

HALOCARBON SOLVENTS; ANALYSIS, ENVIRONMENTAL OCCURRENCE AND
PHYTOTOXIC SECONDARY AIR POLLUTANTS.

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ABSTRACT: Representative levels of the halocarbon solvents dichloromethane, 1,1,1-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloroethene and tetrachloroethene at rural and mountain forest sites have been assessed by automated gas chromatography/data processing. The principal atmospheric oxidation product of C₂-chlorocarbons, the phytotoxic trichloroacetic acid (TCA), has been determined in the foliage of conifers at levels between 10 and 100 ppb, suggesting its involvement in mountain forest decline.

INTRODUCTION: The C₁- and C₂-haloalkanes dichloromethane, 1,1,1-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloroethene and tetrachloroethene have found wide industrial application as solvents, degreasers, paint strippers and blowing agents for foam-polymers. Their most important features in this regard are non-inflammability, low acute toxicity, and high volatility. Depending upon source, data on production and emission may differ [1], but their annual global production rates are estimated as between 2.5 and 3 million tons. A quarter to a third is produced in Western Europe, about a tenth in West Germany.

Emissions into the atmosphere have been suggested as 60 to 90 % of production [1]. Under steady-state conditions, more than 99 % may be expected to equilibrate into the atmospheric compartment due to their large Henry constants [2]. As the only significant removal process is photooxidation, the latter fact is relevant to atmospheric formation of secondary air pollutants and chlorine recycling.

Data for assessment of background levels and long-term developments of persistent haloalkanes have been established in the mid-seventies [3]. As they have atmospheric lifetimes of several decades, the levels in well-mixed air at remote sites reflect diffuse global burden; this applies also to 1,1,1-trichloroethane and 1,1,2-trichloro-1,2,2-trifluoroethane which have tropospheric lifetimes of a decade or more. Dichloromethane, trichloroethene and tetrachloroethene are short-lived (lifetimes of a week to several months) but are still sufficiently stable to be ubiquitous on the Northern hemisphere; their atmospheric levels in industrialized countries vary widely. Determinations of actual levels on the European and North American continent are scant but suggest that tropospheric concentrations at rural sites of industrialized countries may have risen during the seventies. In order to judge the relevance of airborne halocarbons in respect to phytotoxicological phenomena such as mountain forest decline [4], representative air levels and the occurrence of phytotoxic secondary air pollutants derived thereof have been monitored.

METHODS: Halocarbon levels in ambient air are determined with a specially designed sorbent sampling and thermodesorption injection system [5] on a gas chromatograph (Sichromat, Siemens) equipped with thick-film capillary and electron-capture detector. Data acquisition and processing are performed with chromatographic integration software (PE Nelson 2600) and data management software (Lotus 123) installed on a personal computer (Tandon AT). Air samples are collected and injected every half hour by means of a 6-port rotary valve. Repetitive automated and coordinated operation of rotary valve, thermodesorption unit, gas chromatograph and data system is enabled with an electronic timer with EPROM-memory [6]. Air levels at sites without electric power supply are determined by collecting samples with sorbent cartridges; actual analyses are performed on a laboratory gas chromatograph as described previously [7].

Trichloroacetic acid in spruce needles is determined by homogenization under liquid-nitrogen, internal standardization with 2,2-dichloropropionic acid, extraction with water and ether, derivatization to the corresponding methyl ester and thick-film capillary gas chromatography, as described elsewhere [8].

RESULTS AND DISCUSSION: Representative ambient air concentrations have been determined with an automated gas chromatographic monitoring system. As air levels at a given time and location are highly variable, numerous analyses need be performed at random under different meteorological conditions.

Atmogenic data are statistically not normal-distributed [9]; however, cumulative frequency distributions illustrate the typical differences between various locations (fig. 1). Comparison based upon 40-50 individual data for

each location illustrate the relatively high levels of the C₂-chlorocarbon solvents in Central Europe as compared to Atlantic sites [10]. For tetra-chloromethane, the direct anthropogenic emissions are small and correspondingly the levels are similar at the different sites (not shown); trichloro-methane is higher at oceanic than at continental sites (not shown).

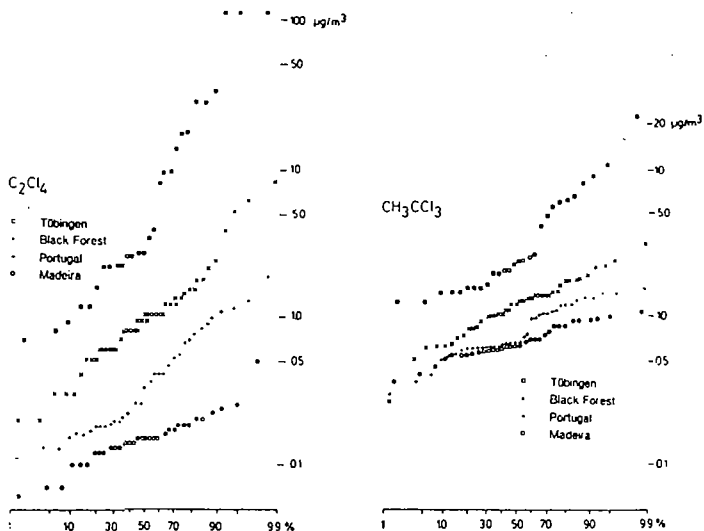


Figure 1: Frequency distributions of ambient air concentrations of tetra-chloroethene (left) and 1,1,1-trichloroethane (right) in Central Europe (Tübingen, Black Forest), at the Atlantic coast of Portugal, and on Madeira.

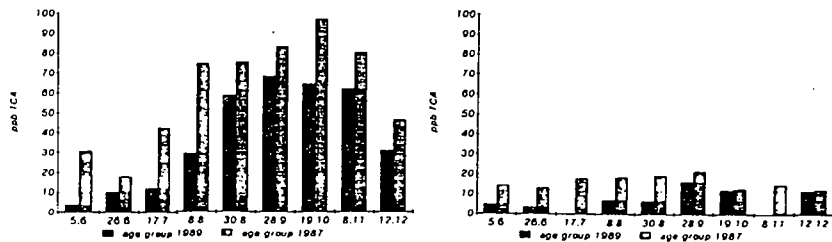


Figure 2. TCA-concentrations during summer 1989 in spruce needles from two forest observation sites with average needle loss of 32 % (left) and 20 % (right).

Atmospheric degradation reactions of airborne compounds including halo-carbons are OH⁻-dependent; the kinetic rate constants and the observed atmospheric lifetimes correlate relatively well. The principal products of photo-

oxidation of the C₂-chlorocarbons 1,1,1-trichloroethane, trichloroethene and tetrachloroethene are chlorinated acetic acids. In fact, photooxidation of tetrachloroethene to trichloroacetic acid had been reported already in 1845 [11]. Dichloroacetic acid, probably an oxidation product of trichloroethene, has been found in rain water [12], and trichloroacetic acid is a ubiquitous pollutant present in forest soil and the foliage of trees (figure 2) [6,13].

Short-chain chlorinated aliphatic acids have been known since the late forties for their strong phytotoxicity [14], and trichloroacetic acid has been employed in the fifties and sixties as herbicide against perennial grasses. Preliminary experiments show that TCA is acutely phytotoxic also to conifers [13].

The relatively high atmospheric levels of ubiquitous C₂-chlorocarbons in Central Europe, their efficient oxidation to chlorinated aliphatic acids, and uptake of the latter by plants is likely to constitute a chronic phytotoxic stress upon mountain forest trees exposed to low levels of the common inorganic air pollutants.

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