PERSISTENCE OF SELECTED ORGANOPHOSPHATE AND CARBAMATE INSECTICIDES IN WATERS FROM A COASTAL WATERSHED

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INTRODUCTION
Organophosphate and carbamate insecticides have been widely used in both agricultural and urban settings for insect control. Studies have shown that runoff and volatilization can cause off-site transport of these compounds and subsequent contamination of surface water [1–7]. Many organophosphate and carbamate compounds have acute and chronic toxicity to fish and aquatic invertebrates. For instance, the 50% lethal concentration for Ceriodaphnia dubia, a common indicator species for freshwater invertebrates, is 0.4 μg/L for diazinon and 0.08 μg/L for chlorpyrifos [8,9]. To restore water quality in surface water bodies, a large number of pesticide-related total maximum daily loads are being developed throughout the United States.

The Newport Bay–San Diego Creek watershed located in central Orange County, (California, USA) encompasses 154 square miles and is encircled by mountains on three sides and the Pacific Ocean on the other (Fig. 1). Runoff from the surrounding mountains drains across the Tustin Plain and enters the Upper Newport Bay (UNB) via San Diego Creek (SDC) (Fig. 1). The largest contributor of freshwater to the bay is SDC (95%), which receives water primarily from SDC Reach 2, which drains 49% of the watershed area, and Peter’s Canyon Wash (PCW), which drains 29% of the watershed area. Newport Bay is a highly developed commercial and recreational area, where the water has many beneficial uses for both human activities (e.g., boating and fishing) and wildlife. However, monitoring showed that surface water throughout the watershed was contaminated with various pesticides, including diazinon, chlorpyrifos, and occasionally malathion and carbaryl [5,6]. Pesticide loads to the surface streams in this watershed are believed to derive from runoff of pesticides from urban use, primarily use around structures [10]. The detection of these pesticides prompted the recent adoption of a diazinon total maximum daily load (SDC) and two chlorpyrifos total maximum daily loads (SDC and UNB) in the watershed [6].

The implementation of pesticide total maximum daily loads requires a comprehensive understanding of the fate and transport of pesticides in the target water bodies under relevant environmental conditions. One important variable that affects pesticide behavior in surface water bodies is pesticide persistence in water. This is especially true for organophosphate and carbamate compounds because they are weakly sorbed to sediment and relatively water soluble. Although degradation of organophosphate and carbamate insecticides in water was previously well studied [11–19], it has not been examined within the scope of a watershed. The objectives of this study were to evaluate persistence of diazinon, chlorpyrifos, malathion, and carbaryl in natural waters from different locations within the Upper Newport Bay–San Diego Creek watershed and to identify the deterministic factors. Because the watershed is representative of other coastal watersheds along the west coast of the United States, the information may be useful for understanding and managing pesticide pollution in this and similar watersheds.

MATERIALS AND METHODS

Chemicals
Standards of carbaryl (99.0% purity), diazinon (98.3% purity), malathion (98.6% purity), and chlorpyrifos (99.5% purity) were purchased from Chem Service (West Chester, PA, USA). MethElute used in derivatization of carbaryl was pur-
Surface water samples

Surface water samples were taken from four locations in the Upper Newport Bay–San Diego Creek watershed (Fig. 1). The sampling points included SDC, PCW, San Joaquin Marsh (SJM), and UNB. San Joaquin Marsh is a freshwater wetland along SDC and sections of the marsh currently are being utilized for diversion of flow from SDC for water-quality restoration projects. Upper Newport Bay connects the freshwater streams with the Lower Newport Bay, where many beneficial uses of the bay exist. Therefore, SDC and PCW serve as the main sources of pesticide load to Newport Bay, SJM serves as a mitigation site, and Upper Newport Bay serves as the initial receiving saltwater body. Water samples were collected manually at about 5 cm below the surface by filling 4-L pre-cleaned plastic bottles. All samples were transported to the laboratory within 4 h from the time of sampling and were kept at 4°C in the dark before use. Samples collected from the same site were combined and homogenized manually in a glass tank. A 4-L aliquot was removed for each sampling site and sterilized in an autoclave for 1 h at 121°C under 13 psi. Sterilization treatment was used to remove microbial activity in the water samples.

Solution pH, conductivity, dissolved oxygen, biological oxygen demand, total organic carbon, total suspended solids, and selected anions were determined for each water sample (Table 1). Dissolved oxygen and biological oxygen demand were determined by following standard methods [20]. Dissolved oxygen was measured by titration and biological oxygen demand was determined as the difference in dissolved oxygen before and after 5 d of incubation at 21 ± 1°C in the dark. Total organic carbon was analyzed on a Shimadzu total organic carbon analyzer (Shimadzu, Kyoto, Japan). Total suspended solid content was determined by weighing after filtration through a 0.7-μm glass fiber filter. Analysis of anions was carried out on a Dionex DX-500 ion chromatograph (Dionex, Sunnyvale, CA, USA) with an Ion Pac AS11-HC column (Dionex).

Degradation experiments

Four liters of the sterile or nonsterile water in a precleaned glass bottle was spiked with 40 μl of acetone solution containing 400 μg of diazinon, chlorpyrifos, malathion, or carbaryl and the treated samples were thoroughly mixed. The initial concentration was thus 100 μg/L for each pesticide. Aliquots of 200 ml were transferred to 250-ml glass Erlenmeyer flasks and the flasks were loosely covered with aluminum foil to exclude sunlight. The sample flasks were kept at room temperature (21 ± 1°C) or in an incubator at 10 ± 0.5°C. The above treatments therefore consisted of four variables: water sampling location, biological activity (sterile or nonsterile), type of pesticides, and temperature (10 or 21°C). The sample flasks were checked for water level on a weekly basis from Pierce (Rockford, IL, USA). Solvents and other chemicals were all gas chromatographic or analytical reagent grade.

Table 1. Physical and chemical properties of waters used in the study

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>DO (mg/L)</th>
<th>BOD-5 (mg/L)</th>
<th>TOC (mg/L)</th>
<th>pH</th>
<th>EC (mS/cm)</th>
<th>TSS (mg/L)</th>
<th>Cl− (g/L)</th>
<th>NO3− (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Newport Bay</td>
<td>5</td>
<td>0.7</td>
<td>5.36</td>
<td>7.98</td>
<td>23.4</td>
<td>18.2</td>
<td>10.09</td>
<td>4.4</td>
</tr>
<tr>
<td>San Joaquin Marsh</td>
<td>4.9</td>
<td>0.6</td>
<td>4.46</td>
<td>8.07</td>
<td>2.44</td>
<td>28.6</td>
<td>0.33</td>
<td>41.2</td>
</tr>
<tr>
<td>Peter’s Canyon Wash</td>
<td>5</td>
<td>3.25</td>
<td>10.55</td>
<td>8.86</td>
<td>1.22</td>
<td>30.0</td>
<td>0.35</td>
<td>0.29</td>
</tr>
<tr>
<td>San Diego Creek</td>
<td>4.3</td>
<td>2.0</td>
<td>7.07</td>
<td>8.02</td>
<td>2.44</td>
<td>72.8</td>
<td>0.33</td>
<td>50.9</td>
</tr>
</tbody>
</table>

*DO = dissolved oxygen; BOD-5 = biological oxygen demand with 5 d of incubation; TOC = total organic carbon; EC = electric conductivity; TSS = total suspended solids.
basis and deionized water was added to compensate for water loss.

Triplicate flasks were removed from each treatment after 0, 2, 6, 14, 28, and 56 d of incubation. To facilitate pesticide extraction, 10 g of sodium chloride was added to each sample and the solution was quantitatively transferred to a 250-ml separatory funnel. The flask was rinsed with 30 ml of methylene chloride and the solution was transferred to the separatory funnel. The samples in separatory funnels were mixed by shaking for 1 min, and after the methylene chloride phase was collected, the remaining water phase was extracted two additional times with fresh solvents. The solvent phases were combined, dehydrated with 30 g of anhydrous sodium sulfate, and then concentrated to approximately 5 ml on a rotary evaporator at 38°C. Before concentration, 20 μg of tributylphosphate in acetone was added as internal standard for calibration. The volume of the final extract was further reduced under a gentle nitrogen stream to 250 μl for analysis by gas chromatography. The thermally labile nature of carbaryl required an additional step for its analysis [21; http://www.thermo.com/]. The final extract was mixed with 50 μl of MethElute: methanol (1:1, v/v) and an aliquot was injected into the gas chromatograph for quantification of the carbaryl derivative.

Analysis

Pesticide analysis was carried out on an Agilent 6890N gas chromatograph equipped with a split–splitless inlet and a 7863 autosampler (Agilent, Wilmington, DE, USA). Detection was conducted by using a nitrogen phosphorus detector. Separation was achieved on a HP-5MS capillary column (30 m × 0.25-mm inner diameter × 0.25-μm film thickness) with a flow rate of 1.0 ml/min (helium). The inlet temperature was 250°C and detector temperature was 300°C. The detector gas consisted of hydrogen at 3 ml/min, air at 60 ml/min, and nitrogen at 10 ml/min. The oven temperature was initially set at 80°C (1.0 min), ramped to 150°C at 20°C/min, then to 230°C at 6°C/min, and finally to 275°C at 30°C/min. The method detection limits calculated as the standard deviation of triplicate analyses with a 95% confidence level were 0.01 μg/L for malathion and 0.1 μg/L for diazinon, chlorpyrifos, and carbaryl. The method recoveries were 104.4 ± 1.5% for diazinon, 105.5 ± 1.2% for chlorpyrifos, 107.8 ± 5.4% for malathion, and 110.0 ± 14.5% for carbaryl.

RESULTS AND DISCUSSION

Pesticide concentrations measured after different intervals of incubation were fitted to first-order kinetics to estimate the rate constant k (d⁻¹) and half-life \( t_{1/2} \) (d). Pesticide persistence was evaluated by using the estimated k and \( t_{1/2} \) values with respect to sampling location within the watershed, contribution of microbial transformations, type of pesticides, and temperature. Differences were tested statistically at the 95% confidence interval whenever comparisons were made between treatments.

Sampling location

Water samples collected from the different locations within the watershed had different physicochemical properties (Table 1). The water from UNB differed from the other waters with respect to its high chloride content and high electric conductivity, which are characteristic of seawater (Table 1). Water from UNB and SJM had significantly lower biochemical oxygen demand and total organic carbon content than water from PCW or SDC, suggesting that the lack of flow and other conditions in UNB and SJM facilitated removal of suspended solids and organic matter. Water from both SDC and SJM also contained substantially higher levels of nitrate than that from PCW and UNB. The pH for water from PCW (pH 8.86) was substantially higher than that of the other waters (pH 8.0; Table 1).

The different characteristics of waters from the different locations were expected to affect pesticide behavior in water. At 21°C, both malathion and carbaryl were rapidly degraded in all water samples (\( t_{1/2} \leq 2.2 \) d), and the degradation in water from PCW was so fast that the pesticides became nondetectable 2 d after the treatment, which prevented calculation of k from regression (Table 2). However, persistence of diazinon or chlorpyrifos was consistently longer in UNB and PCW than in SDC or SJM (Table 2). The estimated \( t_{1/2} \) for diazinon in UNB (54.5 d) was 3.9 times that in PCW and approximately 8.5 times that in SDC or SJM (Table 2). The persistence of diazinon increased in the order SDC ≈ SJM < PCW < UNB, and the difference was significant at \( \alpha = 0.05 \). Similar trends were observed for chlorpyrifos, where \( t_{1/2} \) increased in the order SDC ≈ SJM < PCW < UNB (Table 2). At 10°C, slower degradation of malathion and carbaryl allowed estimation of \( t_{1/2} \) for all water samples through regression (Table 2). Persistence of both malathion and carbaryl followed a similar trend, with very rapid degradation in PCW, but slower degradation in UNB (Table 2). The persistence increased in the order PCW < SDC ≈ SJM < UNB and the difference was significant at \( \alpha = 0.05 \). A slightly different trend was observed for diazinon and chlorpyrifos at 10°C. Although the longest persistence occurred in UNB for both diazinon and chlorpyrifos, \( t_{1/2} \) in PCW became statistically similar to that in SDC or SJM, and \( t_{1/2} \) increased in the order SDC ≈ PCW ≈ SJM < UNB (Table 2).

Organophosphate and carbamate compounds are known to degrade via both biotic and abiotic pathways in water and abiotic transformations may include chemical hydrolysis and photocatalytic reactions [16–18,22,23]. Photolysis of pesticides was suppressed in this study by the experimental conditions used. No apparent correlation was found between diazinon or chlorpyrifos persistence and pH, because the \( t_{1/2} \) in
PCW (pH 8.86) was similar or even longer than that in SDC or SJM (~pH 8.0). However, the high pH in PCW likely contributed to the enhanced degradation of malathion and carbaryl in this water and the effect was more discernible at 10°C because of the overall slower degradation (Table 2). The greatest effect of sampling location was the significantly slower degradation of diazinon and chlorpyrifos in UNB than in the other waters, which may be attributable to the seawater properties of UNB. It is likely that the high osmotic potential and low organic matter and nitrate concentrations of UNB inhibited microbial transformations of these pesticides. However, similar inhibition did not occur with malathion or carbaryl, which suggests that these compounds were either degraded abiotically or by microorganisms that were present in both seawater and freshwater.

Very few studies have been reported in which degradation of organophosphate and carbamate compounds was compared between freshwater and seawater. Lartiges and Garrigues [15] measured $t_{1/2}$ of diazinon and other compounds in a river water and a seawater. The $t_{1/2}$ of diazinon was found to be less in seawater (50 d) compared to river water (80 d). However, the seawater (pH 8.1) used in the study had a significantly higher pH than the river water (pH 7.3), which likely contributed to the increased degradation in seawater. Our study suggests that under similar pH conditions, the persistence of certain organophosphate insecticides may be prolonged in seawater. The increased persistence of diazinon and chlorpyrifos in seawater may have important implications. The slow degradation of diazinon and chlorpyrifos, when coupled with their enhanced aquatic toxicity in seawater [6], suggests that the overall eco-toxicological risks of these compounds may be greater for seawater than for freshwater ecosystems. On the other hand, if natural attenuation of diazinon and chlorpyrifos occurs more extensively in freshwater tributaries than in seawater tributaries, then mitigation practices should be implemented before pesticides reach the saltwater body. The relatively short persistence of diazinon and chlorpyrifos in SJM implies that abatement practices such as diversion of flow to wetlands or settling ponds may be effective for reducing pesticide output to downstream water bodies [24].

**Microbial activity**

The role of microorganisms in pesticide degradation was studied by evaluating the rate of pesticide degradation in the absence of microbial activity. Half-lives of malathion and carbaryl remained essentially unchanged in sterile water when compared to the nonsterile water (Table 2). Malathion and carbaryl both were degraded rapidly in sterile water, with $t_{1/2} \leq 2.6$ d. Again, the most rapid degradation occurred in PCW, where the pesticide concentration decreased below the detection limit 2 d after treatment. These results suggest that degradation of malathion and carbaryl in water was primarily abiotic and high pH further enhanced pesticide degradation.

However, sterilization greatly increased persistence of diazinon and chlorpyrifos in freshwater, with an increase in $t_{1/2}$ ranging from 3.9 to 8.5 times for diazinon and 2.4 to 4.0 times for chlorpyrifos (Table 2). Assuming that pesticide dissipation due to abiotic and biotic processes follows first-order kinetics, the overall rate constant $k$ (d$^{-1}$) would be the sum of the rate constant for abiotic degradation ($k_a$ [d$^{-1}$]) and that of biotic degradation ($k_b$ [d$^{-1}$])

$$k = k_a + k_b$$
increased in the order carbaryl < malathion < chlorpyrifos < diazinon (Fig. 3), and this order was observed in almost all water samples at both 10 and 21°C (Tables 2 and 3). In previous studies, great variations also were observed among different organophosphate and carbamate compounds in their persistence in water. Frank et al. [13] reported that the persistence of diazinon and chlorpyrifos in water from Chesapeake Bay also was affected by copper concentration. It is also likely that adsorption to sediment may increase pesticide persistence in surface-water systems under field conditions. Because chlorpyrifos is adsorbed to soil or sediment more strongly than are the other compounds, partitioning to sediment may have a greater impact on the behavior of chlorpyrifos [26]. In a previous study, chlorpyrifos was found to be moderately persistent in sediments under aerobic conditions but very persistent under anaerobic conditions, and its adsorption to sediment also increased with time [27]. Therefore, the frequent detection of chlorpyrifos in surface-water bodies may be partly attributed to its adsorption to sediment and subsequent desorption into the overlying water.

Temperature

The effect of temperature was determined by comparing pesticide degradation rates at 10 and 21°C. Persistence of all compounds significantly increased at 10°C when compared to 21°C. The effect of temperature on pesticide persistence appears to depend on both the type of pesticides and water location. For diazinon, the change in the $t_{1/2}$ ranged from 1.8- to 4.4-fold for the 11°C temperature difference, with the greatest change occurring in SDC (4.1 times) and SJM (4.4 times), and the smallest change in PCW (1.8 times) and UNB (2.3 times). Smaller variations were observed for the other pesticides, with the $t_{1/2}$ of chlorpyrifos varying by 2.4 to 3.4 times, malathion by 3.2 to 3.5 times, and carbaryl by 4.3 to 5.0 times. The greater effect of temperature on diazinon degradation in SDC and SJM may be caused by a higher rate of biodegradation, whereas the limited effect in UNB may be due to a lack of microbial activity in the water.

The measured $k$ values (d$^{-1}$) were further fitted to the linear form of Arrhenius equation

$$\ln k = \ln A - E_a/RT$$

where $E_a$ is activation energy (kJ/mol), $A$ is the pre-exponential factor, $T$ is temperature (K), and $R$ is the gas constant (8.3 J/mol/K). From the estimated $E_a$ values (Table 3), temperature changes will have a greater effect on the persistence of carbaryl than on the other pesticides. For diazinon, temperature will have a much greater influence for SDC and SJM than for PCW or UNB. Significant effects of temperature were observed in other studies during degradation of organophosphate and carbamate insecticides in water. In river water, Frank et al. [13] observed that the $t_{1/2}$ of diazinon increased from 14 d at 21°C to 45 d at 4°C. In a different study, the $t_{1/2}$ of diazinon, malathion, and carbaryl increased by many times when the temperature was decreased from 22 to 6°C [15]. Because water temperature generally varies as a function of location and seasonality, temperature dependence should be considered when predicting the fate and transport of pesticides in a watershed. For watersheds along the west coast of the United States, storm-water runoff typically occurs in the winter months when the water temperature is typically low. Water temperature also is usually lower in coastal tributaries than in inland streams. Therefore, variations in temperature may cause spatial and

![Graph](image)

Fig. 3. Degradation of diazinon, chlorpyrifos, malathion, and carbaryl in surface waters at 21°C. (A) water from San Diego Creek and (B) water from Upper Newport Bay (California, USA).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>SDC</th>
<th>PCW</th>
<th>SJM</th>
<th>UNB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diazinon</td>
<td>88.2</td>
<td>36.5</td>
<td>93.5</td>
<td>51.7</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>77.0</td>
<td>56.0</td>
<td>74.2</td>
<td>74.1</td>
</tr>
<tr>
<td>Malathion</td>
<td>75.3</td>
<td>—</td>
<td>73.4</td>
<td>78.0</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>91.3</td>
<td>—</td>
<td>101.2</td>
<td>90.7</td>
</tr>
</tbody>
</table>
temporal effects on pesticide distribution and should be considered in understanding the ecotoxicological effects of these compounds within a watershed.

This study shows that many factors can affect the persistence of organophosphate and carbamate insecticides in surface water. The interaction of these factors may determine the spatial and temporal distribution, and hence ecotoxicological risks, of these compounds on a watershed scale. The deterministic factors may include location, biotic and abiotic characteristics of the water column, temperature, and type of pesticides. It appears that different pesticides are selectively degraded by microorganisms, and variations in water properties as a function of location and temperature can influence pesticide persistence by affecting the role of microbial degradation. From this study, malathion and carbaryl were nonpersistent under most conditions, which suggests that contamination of surface water by these compounds would be transient. In contrast, longer persistence may be expected for diazinon and chlorpyrifos, especially in seawater. Because all pesticides were found to degrade relatively rapidly in freshwater and at warm temperature, in situ mitigation practices, such as freshwater wetlands and holding ponds, may be effective in reducing pesticide load to downstream water bodies.

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REFERENCES


