Sampling and Analyses of Balsam Fir Foliage and Soil-air; Mt. Mansfield, Vermont; June, 1995
(Sources and Sinks of Chloroform and its Precursors)
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The purpose of the expedition was to investigate further the hypothesis that chloroacetic acids may be involved in forest decline. These compounds are formed in the atmosphere through the degradation of certain chlorinated solvents used in metal cleaning and dry cleaning, including methyl chloroform, perchloroethylene, and trichloroethylene. Researchers in Germany have found surprisingly high levels of chloroacetic acids in the foliage of forest trees, and they have reported that the concentrations of these substances in the foliage are correlated with needle loss.[1] Both monochloroacetic acid and trichloroacetic acid (TCA) have herbicidal properties; in fact, TCA was marketed as a herbicide at one time. . One study also found high levels of chloroform in soil gas compared background atmospheric levels.[2] The chloroform could possibly have come from chemical reactions in the soil, probably biologically mediated, which degraded trichloroacetic acid.

The expedition to Mt. Mansfield was an effort to observe first-hand the symptoms of high-altitude forest decline and to replicate the findings of chloroacetic acids in foliage of high-altitude conifers and of chloroform in the soil gas of these forests. I was assisted by Beorn Sunflower and Gabriel Aucott.

On the first day, June 9, 1995, we met with Sandy Wilmot, Monitoring Coordinator for the Vermont Monitoring Cooperative. It was determined that we would sample along the Halfway House Trail, which starts at about 2000 feet and goes up fairly steeply to the summit of Mt. Mansfield.

On the first day, we hiked this trail to get a general idea of the terrain and to identify areas and particular trees which looked like good sampling subjects. We determined that there were not enough red spruce to provide samples at a variety of altitudes, and decided to take samples from balsam fir, which is present from about 2000 feet to the tree line at about 3900 feet. We used a portable altimeter, whose response is geared to air pressure changes, to indicate our altitude. The meter readings seemed to correlate well with the altitude stated on our trail map and Geological Survey map, provided that the meter was calibrated first at a known altitude.

On the second day, we again hiked to the summit along the Halfway House Trail, and then began the sampling on our descent. Locations were picked at 3850 feet, 3620 feet, 3050 feet, 2590 feet, and 2050 feet. Most of the initial foliage sampling was done by removing tips of branches from selected balsam fir trees at a height of 20 to 30 feet using a tree-pruner on a three-piece extendable aluminum and fiberglass pole. Smaller pieces were clipped from the branches so obtained and placed in glass vials. At each spot, I also set up the pump to obtain samples of soil gas. Two samples were also taken of the ambient air on Mt. Mansfield. The pump, a battery-powered constant-volume type, was then hooked with a plastic tube to a tenax-filled tube type trap, which was in turn hooked to a stainless steel probe with small holes on the end. The probe was poked into the soil to about a 20 cm. depth. When the pump was turned on, in pulled soil gas from the interstitial spaces in the soil. The gas passed through the tenax-filled trap.

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[1] Frank, H., "Airborne Chlorocarbons, Photooxidants, and Forest Decline," Ambio, Vol. 20, 1991.

[2] Frank, H., Frank, W., and Thiel, D., "$C_1$and C_2-Halocarbons in Soil-air of Forests," Atmospheric Environment, Vol. 23, pp. 1333-1335, 1989.

Upon returning to camp, the foliage samples were placed in the refrigerator of the forest rangers at the campsite, Underhill Center. The next morning, they were placed in a ice chest.

The foliage samples were taken to the lab at Rutgers University, and portions of last year's growth were analyzed for dichloroacetic acid (DCA) and TCA on June 13. The tenax traps were analyzed for chloroform several days later. The analysis procedures involve extracting the chloroacetic acids from the needles and them converting them to ester derivatives which are volatile enough to be measured with a gas chromatograph.[3] [4] The gas samples were desorbed by heat from the tenax tubes and also analyzed with a gas chromatograph.

The results indicate that there are modest levels of DCA and TCA in the balsam fir foliage, with no particular correlation with altitude. The levels are comparable to some of the lower values reported in the European studies. This may be typical of fir foliage early in the season; at least one study has shown fir trees to have lower levels of the chloroacetic acids than spruce or pine, and most studies in the literature show lowest levels in late winter and spring and highest levels in late summer and early fall. There is much variation in the chloroform data, but two samples appear to show significantly higher levels than ambient air.

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[3]Frank, H., H. Scholl, D. Renschen, B. Rether, A. Laouedj, Y., Norokorpi, "Haloacetic Acids, Phytotoxic Secondary Air Pollutants," Environ. Sci. & Pollut. Res., Vol 1, pp 4-14, 1994.

[4]Frank, H., D. Renschen, A. Klein, H. Scholl, " Trace Analysis of Airborne Haloacetates," J. High Resol. Chromatogr., Vol. 18, 1995.