# TRICHLOROACETIC ACID IN CONIFER NEEDLES IN POLLUTED AND CLEAN ENVIRONMENTS

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## INTRODUCTION

Trichloroacetic acid (TCA) is a lipophilic and watersoluble organic acid which has been widely used as a herbicide against grasses and certain broad leaf weeds in the 1950-60's. TCA is no more in common use as a herbicide. However, it has been found in tree needles and leaves; concentrations between 5 and 150 ng/g have been reported from Central- and North-Europe[2,4,5]. TCA has also been observed in soil and rainwater. It has been assumed that TCA would be phytotoxic to conifers and thus, may have a role in the forest decline. The origins of TCA are the reactions of chlorinated $C_2$-hydrocarbons (1,1,1-trichloroethane, trichloroethene, and tetrachloroethene). Their annual global emissions are about $1,6 \times 10^6$ tonnes. The use of these compounds has increased during the last decades[7]. These compounds are mostly emitted from textile and metal industries. The emissions of pulp mills also contain these chlorinated compounds[6,8].

In this study TCA levels in pine needles in the surroundings of a pulp mill were compared to TCA levels in urban and rural areas.

## METHODS

Needle samples were collected from pine branches within one week from three different areas of eastern Finland in May 1992, i.e. an urban area, a rural area, and the vicinity of a pulp mill. The pulp mill and the urban area were situated about 100 km from the rural area in opposite directions. There were nine sampling sites (three trees per site) at the distances of 0.5 km, 3 km and 18 km from the pulp mill in

different compass directions. Southerly winds were most common in the mill area. In the rural and urban study areas there were three sampling sites (four trees per site) about 5 km from each other. All samples were stored below -40 °C until analysis.

The samples were prepared and analyzed as described earlier[2,5]. Needles were crushed under liquid nitrogen and the internal standard (2,2-dichloropropionic acid) was added. Samples were extracted with 6 ml of Millipore water, reextracted with ether and methylated with diazomethane. Analysis was done by using negative chemical ionization with GC-MS (GC/NCI-MS/SIR). Methane was used as an ionization gas. The mass fragments m/z 35 and 37 were monitored. The column was an HP-5 (25 m x 0.2 mm with 0.1 μm film). The detection limit of TCA was 10 pg.

## RESULTS AND DISCUSSION

TCA was detected in all samples. TCA was present in the older needles at higher levels than in the younger ones (Table 1). Quite large natural variations among trees growing close to each other were noticed.

Table 1. Trichloroacetic acid (TCA) concentrations, mean ±SD (min. - max.), in 1.year needles (= 1.yn) and 3.year needles (= 3.yn) of pines in the study areas. (FW: fresh weight)

| | n | RURAL AREA (ng/g FW) | n | URBAN AREA (ng/g FW) | n | PULP MILL (ng/g FW) |
|---|---|---|---|---|---|---|
| 1.yn | 11 | 19 ±14 (3-50) | 12 | 24 ±12 (6-42) | 27 | 16 ±12 (2-50) |
| 3.yn | 11 | 58 ±38 (17-135) | 12 | 56 ±35 (18-128) | 27 | 37 ±29 (5-98) |

TCA concentrations in the urban area were similar to those in the rural area. It seems that the emissions from an area source (Table 2) are diluted effectively and thus, no changes in needle TCA concentrations could be observed. High TCA levels in the rural area show that there exist no areas free of TCA. This is due to the long atmospheric lifetimes of the precursor chlorocarbons, which are effectively transported over long distances. TCA concentrations determined in this study are comparable to those reported previously[2,4].

Table 2. Atmospheric emissions (t) from the study areas in 1992.

| | RURAL AREA | URBAN AREA | PULP MILL |
|---|---|---|---|
| $SO_2$ | 0 | 2000 | 420 |
| $NO_x$ | 0 | 5100 | 250 |
| $Cl_x$ | 0 | 5-30[+] | 60[++] |

[+] = total amount of halocarbons
[++] = total amount of chlorinated compounds calculated as chlorine

The lowest average TCA levels were found in the surroundings of the pulp mill. However, due to the high concentration variation the differences were not statistically significant. The levels downwind of the most common wind direction from the pulp mill were lower than the levels upwind (Figure 1). The emissions of nitrogen oxides from the pulp mill may inhibit TCA formation from its precursors[1].

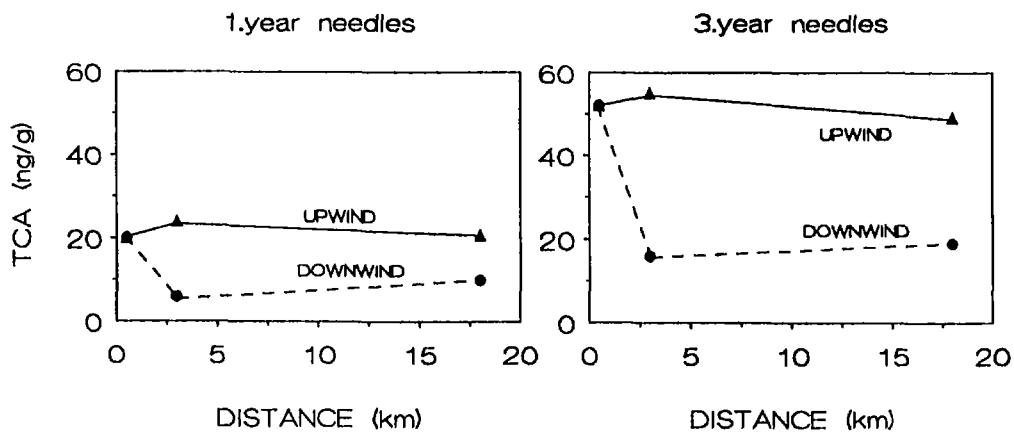


Figure 1. Average TCA concentrations in pine needles downwind and upwind the most common wind direction with increasing distance from the pulp mill.

## CONCLUSIONS

Trichloroacetic acid concentrations in pine needles in rural, industrial and urban environments were compared. Similar concentrations were observed in urban and rural areas which shows that TCA is a ubiquitous compound. The levels of TCA were lower in the surroundings of a pulp mill than in urban and rural areas. There might be atmospheric reactions due to pulp mill emissions which inhibit TCA formation.

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