Pine Needles as Biomonitors of Short-Chain Aliphatic Halocarbons in Air

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1. Introduction

Short-chain aliphatic halocarbons (SCAHs) are ubiquitous mainly, except for methylhalogenides, anthropogenic air pollutants[1)]. For example chloroform can be formed through in vivo haloform reaction in sea. Algae and volcanic activities produce remarkable amounts of tetrachloromethane, dichloromethane, trichloroethene and tetrachloroethene into the atmosphere[2)]. Dichloroacetic acid and trichloroacetic acid are the main oxidation products of tri- and tetrachloroethene and trichloroethane in the atmosphere[3)].

The most important physical-chemical properties affecting the fate and distribution of chemicals in the environment are the water solubility, vapor pressure, Henrys law constant and octanol/water partition coefficient (K_{OW}). These factors are also regulating the formation of equilibrium distribution between the concentration of chemicals in air and in needles. For example in case of tetrachloroethene the equilibrium between the concentration in air and the concentration in needle has been shown be achieved already in one hour[4,5)]. For some semivolatile or low-volatile compounds, such as DTT, the time to achieve the equilibrium may be several years[6-8)]. At equilibrium the concentrations of chemicals in air could be calculated from the concentration in needles and from the partition coefficient concentration in air versus concentration in needle[9)]. Some relevant physical-chemical properties of the SCAHs analyzed in this investigation are shown in Table 1. SCAHs have relatively high water solubilities. Log K_{OW} values are in the range of 2 to 3. The vapor pressures are high enough for evaporation and fast distribution in the environment after release to air phase. The atmospheric lifetimes of SCAHs are long enough for the transport of these from industrialized and urban areas to rural and forest areas[10-13)]. The concentration levels of SCAHs in urban and rural air usually do not differ greatly[14)]. The atmospheric concentration levels of SCAHs vary over several orders of magnitude. The air concentrations of C_1- and C_2-halocarbons have been found to be in the range of 0.1 to 20 $\mu g/m^3$ or even higher[15-17)].

Halocarbons have a tendency to accumulate in the lipophilic compartments of needles and leaves[14)]. Pine needles can be used to monitor the air concentrations of SCAHs. In this study pine needle samples collected from the vicinity of a metal reclamation plant were analyzed for eight SCAHs. Reference samples were collected from forest in the Central Finland. The analyses were done by purge and trap GC/MS to minimize the use of organic solvents and chromatographic materials.

Table 1. Physical-chemical properties of the SCAHs at 25°C (from EPA, Environmental Database).

compound	molecular weight	solubility in water g/m^3	vapor pressure $Pa x 10^3$	H Pa m^3/ mol$x10^3$	log K_{ow}
carbontetrachloride	153.8	800	15.097	2.968	2.64
1,1,1-trichloroethane	133.4	5500	17.023	0.413	2.47
chloroform	119.2	9600	26.344	0.343	1.97
1,2-trans-dichloroethene	96.9	6300	26.648		
dichloromethane	84.9	16700	60.694	0.323	1.25
1,1,2,2-tetrachloroethane	167.8	2900	0.533	0.038	2.39
trichloroethene	131.4	1100	10.266	1.185	2.53
tetrachloroethene	165.8	150	2.533	1.908	2.53

2. Experimental

The analytical procedure for the determination of SCAHs is described in Fig.1. Pine needles from the surroundings of a metal scrap plant were collected. The needles representing different periods of growth were separated. The samples were stored in twofold aluminium foils at -20°C until analysis. The analyses were performed as soon as possible.

A Tekmar LSC 2000 Purge and Trap equipment was used to isolate the SCAHs from fresh pine needles. About 0.2 grams of needles were taken for each analysis. The needles were crushed under liquid nitrogen just before analyses. The samples of crushed needles were moved into sealed sample vessels and bromoform was added as internal standard. The needles were purged for 10 min at 60°C with helium (40ml/min) and the volatile compounds trapped into solid sorbent material (Tenax) and then thermally desorbed from Tenax trap (3 min in 190°C) and removed to a cryofocusing module (-130°C) and further to the GC column. Fig. 2. shows the purge and trap system. VG AutoSpec high resolution mass spectrometer connected to a HP 5890 Series II Gas Chromatograph was used in the GC/MS analyses of the samples. The resolution of the mass spectrometer was adjusted to 5 000. The column was a 25 m Nordibond SE-54 (0.32 mm, 1 μm) and the temperature program was 40°C(5 min)-5°C/min-100°C-10°C/min-250°C. The temperature of transfer line was 280°C and the temperature of ion source 260°C. The electron ionization potential was 70 eV. The following eight compounds were analyzed by selected ion monitoring (SIM) GC/MS: dichloromethane (83.953, 85.950), chloroform (82.946, 84.943), tetrachloromethane (116.907, 118.904), 1,1,2,2-tetrachloroethane (82.946, 84.943, 130.922, 132.919), 1,2-dichloroethene (95.953, 97.950), 1,1,1-trichloroethane (96.961, 98.958), trichloroethene (129.914, 131.911) and tetrachloroethene (163.875, 165.872).

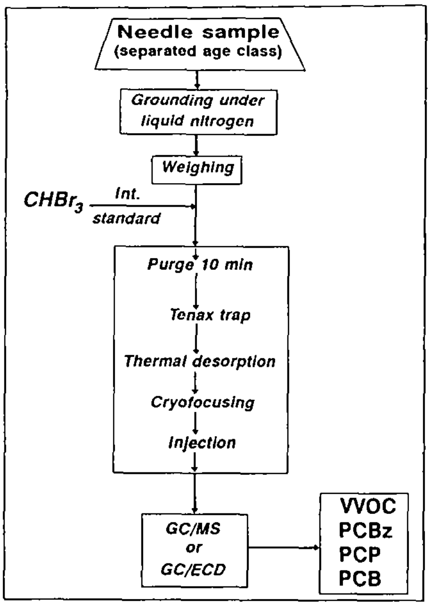

Fig. 1. The analytical procedure for the determination of SCAHs.

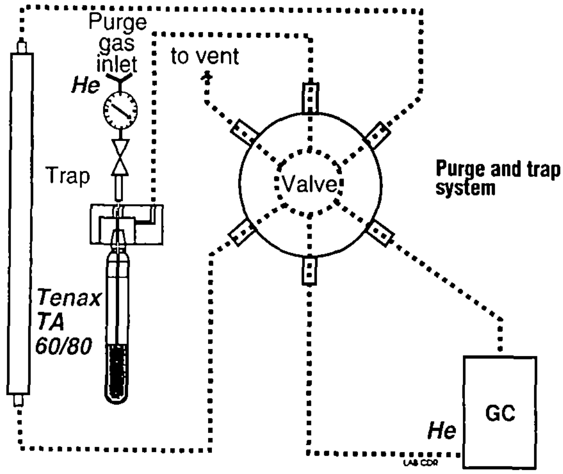

Fig.2. The purge and trap system used in the isolation of SCAHs.

3. Results and conclusions

The concentrations of dichloromethane, chloroform, dichloroethene and tetrachloroethene were calculated. The concentrations of dichloromethane were highest, in the range of 2-20 µg/g. The concentrations of chloroform were in the range of 6-35 ng/g, those of dichloroethene 2-115 ng/g and those of tetrachloroethene in the range of 100-350 ng/g.

The purge and trap GC/MS is quite fast and sensitive method for determination of SCAHs in pine needles. The method does not include any solvent extractions or chromatographic purifications. Common solvents and chromatographic materials may contain disturbing amounts of some SCAHs. A large number of samples should be analyzed to obtain reliable knowledge of the distribution of SCAHs and of the probable source of these. In the surroundings of the metal scrap plant there are also other possible sources of SCAHs. There is a new motorway quite near the plant, and traffic is known to be one of the major sources of SCAHs. There are also some small industrial plants situated in the vicinity of the metal scrap plant. These can act as small point sources of SCAHs.

4. References

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