

Water Analysis of Pesticides at Aquatic Park

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Introduction

Aquatic Park is a 97-acre park on the Berkeley Waterfront (Figure 1). Nearly 63 acres of the Park are covered with a shallow, salt-water tidal lagoon, and the Park provides refuge for fish, small mammals, and a host of birdlife. Contact uses of the water, such as boating and water-skiing are allowed, but due to poor water quality, swimming is forbidden. The Regional Water Quality Control Board (RWQCB) recommends there be "no detectable levels of pesticides present in surface waters" (RWQCB, 1975), and thus an investigation of possible pesticide contamination could make a significant impact on future use and planning policies. This report investigates the water quality at Aquatic Park by testing for sixteen organochlorine pesticides in the surface waters and attempts to identify the contaminants of highest concentration found in the lagoon water samples.

Past Studies

Past studies of Aquatic Park waters have identified bacterial contaminants (Betts, 1983) and characterized basic physical and chemical parameters (Altamirano, 1983) affecting the water quality. However, there have been no studies of pesticide contaminants in Aquatic Park waters.

Site Description

Aquatic Park is noted in Berkeley's 1977 Masterplan as "a unique, close-at-hand resource, which should be retained and improved" (Berkeley, 1977). Since this designation, the City of Berkeley has made efforts to increase use and accessibility and to maintain or improve the water quality in the park.

The lagoon water originates primarily from San Francisco Bay through a series of seven tidal gates (all but two of which are currently blocked). It is also subject to contaminants from city storm drains and run-off collected from surrounding urban and industrial areas. The

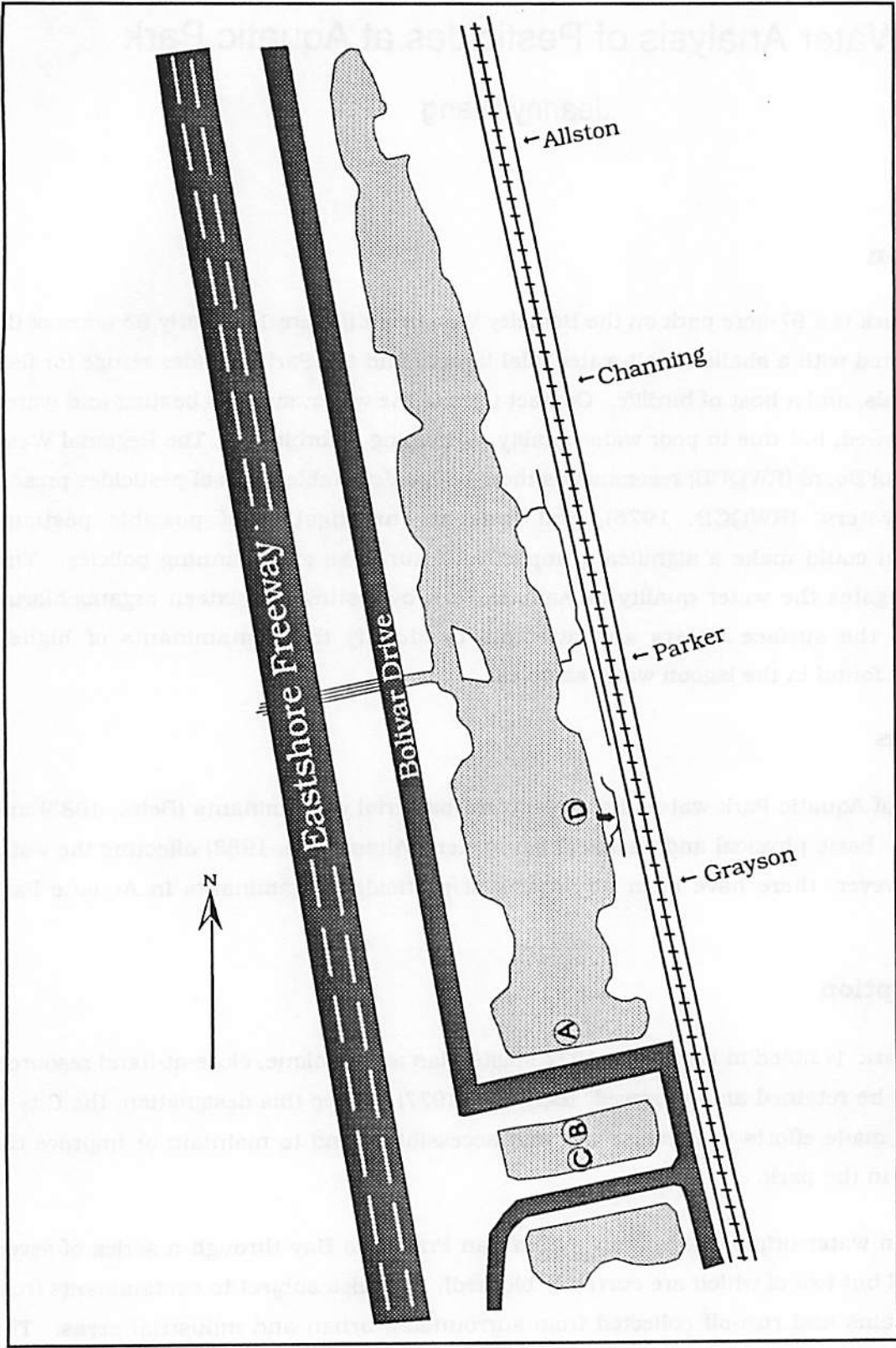


Figure 1. Aquatic Park and sampling locations (adapted from Ferlin, 1983); not drawn to scale.

waters suffer from recurrent excess algal growth and decay problems, limited circulation, and possible chemical contamination.

Although the City of Berkeley discourages the use of pesticides and herbicides in park and grounds maintenance, there is nevertheless widespread use in Berkeley and neighboring cities of many different chemicals in landscape maintenance, structural pest control, as well as in local industries. Over 115 different types of pesticides were used in Alameda County in June 1987 alone (California Dept. of Food and Agriculture, 1987).

Pesticides

There are many different types of pesticides used agriculturally and residentially for insect and fungus control. Two major classes include the organophosphate and the organochlorine pesticides. The former is an example of a "nonpersistent" or nonresidual pesticide, and the latter, a "persistent", or highly residual pesticide. The environmental half-life of a persistent pesticide reflects the time required for the pesticide residue to degrade in its surroundings. Persistence times vary with environmental conditions, and the generalizations about the classes are subject to exceptions by individual pesticides within the class (Klaasen et al., 1986).

Chlorinated hydrocarbon insecticides are a group of organochlorine pesticides that include DDT, its major breakdown product DDE, methoxychlor, and the cyclodiene insecticides: aldrin, dieldrin, endrin, heptachlor, chlordane; mirex, and kepone, lindane, and toxaphene (Klaasen et al., 1986). They are highly soluble in lipids and most organic solvents, but have low water solubilities and very low vapor pressures. Degradation of the chlorinated hydrocarbons is quite slow compared to other classes of insecticides, and in soil and water this degradation is mainly due to the action of microorganisms and photolysis in sunlight.

Because of their persistence, chlorinated pesticides tend to linger in the environment, and thereby pose a possible danger to organisms that live in the water or feed on the sediment. Birds in turn feed on the smaller organisms, and pesticide residues bioconcentrate in their tissues. The well known example of eggshell thinning caused by DDT and DDE (Fyfe, 1988) remains an unresolved problem, though DDT's use was discontinued in the early 1970's. One reason for this lingering problem involves the use of Kelthane[®], a miticide of widespread agricultural and residential use until its ban in March 1989. A major impurity in Kelthane breaks down into DDE, which continues to endanger predatory birds as the pesticide is concentrated in the food chain (Zenone, 1989).

DDT is only one of the many different types of chlorinated pesticides. Characteristic of them all is their persistence in the environment, and because of this, they would be the most likely class of pesticides to be present at Aquatic Park. Although the water solubility of these compounds is low, their presence in the sediment may allow for a constant leaching of the compounds into the water. This study will analyze for sixteen specific organochlorine pesticides.

Methodology

Introduction: Analysis for chlorinated pesticides was performed using standard methods (US EPA, 1986) with slight modifications (Ewing, 1989, pers. comm.). The sixteen compounds tested for are listed in Table 1.

a-BHC	dieldrin
b-BHC	4,4'-DDE
g-BHC	endrin
d-BHC	endosulfan II
heptachlor	4,4'-DDD
aldrin	endrin aldehyde
heptachlor epoxide	endosulfan sulfate
endosulfan I	4,4'-DDT

Table 1. Compounds tested for in Aquatic Park water samples

Grab samples of water were taken from various sites at Aquatic Park (see below). Organic compounds in the water were extracted using a liquid/liquid extraction and then concentrated and analyzed to see if any organochlorine pesticides were detectable. The analysis used gas chromatography techniques to verify whether any of the sixteen pesticides (listed in Table 1) were present in the concentrated water extracts and in what concentrations. To do this, the samples were compared with standards of known concentration. Mass spectrometry was used to verify similar time peaks, thereby making a compound-specific analysis based on a spectrographic pattern possible.

The study procedures are summarized as follows.

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|--|---|
| 1. Sampling | -total of six samples at three sites |
| 2. Sample extraction and concentration | -solvent extraction to remove organics |
| 3. Analysis - Gas Chromatography (GC) | -gases carry compounds through column |
| 4. Comparison of retention times | -compounds exit column at different times |
| 5. Mass spectra (MS) of specific peaks | -compare spectral pattern and ion masses |

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|--|--|
| 6. Identification of compound | -peaks and mass spectra match up |
| 7. Calculation of concentration | -from concentration of standards |
| 8. Identification of other contaminants found in greatest concentration (GCMS) | -verify highest peaks in GC runs with MS |

The outline of this study was based primarily on methods used in EPA analytical procedures and guidelines found in American Public Health Association (1986). For further reading or more detailed procedures, consult EPA analytical manual, Method 8080 (1983) and related articles (US EPA, 1980).

Gas Chromatography: In gas chromatography a *mobile phase* (carrier gas) and a *stationary phase* (column packing) are used to separate individual compounds. The *stationary phase* is a silicon-based polymer that has been coated on the inner wall of glass capillary tubing. This is called a *column*. The column is installed in an oven, so that the inlet is attached to a heated injector block, and the outlet is attached to a detector (Figure 2). The *mobile phase* (gases such as nitrogen, helium, oxygen) carry the sample from the injector block through the column packing to the detector. Precise and constant temperature control in the injector block, oven, and detector is maintained.

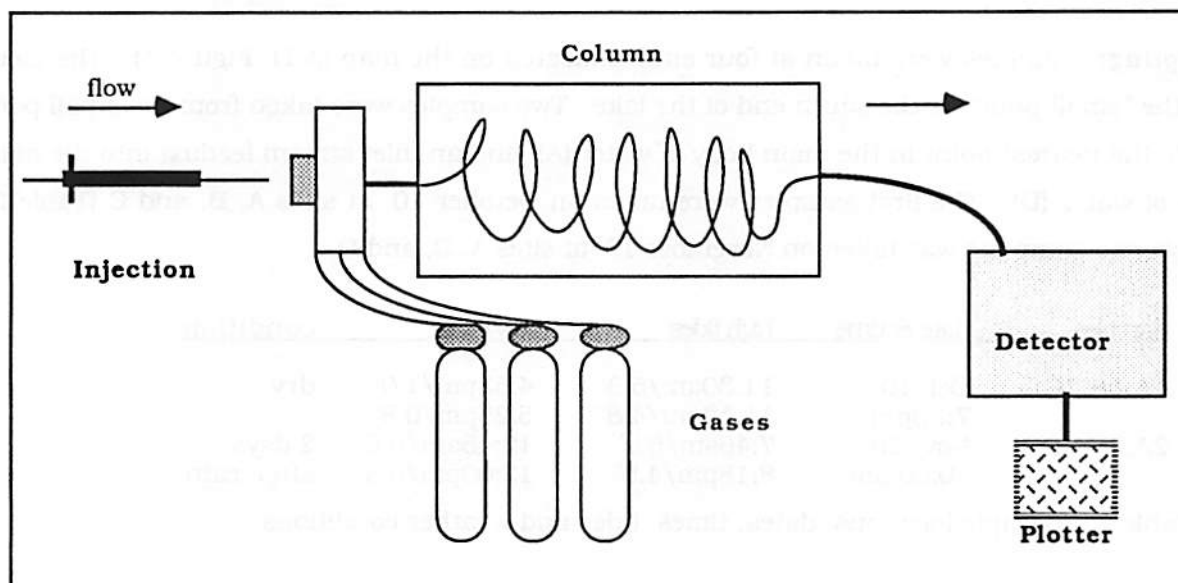


Figure 2. Diagram of a Gas Chromatograph and Detector

Since compounds have different polarities, vapor pressures and molecular weights, they pass through the column and are retained by the stationary phase for different lengths of time under set conditions. The detector will record the amount of time a compound is held on the

column, the *retention time*, before the compound exits the column and produces a peak whose area corresponds to the concentration of that compound. Each peak has a calculable area that can be integrated and thereby quantified in relation to a known concentration of a standard. Therefore, to do any quantification, a *standard* of known concentration must be injected prior to or following an identification run of an unknown sample. The amount of compound present can also be calculated by estimating and comparing the peak heights (usually gauged on the left hand side of each graph) that occur at similar retention times in subsequent runs. In this manner, positive identification and quantification of compounds present in unknown concentrations are possible.

If the retention time of a compound and a standard are identical, there is a good probability that they are the same compounds. Mass spectrometry can confirm this suggestion. For each incremental time segment on the x-axis of the gas chromatogram, ionic spectra can be analyzed. Each vertical peak in the mass spectrum represents an ion identified in atomic mass units (amu). A spectrum of given pattern is compound specific; therefore, the greater the number of major ions common to both standard peaks and samples, the more likely it is that the compounds are identical. If the compound is very dilute, the spectral pattern that can be obtained may be sparse, though still readable. Such is the case for the samples described here.

Sampling: Samples were taken at four sites indicated on the map (A-D, Figure 1). The focus was the "small pond" at the south end of the lake. Two samples were taken from the small pond (B, C), the nearest point in the main body of water (A), and an inlet stream feeding into the main body of water (D). The first samples were taken on October 10 at sites A, B, and C (Table 2). The second sampling was taken on November 19 at sites A, B, and D.

Samples	date & time	high tides	low tides	condition
1A,1B,1C	Oct. 10	11:30am/5.3'	4:53pm/1.0'	dry
	7:30pm	11:52pm/4.8'	5:25pm/0.8'	
2A,2B,2D	Nov. 19	7:46am/6.0'	12:45am/0.8'	2 days after rain
	10:00 am	8:18pm/4.5'	12:00pm/0.8'	

Table 2. Sample locations, dates, times, tides and weather conditions

During each sampling, clean 1-gallon or 4-liter glass jugs were used. The containers were rinsed once with water at the site, and grab samples were taken from the shore or dock.

Preparation for Analysis: Samples were then taken to the laboratory, where 500-milliliter volumes of each sample were promptly extracted with methylene chloride. This procedure separates the water from the solvent (methylene chloride), which effectively traps the organic

compounds of interest. The water is discarded and the solvent extract can be concentrated for analysis. Concentration of the sample involved transferring the extract to a pear-shaped flask, rotor-evaporating it to a volume of several milliliters, and pipetting it into a vial. The solvent was then evaporated off to dryness under nitrogen, and one milliliter of toluene was added to the vial. Toluene served as the medium for all samples in the analysis. (To get more concentrated samples, one half milliliter of solvent may be sufficient.) The vials were stored in a freezer until analysis could be carried out.

Analytic Methods: Compound comparison and identification were done using gas chromatography (GC) techniques. Equipment used included a Hewlett Packard 5890A Gas Chromatograph, an HP 7673A Controller, and an HP 3393A Integrator. Sample injections of 2 μ l were run parallel with control standards. Verification was provided by mass spectroscopy techniques, using the HP 5840A - GC connected to a Mass Spectrograph (MS) detector (HP 3000 + Integrator).

Temperatures were generally set between 120°C and 215°C, and the running time for each sample was 25 to 36 minutes. Variables were set to maximize clarity in data analysis. See Table 3 for final program conditions. Conditions 1 were the initial conditions used in the GC runs (Figure 3), and Conditions 2 were the final conditions used in the GCMS verification runs (Figures 4 and 5).

	Conditions 1	Conditions 2
column type	30m x 0.53mm x 0.25 μ m thickness SPB-1 glass capillary column	60m x 0.575mm x 1 μ m thickness SPB-5 glass capillary column
carrier gases and flow rate	helium at 7ml/min and argon/methane at 8ml/min..	helium at 5ml/min and
program temp.	180°C; 8°/minute to 300°C	120°C to 215°C.
injection temp.	250°C	250°C
detection temp.	300°C	300°C
detector	electron capture	mass spectrometry
run length	25 minutes	36 minutes.

Table 3. GC and GCMS conditions: column type, gases, flow rates, temperatures, detector and run length

Control Standards: The control standards of the compounds tested for (Table 1) were Supelprime-HC Pesticides Mix (Catalog No. 4-8903) supplied by SUPELCO. The original concentration of 2000 μ g/ml in a toluene:hexane (50:50) solvent was diluted to 0.1 ng/ μ l in

toluene. Relative concentrations were evaluated in proportion to the new concentration. Bottled deionized water was extracted in the same manner as the samples to serve as an analytical blank. Toluene washes were run between sample sets to check for residual compounds, and standards were injected at the beginning and end of each run.

GCMS verification was performed with 1 μ l injections of the standards, the lab water extract, and samples 1C and 2D. The identities of unknown chromatographic peaks were individually verified by comparing each peak occurring at a retention time similar to one of the standards. Mass spectra of similar peaks were displayed and checked for corresponding ion abundance. Major peaks occurring at times not corresponding to the standards were checked as well. Relative concentrations indicated by identified peaks were calculated with respect to the concentration standard of 0.1 ng/ μ l.

Results

Pesticides: The compounds tested for were found in low or negligible concentrations. Residual amounts of endrin aldehyde and DDE were detected in sample 2D. Preliminary chromatographs showed a great number of unknown peaks. Once acceptable conditions (Table 3) and clear signals were obtained, a series of injections were sequentially run in the order: standards, toluene wash, water blank, samples, toluene, water blank, standards. This final sequence showed the most interpretable results (see Figure 3).

Low peak signals were noted at retention times similar to a number of the pesticides in the standard. However, the peak areas are less than one fifth the size of peaks seen in the pesticide mix. This corresponds to levels lower than 0.1 pg/ μ l. This low response indicates concentrations that are statistically insignificant. In solvent washes one notes the similar low level peaks at pesticide retention times as well. This suggests incomplete wash out and that the column is holding some of the compounds from prior runs.

Since it is difficult to verify complex samples with only a few standards, two samples (1C and 2D) were again analyzed using GCMS with the sixteen standards and the purified water blank (Figure 4). Matches with similar retention times were checked and the mass spectra drawn for each correlated peak. No matchable spectra (pesticide traces) were observed in sample 1C or in the water blank. However, in sample 2D, peaks observed at 23.11 and 22.24 minutes exhibit mass spectra that look similar to endrin aldehyde and DDE, respectively (Figure 4). Major common ions are identified on the chromatograms in Figure 5 and listed along with retention times. Assuming a linear response over the concentration range

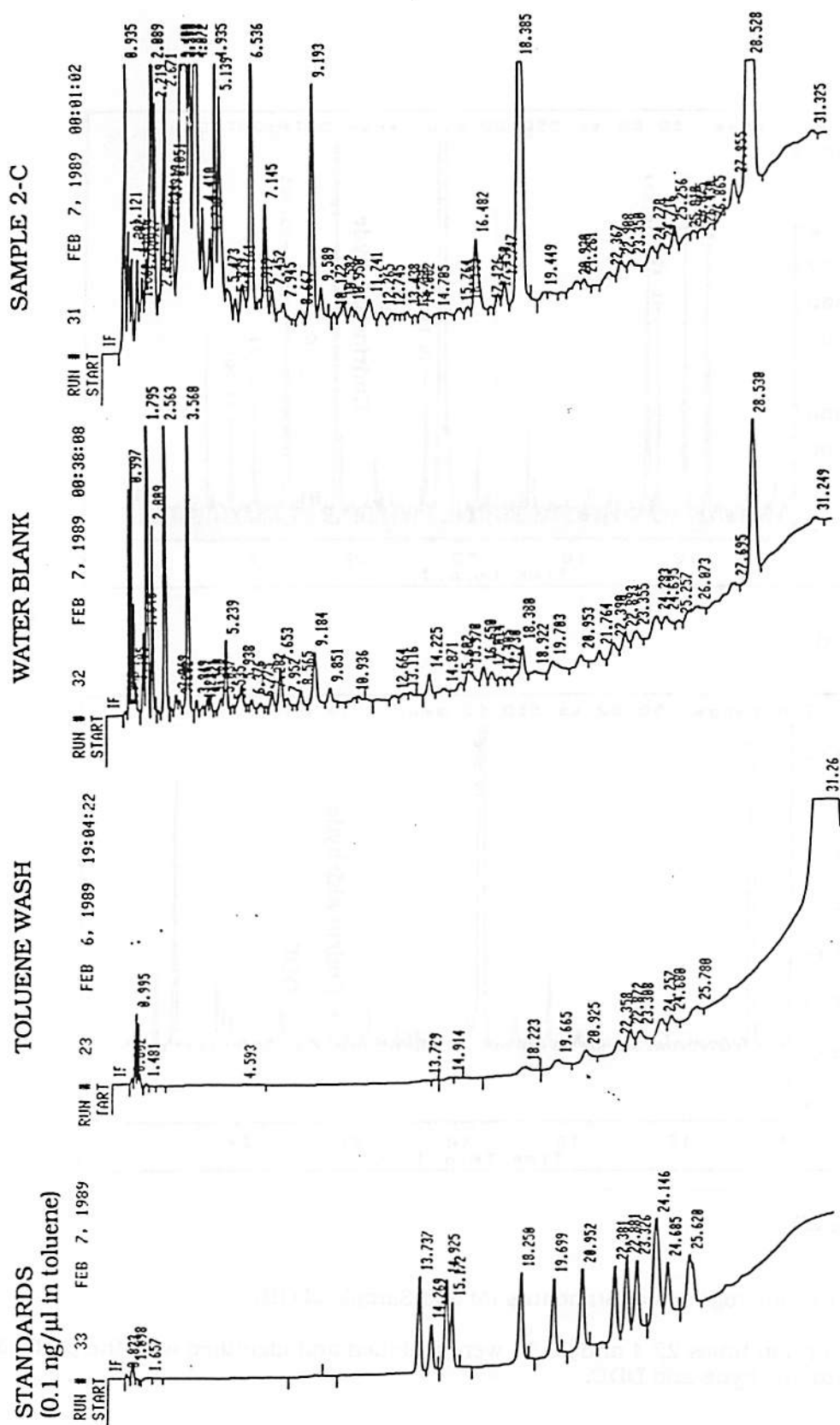
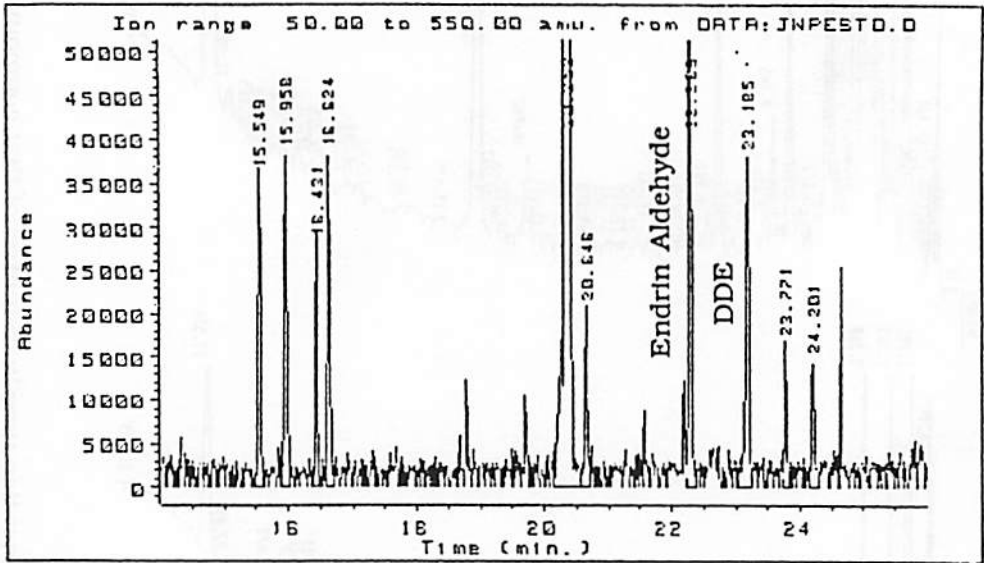
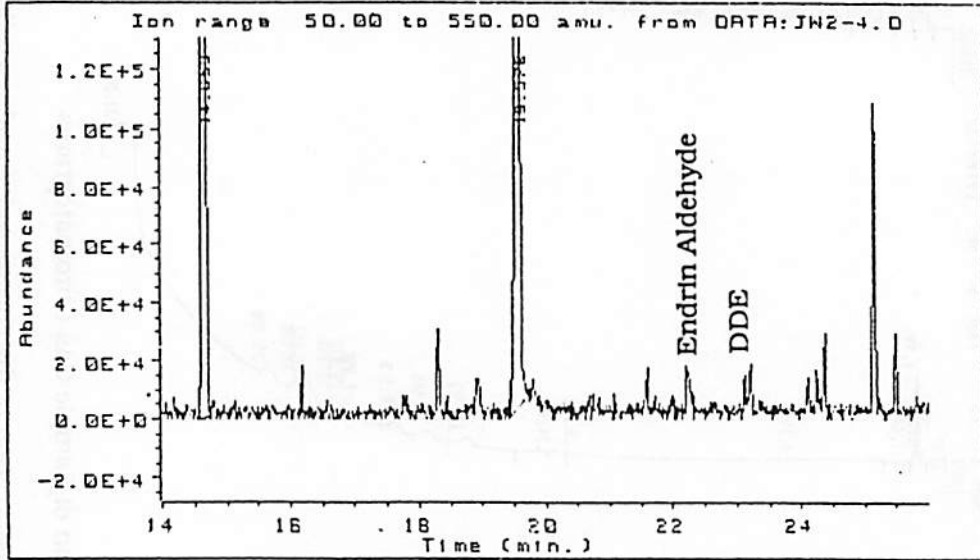


Figure 3. A Comparison of Sample Gas Chromatograms

Peaks suggest the concentration of the compound; numbers indicate the retention time (in minutes) of that compound. The greater number of peaks at the beginning of each run is primarily solvent washout. The chlorinated pesticides in question exhibit retention times between 14 and 26 minutes.



A. Standard

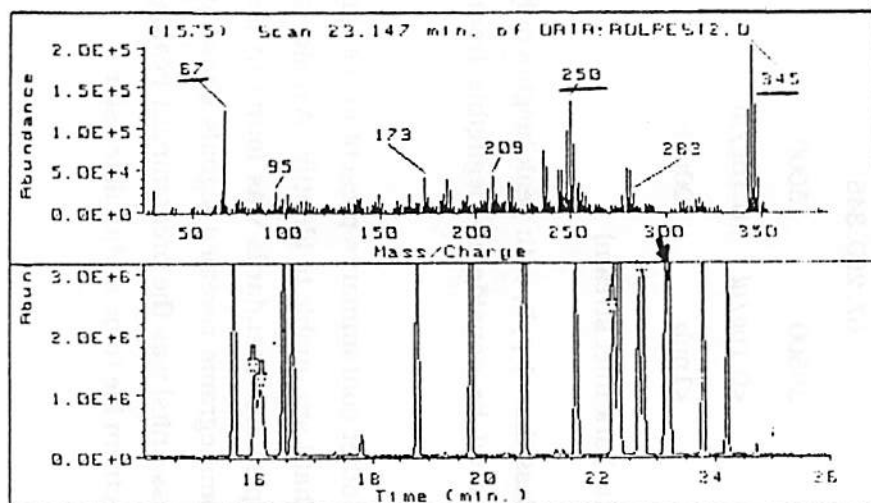


B. Sample 2D

Figure 4. GCMS Chromatograms of Standards (A) and Sample 2D (B).

Peaks found at retention times 22.4 and 23.11 were matched and identified with the pesticide standards of endrin aldehyde and DDE.

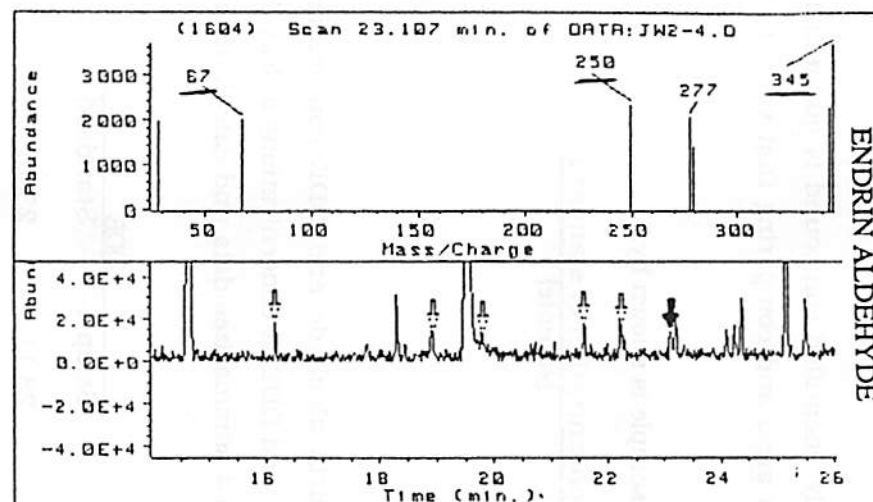
STANDARDS



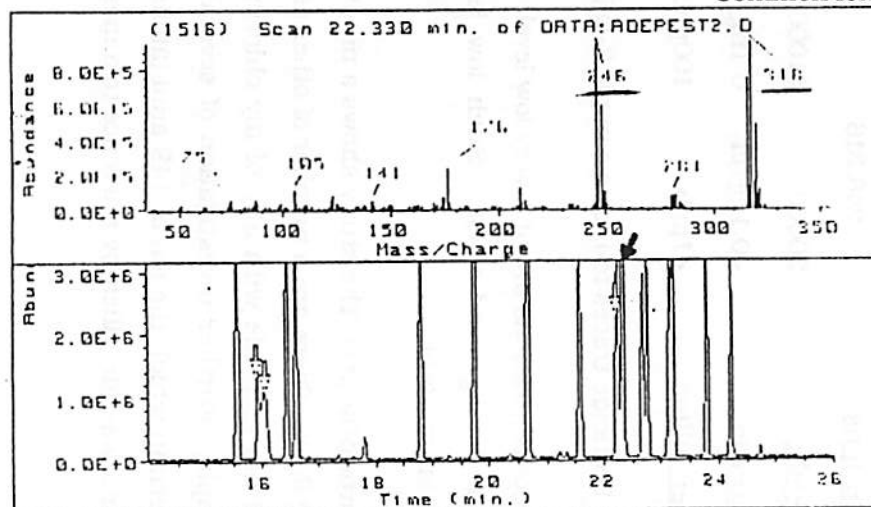
Retention Time: 23.15 minutes

Common Ions: 67, 250, 345

SAMPLES

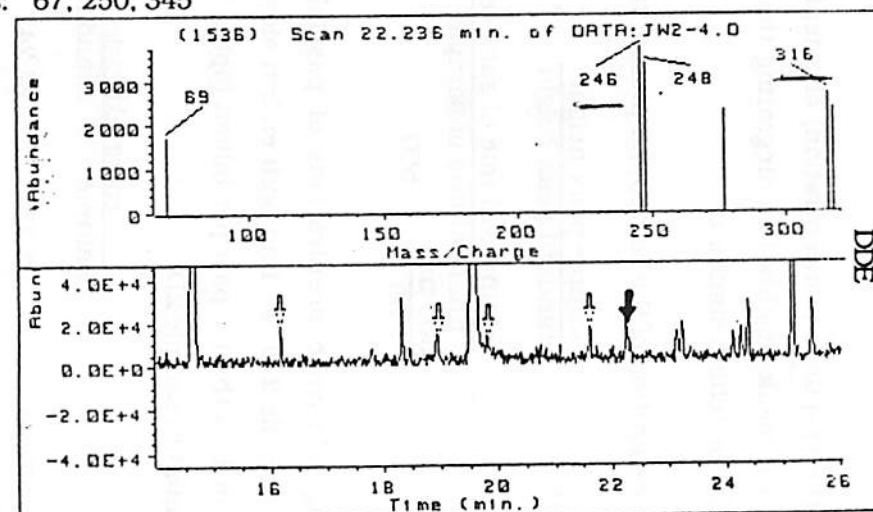


Retention Time: 23.11 minutes



Retention Time: 22.33 minutes

Common Ions: 246, 316



Retention Time: 22.24 minutes

Figure 5. GCMS Verification of Sample 2-D for Endrin Aldehyde and DDE

observed, the response (concentration) of a tentatively identified compound is quantified by estimating the peak heights (or integrating the peak area) and comparing that value to the response of a matching standard.

The concentration of the compound present in the sample is shown by:

$$\begin{aligned} \text{concentration} &= \frac{\text{sample peak height}}{\text{standard peak height}} \times \frac{\text{concentration of standard}}{[\text{sample}]} \\ \text{where} \\ [\text{sample}] &= \frac{\text{original volume of sample}}{\text{final volume of sample}} \\ &= \frac{500 \text{ ml}}{1 \text{ ml}} = 500 \end{aligned}$$

Calculating relative concentrations of possible endrin aldehyde and DDE contaminants present in Sample 2-D, we find both endrin aldehyde and DDE at concentrations of less than 0.1 pg/ μ l, or less than 1 part per billion (ppb). Table 4 summarizes data and calculations for residues found in sample 2D.

	<u>endrin aldehyde</u>		<u>DDE</u>	
	<u>Sample</u>	<u>Standard</u>	<u>Sample</u>	<u>Standard</u>
<u>Retention Time</u> (minutes)	22.33	22.24	23.11	23.15
<u>Common Ions</u> (amu)	246, 316		67, 250, 345	
<u>Peak Height</u>	20000	51000	35500	15000
<u>Concentration</u>	<0.1pg/ μ l	0.1ng/ μ l	<0.1pg/ μ l	0.1ng/ μ l
<u>Parts per billion</u>	<1ppb	100ppb	<1ppb	100ppb

Table 4. Pesticide traces found in sample 2-D (Aquatic Park inlet stream)

These concentrations are at a very low level, each less than 1 ppb, with peak heights only 2-3 times the background noise. Such low levels could be considered negligible from an analytical standpoint.

Other Contaminants: The study shows a number of other contaminants present in the waters at Aquatic Park. There are a number of other peaks that I am unable to identify. A major peak which did not coincide with any of my chlorinated pesticide standards was found in nearly every sample. Further investigation of several chromatograms revealed signals showing an ionic pattern in which the ion of 149 amu (atomic mass units) was the predominant peak. The contaminant was identified by reference to a mass spectrum file to be a phthalate ester.

Phthalates are ubiquitous impurities found in the environment, since they are common components of plasticizers (tubing, cap liners, gaskets) and chromatographic column packings (McLafferty, 1980). The two most commercially abundant phthalate ester plasticizers are di-2-ethyl-hexylphthalate (DEHP) and di-n-butylphthalate (DBP). Phthalates have been found complexed with the fulvic acid components of humic substances in soil (Ogner and Schnitzer, 1970, cited in Klaasen et al., 1986) and in both marine and estuarine waters. Fulvic acid apparently mediates the transport of phthalates in soil and water by making it more soluble. DEHP and DBP may also be detrimental to the reproduction of some aquatic organisms at low concentrations. *Daphnia magna* reproduction was decreased by approximately 80 percent by continuous exposure of 30 $\mu\text{g/l}$ (30 ppb) DEHP for up to 21 days. Reproduction in zebra fish and guppies was also decreased by low concentrations of DEHP (Mayers and Sanders, 1973, cited in Klaasen et al., 1986). Though ubiquitous, the lipophilic nature of phthalates are of toxicological concern to certain aquatic populations, and organisms that may be present at Aquatic Park.

In all representative samples (Water Blank, Sample 2-D, Sample 1-C) ion 149 was traced and relative abundance integrated. Concentrations up to 300 ppb were present in the water extracts. This is 10 times the amount seen to have effects in the Mayers and Sanders study. If this amount is actually present in the water at Aquatic Park, and not merely a contaminant resultant from sampling and analysis techniques, it may be possible that the fish in Aquatic Park are subject to reproductive hazards from phthalate contamination. An array of phthalates are present including DBP and DEHP.

Discussion

Residual traces of DDE and endrin aldehyde are present in extracts from Aquatic Park water samples. However, due to questions about the accuracy of the conditions used in my gas chromatographs, even these low levels may be unreliable. For instance, toluene washes show a small degree of carry-over from one run to the next, indicating incomplete washout. Therefore, for the compounds for which I have tested, levels of organochlorine pesticides present in the waters at Aquatic Park can be considered negligible. However, this does not mean greater concentrations of these and other pesticides are not present at Aquatic Park. Further sampling is necessary.

Although chlorinated pesticides are persistent, they are primarily lipid soluble and are more likely to be bound up in the soil or taken up by fish, which are lifetime samplers. If pesticides were present in the sediment or the water at Aquatic Park, their presence would also

be easier to detect by sampling since they would be in higher concentrations. A more accurate study should involve one of these potential sources rather than grab samples of water, a dilute medium which undergoes daily tidal influx.

Phthalate contamination in some samples is almost three times the concentration of the pesticide standards. There are a number of possible sources for the detected phthalates. Either they are present in Aquatic Park in notable concentrations (0.3 ng/ μ l or 300 ppb) or sampling techniques or container top linings could have caused contamination before analysis. Water leaches these materials from plastics, such as plastic bottles and tubing, and phthalates themselves are notorious for contamination of samples. The water extraction sample showed phthalate levels 10-20 times lower than the samples; therefore, it is possible that the detected levels are indeed found in the Aquatic Park water and did not come from sample bottles or faulty techniques. On the other hand, that phthalates were detected at all in the water blank would cast some uncertainty on the levels found. By repeating samplings and analysis, one can easily verify this.

Conclusion

Except for phthalate esters, insignificant quantities of contaminants and no solid evidence of chlorinated compounds were detected in the surface water at Aquatic Park. However, further testing of chemical and pesticide contaminants is recommended. For a further investigation of chlorinated compounds, different media should be sampled, such as sediment or fish. To test for other compounds involving water samples, a greater quantity of water should be collected and concentrated if it is to be used for analysis. This may help avoid problems in the analysis of samples that are very dilute. The analyst should also note that future pesticide studies should involve compounds of greater solubility in water. In addition, a greater number of samples taken from various portions of the lake may help increase validity of the results found. Finally, additional chemical or pesticide standards should be utilized for comparison. A computer-operated priority pollutant library would be a useful tool that would facilitate more rapid checking of compound peaks with GCMS data.

Pollution problems may lie with other physical parameters such as lead from I-80 exhaust deposition, storm drain run-off, or biological parameters such as excess nitrogen or phosphorus that cause excessive algal growth or decay. Some effort to trace contaminant sources would also be beneficial. Major human health hazards from chlorinated pesticides at Aquatic Park are not apparent at the moment. Those that would suffer from unnoticed levels of pesticides in the sediment would be the members of the diverse bird population that frequent

the park. Conclusive danger for these birds cannot, however, be drawn from this study. In the best interest of these birds and also of humans enjoying the park, monitoring and further testing is advised.

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