Trichloroacetic acid in conifer needles in an area of kraft pulp mill plume

Juuti S., Norokorpi Y.*, Ruuskanen J.
Department of Environmental Sciences, University of Kuopio, P.O.Box 1627, FIN-70211 Kuopio, Finland; *The Finnish Forest Research Institute, Rovaniemi Research Station, FIN-96300 Rovaniemi, Finland

INTRODUCTION

Understanding the distribution and fate of volatile chlorinated hydrocarbons (VCHs) in the environment has recently become a high priority in the environmental science. There is also a considerable environmental interest in ascertaining the volatile chlorinated organic contaminants around pulp and paper industry. Bleaching of the chemically produced pulp involves the use of bleaching agents which can be chlorine containing compounds like gaseous chlorine (Cl_2) or chlorine dioxide (ClO_2) or nonchlorine compounds like oxygen. When Cl_2 and ClO_2 are used for pulp bleaching, their as well as VCH's atmospheric emissions are of concern in the surrounding areas of the pulp and paper industry.

The various sequences of pulp bleaching involve multistage processes of bleaching and extraction of solubilized organic material to remove residual lignin. Each stage typically includes reaction with bleaching chemical or caustic extraction solution in the retention tower, washing of the product pulp on the washer prior to subsequent operations, and removal of the filtrate via a seal tank. The vents to the atmosphere from towers, washer hoods, and seal tanks may or may not be fan driven, ducted together to common vents, or ducted to gas-liquid scrubbers for emission control. Because ClO_2 is always generated on-site, there is a ClO_2 generator vent that can be a source of emissions of Cl_2 and ClO_2. Besides of direct emissions of Cl_2 and ClO_2 there are emissions of VCHs from wastewater collection and treatment facilities which are a potential concern to treatment operators and downwind receptors. During the bleaching variety of organochloro compounds will be formed; in the spent chlorination/alkali extraction liquor over 250 chlorinated compounds have been identified[1-3]. The data about the atmospheric emissions of VCHs released during different stages of pulp bleaching processes or from the spent liquor is, however, much sparse[4].

Some VCHs, primarily tetrachloroethene and 1,1,1-trichloroethane, react in the atmosphere to produce e.g. trichloroacetic acid (TCA)[5,6]. These chlorocarbons are present in the volatile fraction of chlorinated compounds formed during bleaching of pulp with chlorine containing agents (Cl_2, ClO_2)[4]. Furthermore, the enhanced atmospheric levels of atomic chlorine, due to Cl_2 and ClO_2 emissions, enhance the formation of TCA from tetrachloroethene[7]. It has been suggested that needle TCA levels could act as an indicator for the overall VCH pollution situation[8]. The purpose of this study was to

investigate concentration levels of TCA in pine needles in the plume area of two closely situated pulp mills and to estimate the impact range of the pulp mill plume.

MONITORING SITE

The two pulp mills situated at a distance of about five kilometres from each other in northern Finland by the Gulf of Bothnia (65°75N'24°60'E). In 1992, the pulp was bleached with Cl_2 and ClO_2 with the ratio 50:50. In 1993, when the samples were collected, the use of Cl_2 in bleaching ended totally. Scots pine (Pinus sylvestris L.) needle samples were collected twice in the surrounding areas of the pulp mills. Samples were taken from ten sites situated at distances of 5-120 km from the mills northeast in April 1993, when there was snow cover on the ground and also, trees were partially covered with snow. Third-year needles were taken from six closely located trees in each site. Needles were taken from the branches facing towards the pulp mill from the upper third of the crown. Sampling from the same trees was repeated the second time in the following summer (August 1993). These samples were taken, however, only from five sites at distances of 5-36 km from the mills. In addition, 58 background samples were taken at a distance of 120 km from the mills. TCA was analyzed as its methyl ester with GC-MS using negative chemical ionization. The sample analysis is described in detail elsewhere[9].

RESULTS AND DISCUSSION

The principle of the analysis was to compare TCA concentrations downwind of the pulp mills, at sites within the plume as a function of the distance between the pulp mills and receptor sites. The range of TCA levels was from 6 to 276 μg kg^{-1} at the distances of 5-120 km to the prevailing wind direction (northeast) from the pulp mills. The highest TCA levels (92-276 μg kg^{-1}) were found in the tree needles at the closest sampling site to the pulp mills and the concentrations decreased with the increasing distance from the mills. TCA levels normalized to the background concentrations are presented in Figure 1. TCA levels on the sample plots at 9 km and 32 km distances from the mills, however, differed clearly from the average trend and were lower than expected. These plots located lower down than the surrounding terrain towards the mills. Therefore the topography sheltered the plot sites by reducing wind passage and deposition of airborne pollutants. The impact of the emissions from the pulp mills was estimated to reach 60-80 km downwind of the mills. Behind that range the site average TCA levels were on the background level.

It has been shown that sea spray aerosols may contribute to the source strength of atmospheric chlorine[10,11] and thus, intensify TCA formation from tetrachloroethene. Because the pulp mills located on the coast the influence of sea spray on needle TCA levels was also studied. TCA levels in needles collected at distances of 1-30 km from the coast in a reference area showed a slight decrease when approaching the coast. Thus, the reactions due to sea spray do not enhance needle TCA levels in our study area.

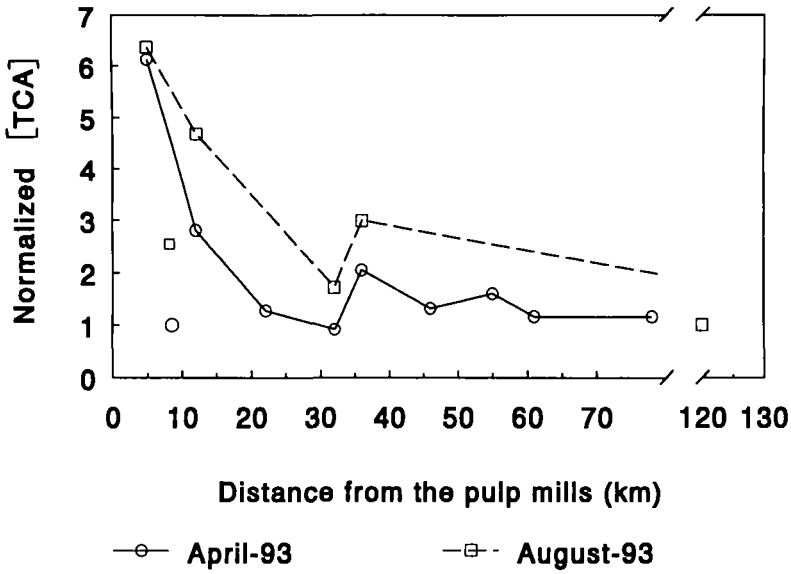

Figure 1. TCA concentrations (average of 5-6 trees; at 120 km average of 58 trees) normalized to the background concentration with increasing distances downwind of the kraft pulp mills.

TCA levels in pine needles close to the pulp mills downwind the prevailing wind direction were considerably higher than the values in rural areas[8,9,12-13]. Thus, the pulp mills where chlorine containing bleaching agents are used could act as emission sources for TCA and its precursors. Considerable accumulation of TCA in needles was noticed with the time, which is obviously due to an intense exposure to the pollutants emitted from the pulp mills. TCA concentrations reached the background levels at the distances of 60-80 km from the pulp mills. It can be concluded that the chlorinated compound emissions from the pulp mills are important on a local scale, but they also contribute to the overall VCH load of the environment.

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