A Search for DDT Residues in the Juneau Icefield, Alaska

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ABSTRACT-The objectives of this study were: 1) to determine if DDT residues occurred in the ice of the Juneau Icefield, and 2) to devise a simple, inexpensive method of sampling glacial ice for pesticide residues. No DDT was found in the samples of ice collected strata spanning the 1963 to 1970 period. However, phthalate plasticizers were found in all samples and were assumed to be due to contamination during collection. The elution time of the phthalate by gas chromatography was identical to that of p,p-DDT. Conversion of DDT to DDD by ultraviolet light was found to remove the phthalate. In the presence of phthalate, DDT could be verified at 25 x 10^-12g per gram of water. In the absence of phthalate the lower of detection of DDT was 1 x 10^-12g water.

Use of DDT in disease control was introduced at the onset of World War II and gained quick acceptance by the military. When released for civilian use, it gained quick acceptance by both health organizations and farmers. In 1970 the National Academy of Sciences estimated the accumulative world production of DDT to be 2 x 10^12 grams. However, DDT was discovered to be highly persistent and widely disseminated worldwide. This finding led to severe restriction or total prohibition of its use in much of the western world by 1970.

DDT is non-polar with very low water solubility (1.2 x 10^-9g DDT/g H2O). These two characteristics contribute to its persistence in the environment, a property desired in an insecticide. Ironically, persistence proved to be the property that eventually caused DDT to lose much of its favor. Residues began to be noticed in non-target areas. Soils throughout the northern hemisphere were found to contain residues of DDT (Woodwell et al., 1969). DDT is very soluble in fat so it is not surprising that residues were discovered in a wide variety of animals in remote Antarctica were found to contain DDT residues in their fat (Brewerton, 1969). Using very large samples, Peterle (1969) reported DDT residues in Antarctic snow in 1969. This remote area, on the interior high plateau about 1,000 km from the nearest coast, had never been treated with DDT, leaving atmospheric transport as the presumed explanation for its occurrence. This discovery was further evidence of the ubiquitous nature of DDT residues.

However, in the late 1960's evidence arose that organochlorine compounds in nature were not always pesticides. This cast doubts on previous reports. Polychlorinated biphenyl (PCB) compounds were found to be widely dispersed in the environment and could be confused for DDT by many analytical techniques used in the late 1960's. Hylin et al. (1969) also reported that naturally occurring organochlorine compounds of plant origin were common and mimicked pesticides in analytical procedures. Furthermore, Brewerton (1969) suggested that much of the DDT found in Antarctica may have been due to its transport by the scientists searching for it either in the form of DDT itself or in the form of mimics or artifacts.

In light of such findings, one of the major problems in environmental assessment of DDT residues, is that prior to 1970 it...
was a two independent studies conducted and analyzed in comparable ways were almost a rarity. Thus, much of the data prior to 1970, and some since that time, cannot be verified as confirmative of the presence of DDT without additional research.

The persistence of DDT has made it a useful “marker” in dating recent surficial deposits such as glacial ice, peat bogs, and sediments. For example, Winderom et al. (1965) determined that the occurrence of talc found in chronological deposits of ice in North American glaciers correlated with its annual use as an extender in pesticide formulations used in the area in question. While it may have little pragmatic importance, the ability to quantify and confirm the presence of picogram quantities of DDT in surficial deposits has considerable academic significance. This study attempted to find an effective and inexpensive way of confirming the occurrence of DDT in ice collected from Alaskan glaciers in the Juneau Icefield in the presence of its mimics or artifacts.

**Collection and Analysis of Glacial Samples**

In 1970 a survey was made by the senior author of several glaciers on the Juneau Icefield north of Juneau, Alaska to determine if existing analytical techniques were adequate to detect the presence of DDT residues. Samples were taken from the surface (1970 snow) down to 1963 ice. The sampling site was on the Taku Glacier west of a research station called Camp 10. Camp 10 is operated by the Foundation for Glacier and Environmental Research, directed by Maynard M. Miller. Crevasses in this area are approximately 30 m deep.

A limited budget necessitated devising methods for sample collection that used simple equipment. To avoid the use of expensive boring equipment, samples were collected from crevasse walls. Crevasses were entered by means of a rope ladder. Several centimeters of surface ice were removed with an ice axe and discarded. A metal container was lowered from the surface by a rope and approximately 20 l of ice removed from the full depth of a given year’s snowfall. The year sampled was determined by visible stratigraphic indicators on crevasse walls, such as relic sun cups, insect inclusions and albedo differences. It was assumed that each year’s snow accumulation was still present in the stratigraphy. Samples were removed to the surface and melted on a gas stove. Duplicate 500 ml samples were then extracted with 25 ml of benzene using a separatory funnel (Konrad, et al., 1969). The extracted samples were placed in 25 ml amber glass containers, covered with aluminum foil and topped with plastic screw-on lids.

After transport to the University of Minnesota laboratory samples were reduced to 1.0 ml with a Kuderna-Danish apparatus. Samples were shaken with 2 g of anhydrous Na2SO4 to remove water, decanted immediately into 10 x 75 mm test tubes and stoppered with corks wrapped in aluminum foil.

All samples were analyzed on a Beckman GC-4 gas chromatograph equipped with a helium ionization electron capture detector. Injection volumes were 1 ul. The operating parameters of the gas chromatograph were: 4 foot glass column packed with 60/80 mesh chromisorb G with 3% silicone SE 30, inlet line temperature 180°C, column temperature 200°C, detection temperature 296°C. Helium gas flow rates were adjusted to maximize sensitivity. Rubber septums were used. DDT standards were dissolved in benzene and analyzed with the same operating parameters.

Almost all samples were found to contain interferences and before further glacial ice analyses were undertaken, techniques were devised to remove the interference, to increase the lower limit of detection and to include verification. The sample size was increased to 2000 ml and 50 ml pesticide-grade hexane was used as an extraction solvent. Samples were concentrated to 1.0 ml by passing nitrogen across the extracts. Ultraviolet light was used to degrade DDT to DDD for verification of DDT. The samples were placed in 10 x 10 x 35 mm glass stopped standard silica cells, normally used for spectrophotometry. The silica cells were laid on a side and a stream of warm air was directed into the cell unit the solvent was evaporated. The lip on the silica cells prevented the solvent from running out during this step. After evaporation the cells were stopped with a ground glass stopper and exposed to ultra-violet light for 15 minutes. After ultraviolet exposure 1.0 ml of hexane was placed in the silica cell to redissolve the sample before reinjection into the gas chromatograph (Banks and Bills, 1968; Gloefsky, 1972). The same gas chromatography and parameters were used as previously except that the detector was replaced with a tritium scandium model.

Plasticizers were removed from samples by placing 0.1 g of Alumina Basic Brockman in a 10 x 75 mm test tube and adding the 1.0 ml hexane sample. After 30 seconds of hand shaking the solvent was immediately decanted to a 10 x 75 mm test tube; injections into gas chromatograph were made directly from this test tube.

During July 1977, samples were again collected from the Taku Glacier using the method described previously. Ice samples were taken from annual deposits from years 1961 through 1966 ice because these were high DDT use years (Brints and Dahl, 1971). A sample from the terminus of the Mendenhall Glacier was also collected to serve as a control. The Mendenhall Glacier terminus is approximately 30 km southwest of the Taku collection site. Ice at the terminus of the Mendenhall Glacier is 100 to

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150 years old, according to the national park ranger present at the site, and would have been formed prior to DDT production.

(The cover illustration is Photo "A" of this paper, and Photo "B" appears on page 6).

Contamination of Samples During Collection

All of the samples collected in 1970 contained unknowns with the same retention time as p,p-DDT. Mass spectographic analysis of these unknowns indicated that they were phthalic acid esters commonly used as plasticizers. A subsequent check of all equipment used on the glacial expedition indicated that the plasticizer was in the climbing ropes used at the sampling site. On the return expedition in 1977 pieces of the climbing rope were observed to flake off and some contamination was unavoidable. The lower limit of detection by the procedures used in 1970 for DDT samples free of interference was 40 x 10^-9 g/g water.

In 1970 Stengle et al. (1971) looked for DDT residues on Mount Logan, Yukon Territory, 323 kilometers northwest of the Juneau Icefield and were unable to detect DDT residues. However, their samples contained polychlorinated biphenyls, which they presumed to be contamination from the coring equipment used. The lower limit of detection in their study was 5 x 10^-12 g/g.

Sensitivity of Analytical Procedure Developed

Recovery of DDD was not quantitative; however a 15 minute exposure of DDT to ultraviolet light gave a well defined DDD peak upon reinjection into the gas chromatograph (Figure 1). Using the new procedure and DDT-spiked samples the lower limit of detection and confirmation was 25 x 10^-12 g/g water in the presence of the plasticizers. If no ultraviolet light treatment was necessary the lower limit of detection was 1 x 10^-12 g/g water.

All samples collected in 1977 were free of DDT residues but did contain chromatography peaks similar to the plasticizers encountered earlier. This contaminant was removed by treating the extracts with Alumina Basic Brockman as described previously (Figure 2). The Mendenhall samples required the least handling in these collections and contained the least contamination.

After "clean-up" all samples from the Juneau Icefield were free of chromatography peaks with the same retention time as DDT. Thus, if DDT residues are present in the Juneau Icefield glaciers the concentration is below 25 x 10^-12 g/g, even for years of high DDT production and use.

The methods used provide easy and inexpensive means of quantifying and confirming the presence of DDT in glacier ice collected in remote locations. Although these methods were not immune to contamination, neither are more elaborate means of sampling. It is worthy of note that the senior author and an assistant left the sampling site and returned to Juneau on skis carrying samples and sampling devices in backpacks. Thus, elaborate equipment was not necessary.

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Taku Glacier study site as observed from Camp 10. Ice measured 300 meters thick in this area.

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