample immediately after collection, homogenized, screened and transported to Germany together with the plant material for subsequent analysis.

Table 1
Geographical limits of the investigation area with typical vegetation and measuring sites (MS)

Unit of geographical structure	Typical nature of vegetation	Measuring sites
Northern slope of the Great Caucasus	Mountain forest	Mountain pass of Kluchor, MS 1 Kislovodsk Mountain station, MS 4
Central part of the Foremost Caucasus	Mountain forest	Kislovodsk Spa garden, MS 2 Kislovodsk Plateau, MS 3 Base terminal of cable railway of Elbrus Mountain, MS 5
Dagestan	Mountain forest	Ahty, MS 6
South-eastern part of the Great Caucasus	Semi-desert	Mahačkala, MS 7
Caspian depression	Semi-desert	Astrakhan Načalovo, MS 9 Krasnyje Jar, MS 8 Čërnyje Jar, MS 10
Hill-range of Ergeni	Steppe of Black Sea	Elista, MS 11 Godschur, MS 12
Central Russian plate	East European mixed forest	Reference MS Zvenigorod

The analytical method used was based on the equilibrium of volatile compounds between the liquid or solid phase of the sample and the gas phase above it in a closed headspace vial. The equilibrium is dependent on the temperature, with higher temperatures causing higher concentrations in the gas phase. An aliquot of the headspace gas was placed in a gas chromatograph. As polar and water soluble compounds such as TCA cannot be measured directly by gas chromatography, the method of thermal decarboxylation of TCA to trichloromethane ($CHCl_3$) was used. Investigations described in Plümacher and Schröder (1994) show that TCA can be quantitatively determined by the following measuring procedure. After 1 h, the first heating of the sample the amount of $CHCl_3$ is measured (first injection). The second injection occurred after 72 h when TCA was completely decarboxylated. The TCA concentration was calculated as the difference between the $CHCl_3$ concentrations of these two injections. Measurements were carried out as using a combination of a HP-7694 headspace sampler and HP-589111 gas chromatograph (Hewlett-Packard) with an electron-capture detector (ECD). The following headspace conditions were used:

Volume of the vials	20 ml
Sample	2.5 gfw (fresh weight) of needles
Equilibrium temperature	65°C
Sample loop temperature	80°C
Transfer line temperature	90°C

The following GC conditions were used:

Capillary column	25 m×0.32 mm i.d. CP-SIL5CB
Film thickness	5 μm
Injector	split, 250°C
Detector	ECD, 300°C
Carrier gas	nitrogen
Make-up gas	nitrogen 57 ml min^{-1}
Temperature program	35°C (3 min) ⇒ 10°C min^{-1}⇒200°C (1 min)⇒30°C min^{-1}⇒260°C (3.5 min)

3. Results

The biomonitoring investigations carried out at the different measuring sites in April and July/August 1997 (Table 2) to survey the TCA imission situation reveal specially differing levels of air pollution by these substances formed in the atmosphere in the area investigated. While at the measuring sites on the northern slope of the Great Caucasus and the central part of the Foremost Caucasus relatively low TCA concentrations were found (3.5–5.3 μg TCA/kg fw). Levels up to approximately 20 times higher were observed at the measuring sites in the north-eastern part of the investigation area between the cities of Astrakhan, Volgograd and Elista (up to 68.9 μg TCA/kg fw). At these polluted locations TCA levels in pine needles were found to be similar to those measured by various authors in central European areas severely polluted by urban and industrial activities. In central Europe, TCA concentrations have been measured in the range of about 25 to 175 μg TCA/kg fw by Frank (1989), Plümacher and Schröder (1994). Moreover, a general rise in the levels of TCA was observed in the indicator trees at all measuring sites in the Caucasus between the transect MS 1 (mountain pass of Kluchor) and MS 5 (base terminal of the cable

Table 2
Concentrations of trichloroacetic acid (TCA; g/kg fw) in 2-year-old needles of Scotch pine (*Pinus sylvestris* L.) and soil samples collected at the same sites in southern Russia in April and July/August 1997

Measuring site	Samples	TCA	
		April	July/August
MS 1: Mountain pass of Kluchor (2200 m ab.sl.) (2.5 km south of Dombai)	pine needles	3.18 ± 0.95	3.54 ± 1.50
	soil	0.04	0.09
MS 2: Kislovodsk Spa garden (300 m a.s.l.)	pine needles	4.99 ± 2.79	–
	soil	0.22	–
MS 3: Kislovodsk Plateau (800 m a.s.l.)	pine needles	4.00 ± 1.12	5.20 ± 1.82
	soil	0.31	0.21
MS 4: Kislovodsk Mountain station (ca. 30 km south of Kislovodsk)	pine needles	3.91 ± 0.88	5.15 ± 1.40
	soil	0.24	0.35
MS 5: Elbrus-Base terminal of cable railway (ca. 2000 m a.s.l.)	pine needles	7.25 ± 3.94	5.28 ± 2.10
	soil	0.46	0.39
MS 6: Ahty (Eastern Caucasus, 1500 m a.s.l.)	pine needles	–	4.29 ± 0.16
	soil	–	–
MS 7: Mahačkala (near the Caspian Sea)	pine needles	–	8.69 ± 1.61
	soil	–	–
MS 8: Krasnyje Jar (ca. 40 km north of Astrakhan)	pine needles	–	3.15 ± 1.39
	soil	–	0.32
MS 9: Astrakhan Načalovo (ca. 10 km east of Astrakhan)	pine needles	20.73 ± 5.80	27.40 ± 9.99
	soil	1.09	1.06
MS 10: Čërnyje Jar (ca. 180 km north of Astrakhan)	pine needles	–	10.37 ± 17.12
	soil	–	n.d.
MS 11: Elista (ca. 6 km east of Elista)	pine needles	6.85 ± 2.71	10.07 ± 2.73
	soil	0.34	0.22
MS 12: Godschur (ca. 120 km south of Wolgograd)	pine needles	28.43 ± 9.44	68.91 ± 37.97
	soil	0.08	0.22
Zve: Zvenigorod (40 km west of Moscow)	pine needles	5.28 ± 0.79	n.d.
	soil	0.10	n.d.

n.d., not detected.

railway of Elbrus Mountain). TCA contamination measured in pine needles from the windward side of the reference measuring site west of Moscow and in the measuring sites to the west of the Caucasus indicate a relatively low pollution of these areas by airborne C_2-chlorohydrocarbons and their decomposition product TCA originating from atmospheric oxidation processes.

4. Discussion

The striking concentration differences bioaccumulated in TCA levels within the investigation area can be traced back to climatic causes. The region at the northern slope of the Great Caucasus described by MS 1 (mountain pass of Kluchor) has a temporal cyclonal climate and is strongly affected by southwesterly air masses from the Black Sea, which after overcoming the wall-like high mountains reach their northern slope, in some areas as the down wind foehn (Walter, 1974). As these air masses do not appear to contain high levels of TCA, it can be assumed that either the substance is already washed out of the atmosphere by extensive precipitation on the southern side of the Great Caucasus, or that low initial airborne concentrations of C_2-chlorohydrocarbons prohibit its formation in the maritime air masses from the south-west.

The slightly higher TCA levels in the pine needles of the indicator trees at MSs 2–4 and MS 5 compared to MS 1 can be attributed to the growing impact of polluted air masses coming from the area of the northern Caspian Sea and reaching the northern slope of the Central Foremost Caucasus. The relatively low TCA levels in the pine needles at MSs 6 and 7 located in the eastern part of the Caucasus, partly in the immediate vicinity of the Caspian Sea, indicate that this region is less affected by TCA depositions owing to the predominating southern wind direction and the hot, dry, continental tropical air masses coming from the Armenian/Iranian highlands, as well as the possible but relatively short atmospheric reaction time in the air masses building up to the east from the direction of the Caspian Sea. By contrast, the pine needles of the indicator trees at MSs 12, 9 and 10 exhibit levels of TCA similar to those found previously by the authors during comparative investigations at reference measuring sites in central and north Germany polluted by industrial and urban emissions.

The results which we obtained tally well with the climatic characteristics in the north-eastern part of the investigation area. In summer, with little cloud and intensive sunshine at the same time, hot easterly to south-easterly winds originating in the deserts of Central Asia which cross the northern part of the Caspian Sea are to be observed, along with north-westerly cyclonal air flows. By contrast, easterly to north-easterly wind directions transporting Siberian air masses predominate in winter. According to Bucharizin (1996), this area of the Caspian Sea is particularly affected by the influx from the Volga and Ural rivers, which contain considerable levels of chemical pollution. The distances concerned and the meteorological conditions described appear to provide favourable conditions for the chemical oxidation in the troposphere of the C_2-chlorohydrocarbons evaporating from the seawater to form TCA and its penetration of the vegetation. However, the topsoils of all measuring sites in southern Russia have TCA levels which do not correlate with the respective TCA levels in the pine needles of the indicator trees growing at the same sites. The sharply differing soil substrates and the unknown microbial activities in soil at the measuring sites (different clay, humus, calcium content) appear to be responsible owing to their ability to sorb both TCA and high-volatile C_2-chlorohydrocarbons (Dural and Chen, 1994; Cowman and Singer, 1996).

5. Conclusions

Different levels of TCA were found in southern Russia in an area between the Caucasus, the Caspian Sea, the Volga and the Ergeni hill range by means of biomonitoring investigations using pine needles (*Pinus sylvestris*) as the indicator system.

Owing to geographical and climatic factors, the north-west of the Caspian Sea is particularly affected by these depositions. This observation supports the hypothesis that high-volatile C_2-chloroorganics (liberated by evaporation from the Caspian Sea, which is severely contaminated by organic and inorganic pollutants) are oxidized by OH hydroxyl radicals during air transport to form compounds such as TCA. It cannot be ruled out that these phytotoxic TCA depositions present a significant ecotoxicological risk for the steppe and semi-desert vegetation, and are also partly responsible for the increasing desertification of the region in south-eastern Europe between the Black Sea and the Caspian Sea.

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