Impact of an Urban Methoxychlor Spraying Program on the Rouge River, Michigan

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Introduction

Since the uses of DDT were restricted in 1969, methoxychlor (2,2-bis (p-methoxyphenyl) -1,1,1-trichloroethane) has been widely used as a replacement for DDT. GARDNER AND BAILEY (1975) reviewed the literature on the effects of methoxychlor on environmental quality. Little is known about the environmental impact of methoxychlor including its persistence, its distribution in aquatic ecosystems, the ability of biological systems to concentrate it, or its chronic effects on the biota. Indications are that methoxychlor degrades rather rapidly in most aquatic systems (BRADSHAW et al., 1972; BURDICK et al., 1968; 1974; MERNA et al., 1972; and WALLNER et al., 1969). METCALF et al. (1971) showed little biological magnification of methoxychlor in model laboratory ecosystems and found that most of those organisms studied rapidly metabolized it.

However, since methoxychlor is concentrated in some organisms such as snails (RHEINBOLD et al., 1971 and METCALF et al., 1971) and since methoxychlor is highly toxic to aquatic organisms (MACEK et al., 1969; MERNA et al., 1972; MERNA and EISELE, 1973; SANDERS, 1969 and SANDERS and COPE, 1966 and 1968) more research is required to assess its environmental impact. MERNA and EISELE (1973) recommended that the study of methoxychlor should be extended to field studies in natural habitats where insect control programs may provide sufficient levels to cause sublethal effects. BRADSHAW et al. (1972) and WALLNER et al. (1969) carried out such field studies but neglected to analyze the sediments and biota as possible storage sites.

The Rouge River drains water from a major portion of the Detroit metropolitan area (Figure 1). Segments of the river are degraded in quality due to inadequately treated municipal and industrial waste discharges and storm water discharges. In 1955 a city-wide Dutch elm disease control program was initiated with DDT as the insecticide. In 1969 DDT was replaced by methoxychlor, which has since been sprayed annually. The neighboring cities of Dearborn (Wayne Co.) and Livonia and Farmington (Oakland Co.) also have yearly methoxychlor spray programs for Dutch elm disease. The study area

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represents a rather "typical" urban watershed receiving widespread applications of methoxychlor.

The purpose of this study was to discover whether or not methoxychlor enters and persists in urban rivers and, if it does, to identify storage areas and levels of concentration.

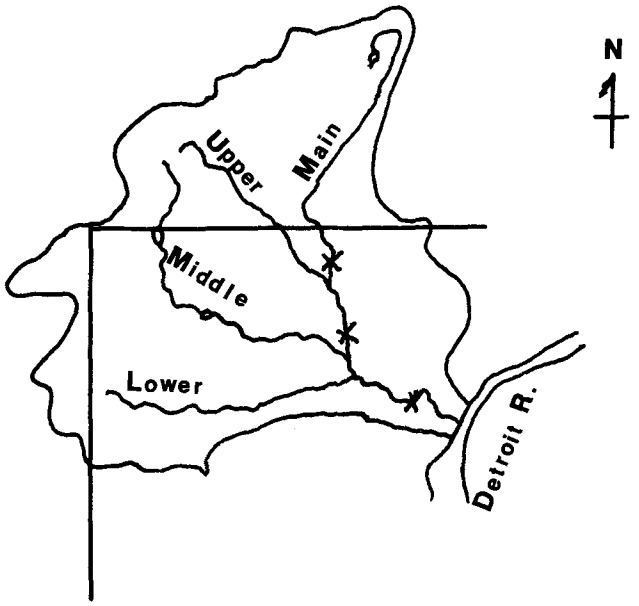

Figure 1. Map of the Rouge River watershed showing the four branches of the river and the location of sampling sites (X). Straight lines encompass Wayne County with the watershed area on the north being Oakland County and on the east, Washtenaw County.

Materials and Methods

Three sampling sites were selected along the Rouge River (Figure 1) and monitored for methoxychlor in the water, suspended solids, sediments and snails (Physa gyrina). Site I was located on the main branch of the river in Eliza Howell Park and was the least organically polluted section of the river studied. Site II was located downstream in Detroit's Rouge Park. Site III was located in a highly industrialized area just upriver from Ford Motor Company's Rouge Plant and was the most polluted segment of the river studied. The sediments consisted of fine sand at site I, pebbles at site II and oil-coated fine silt at site III. Most of the watershed had been drained by the time the river reached the third sampling site.

Each site was sampled biweekly from March 28, 1974 (two

weeks prior to the 1974 elm tree spraying program) until September 1, 1974. Triplicate samples of water, sediment and snails were collected at each site each sampling period and stored for not more than two weeks at -10°C.

Water sampled (200 ml) were collected just below the water surface, filtered through No. 40 Whatman filter paper and extracted three times with ethyl ether-petroleum ether (6:94). Suspended materials on the dried filter pads were extracted and analyzed periodically throughout the study. Snail samples of approximately 0.6 g dry weight were ground with anhydrous sodium sulfate, extracted three times with ethyl ether-petroleum ether (6:94) and cleaned up on activated florisil (MILLS et al., 1963). Sediment samples (approximately 43 g dry wt. per sample) were collected from the upper 3-4 cm of river bottom, extracted and cleaned up by the same procedure used for snails. Solvent from the collected fractions was evaporated to near dryness on a rotary evaporator and quantitatively transferred to glass stoppered sample tubes.

All samples were analyzed on a Beckman GC-4 gas chromatograph equipped with a Beckman discharge electron capture detector. It was fitted with a 6' x 1/4" glass column packed with 3% SE-30 on 80-100 mesh Gas Chrom Q and was operated at a helium flow rate of 40 ml/min and a discharge flow of 120 ml/min. Relevant temperatures were the following: injection port 275°C, column 200°C, and detector 275°C. Operating parameters for the instrument were maximized each morning prior to analysis of samples. Methoxychlor standards were injected at the beginning of each run, after every 3 samples, and at the end of each run.

Spiked samples of water, sediments and snails gave 80-85%, 75% and 80% recovery, respectively, of methoxychlor.

Following gas chromatographic analysis, all samples of each ecosystem component (i.e., all the water sample extracts from throughout the test period, etc.) were combined and reduced to minimum volume. These concentrated samples were run for peak confirmation on a Bell and Howell Type 21-490 mass spectrometer interfaced via a jet separator with a Beckman GC-65 gas chromatograph.

Results and Discussion

Methoxychlor was not detected by gas chromatography in any of the water, suspended matter, sediment or snail samples. No detectable levels of methoxychlor were found in the mass spectrometric analysis of the composite samples. Therefore, we found no detectable buildup of methoxychlor in the Rouge River ecosystem.

This study differs from those previously reported in the

literature (except BRADSHAW et al., 1972) in that most methoxychlor was deposited on land, away from the water, rather than by direct application onto the stream surface.

There are several possible reasons that no methoxychlor was detected in this study. First, methoxychlor may not have been leached into the river from the surrounding watershed. PIONKE and CHESTERS (1973) and EDWARDS and GLASS (1971) have shown that methoxychlor is tightly adsorbed to grass and soil and that losses to aquatic ecosystems through runoff are relatively low when compared to other pesticides. Only BRADSHAW et al. (1972) have reported finding methoxychlor in aquatic ecosystems where runoff from agricultural lands appeared to be the major source.

If the insecticide was leached into the stream, it could have been rapidly degraded and thus not detected. The results of MERNA et al. (1972) and BURDICK et al. (1968) are not directly comparable to this study since both applied methoxychlor directly to the stream surface prior to sampling. MERNA et al. (1972) found a halflife of 7 to 18 days depending on the source of water used, while BURDICK et al. (1968) could no longer detect methoxychlor 36 days after application, thus indicating a rapid breakdown rate.

If methoxychlor had been available in the water and was rapidly degraded, biweekly sampling of the Physa snails should still have detected it, since this genus of snail cannot metabolize methoxychlor. KAPOOR et al. (1970), METCALF et al. (1971) and RHEINBOLD et al. (1971) all found Physa snails capable of retaining relatively high concentrations of methoxychlor once they had accumulated it. Therefore, it seems unlikely that rapid degradation within the aquatic system can explain these results, since no trace of methoxychlor was detected in the snail samples.

One other possible explanation is that the methoxychlor was so diluted by the load of organic matter that it was undetectable in any one sample. REINERT (1970) showed that Lake Erie fish had lower concentrations of chlorinated hydrocarbons than the other Great Lakes (except Lake Superior), due partly to the dilution factor in such a productive lake. There are, however, a number of factors that detract from this hypothesis. HARTUNG and KLINGER (1970) found that sedimented oils markedly concentrated chlorinated hydrocarbons. Site III of our study was similar to their site on the Detroit River, yet we found no traces of methoxychlor in those sediments. Furthermore, BEDFORD et al. (1968) were able to detect levels of methoxychlor in clams in the organically enriched Red Cedar River.

It would seem from the present study, therefore, that methoxychlor did not reach the Rouge River in detectable

quantities.

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