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Pesticides in Marine Sediments Associated with Golf Course Runoff

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Pesticide and fertilizer contamination of surface and groundwater associated with golf courses has drawn increased public concern. A groundwater monitoring study for pesticides and nitrates associated with golf courses on Cape Cod found 10 of the 17 pesticides analyzed although only one, chlordane, was above the health guidance level (HGL)(Cohen et al., 1990). Since chlordane is not registered for use on golf courses, none of the 12 currently registered turf pesticides targeted in this study were detected at 20% of the HGL. These findings are significant since the sandy soils are highly permeable and the depth to groundwater is relatively shallow. Studies of pesticides and fertilizer runoff from turfgrass show that, even under extreme conditions, that only small amounts of water move from sodded slopes (Watschke, 1990). Degradation and sorption in the turf and dilution in receiving waters resulted in pesticide concentrations below drinking water standards in almost all cases.

Metribuzin (SENCOR $^{(R)}$ and LEXONE$^{(R)}$) is a selective systemic herbicide registered for use on golf courses. High water solubility (1220 mg/L), moderate half-life (30 d) and moderate sorption to soils (K_{oc} = 41) contribute to a large leaching potential and medium surface loss potential (USDA, 1989). Deamination followed by further degradation to water soluble conjugates is the major dissipation mechanism in soils (Royal Society of Chem, 1987)(see Figure 1). Chlorpyrifos (DURSBAN$^{(R)}$) is a non-systemic insecticide also registered for golf course use. Low water solubility (2 mg/L), moderate half-life (30 d) and high sorption to soils (K_{oc} = 6070) yield a small leaching potential and a high surface loss potential (USDA, 1989). In soil, the major degradation pathway is hydrolysis to 3,5,6-trichloro-2-pyridinol (Royal Society of Chem, 1987).

Hawaii is economically dependent upon a tourist industry and the associated golf courses are desirable. The Hawaii State Department of Health (HDOH) has imposed conditions for development of new golf courses that include protection

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of surface and groundwater resources (HDOH, 1990). The state is also concerned about the impact of pesticides on marine resources. This investigation examined marine sediments near golf course drainage ditches on the island of Maui, Hawaii for metribuzin herbicide and metabolites and chlorpyrifos insecticide.

MATERIALS AND METHODS

Soils associated with the sampling sites are the Pulehu and Jaucas series (USDA/SCS, 1972). Pulehu soils developed from alluvium washed from basic igneous rock. These silt loam texture soils have moderate permeability and runoff is slow. Jaucas series are excessively drained, calcareous soils usually found in narrow strips on coastal plains near the ocean. They have a fine sand texture, rapid permeability, and slow runoff. The water erosion hazard of both soils is slight.

Marine sediment samples were collected from several sites off the Ka'anapali coast of Maui, Hawaii. Eleven samples were collected in July 1990 and another eight samples were collected in November of 1990. Sample sites were ditches that drained the upslope areas including the golf course and the sewage treatment plant. Most samples were largely composed of sand although some had large amounts of organic matter. Surface sediments (ca. 200 g ea) were collected by stainless steel auger and stored in polyethylene bags. Samples were refrigerated in the field and frozen in the laboratory until analyzed (less than 2 months).

Analytical standards of metribuzin (97.2%) and chlorpyrifos (99.7%) were obtained from EPA (Research Triangle Park, NC), deaminated metribuzin (DA; 99.6%), diketo metribuzin (DK; 98.7%) and deaminated diketo metribuzin (DADK; 84.8%) were obtained Mobay Chem. Corp. (Kansas City, MO), and chlorpyrifos oxon (98.2%) and 3,5,6-trichloro-2-pyridinol (99.9%) were received from Dow Chem. Co. (Midland, MI). Chlorpyrifos and metabolite standards were prepared in acetone, metribuzin was prepared in toluene and metribuzin metabolite standards were prepared in 20% methanol and toluene.

Sediments were thawed and homogenized by stirring before 25 g subsamples were placed into 300 mL round bottom flasks. Fortification was performed by adding a mixture of standards in 0.25 mL of acetone, stirring, and allowing 1 hour for the acetone to volatilize. Ten mL of methanol and 100 mL of ethyl acetate were added before refluxing for 1 hour. After cooling, the sample was filtered (Whatman #4) and quantitatively transferred to a round bottom flask with 0.25 mL of decyl alcohol. The extract was rotary evaporated (30 °C) until only water and decyl alcohol remained. After drying with 40 g sodium sulfate, the sample was rotary evaporated until only decyl alcohol remained. The sample was made to 2.5 mL with ethyl acetate and ready for gas chromatographic (GC) analysis.

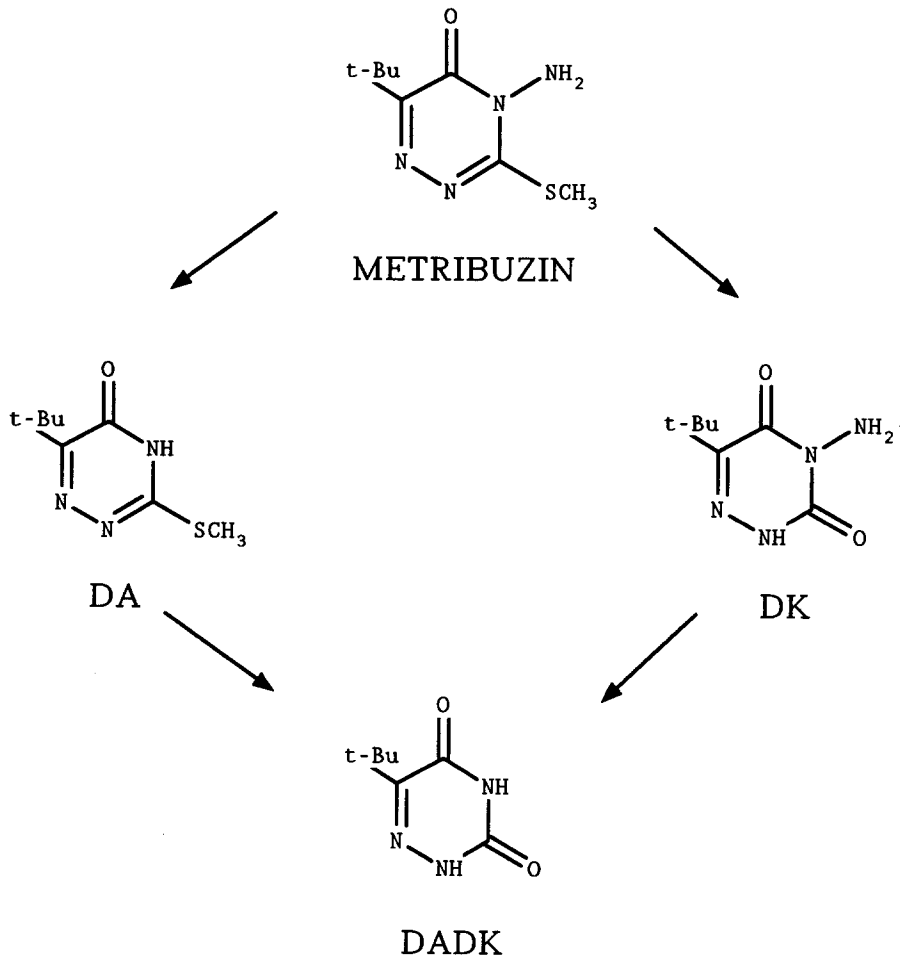

Figure 1. Degradation scheme for metribuzin to the deaminated (DA), diketo (DK) and deaminated diketo (DADK) products.

GC analysis was performed on a Hewlett-Packard 5730 gas chromatograph equipped with a nitrogen-phosphorous detector (NPD). Injector and detector temperatures were 250 °C and 300 °C. A 0.53 mm ID X 15 m (0.5 μm film) Supelco Herbicide wide bore capillary column was used with helium carrier gas (5 mL/min). The column was temperature programmed from 120 °C to 240 °C at 16 °C/min and held for 8 min at 240 °C. Retention times were 3.8 min for DADK, 5.0 min for DK, 6.2 min for DA, 6.4 min for the parent metribuzin, and 6.8 min for chlorpyrifos. Confirmation of chlorpyrifos was performed with a Hewlett-Packard 5890 GC equipped with FPD (250 °C) and splitless injector (250 °C). A 0.53 mm ID X 5 m (2.65 μm film) HP-5 (Hewlett-Packard) wide bore capillary column was used with helium carrier gas (5 mL/min). After 1 min at 120 °C, the column was temperature programmed at 8 °C/min to 240 °C and held for 8 min. Retention time was 13 min for chlorpyrifos. Confirmation also was achieved with GC/mass spectrometry using a Hewlett-Packard 5890 GC and a VG BioTech Trio 2 mass spectrometer (MS). The MS was operated in the electron impact mode (70 eV) and MS source, GC transfer line and GC splitless injector were maintained at 200 °C, 200 °C and 250 °C, respectively. A 0.25 mm ID X 30 m (0.25 μm film) DB-5 capillary column (J&W Scientific) was operated with helium carrier gas (ca. 1 mL/min). After 1 min at 50 °C, the column was temperature programmed at 15 °C/min to 200 °C and held for 5 min. Metribuzin eluted at 14.3 min while chlorpyrifos eluted at 16.2 min.

RESULTS AND DISCUSSION

Metribuzin and its metabolites have been determined in soil and plant tissue by gas chromatography (Balinova, 1978; Jarczyk, 1983) and liquid chromatography (Parker et al., 1988; Norman et al., 1989). Florisil or silica gel column cleanup is often used to remove interferences, but the selectivity of the nitrogen specific GC detector (NPD) can eliminate the need for this cleanup (Jarczyk, 1983).

Gas chromatography with a nitrogen specific detector was chosen for determination of metribuzin, metribuzin metabolites and chlorpyrifos in sediments. The selectivity of the NPD eliminated the need for sample extract cleanup on most sample but interferences were observed in sediments with high organic matter content. We anticipated the need to confirm positive samples with mass spectrometry (MS) and GC/MS was available in our laboratory and had the sensitivity to detect these analytes. Refluxing with a 10:1 mixture of ethyl acetate/methanol yielded good recoveries of all analytes whereas others have used only polar solvents with success on soils (Balinova, 1978; Jarczyk, 1983).

Method detection limits (MDL's) for metribuzin and metabolites was 0.01 μg/g in the sandy sediments while interferences in the high organic matter sediment samples raised the MDL to 0.1 μg/g. Most of the methods described in the literature, including those with cleanup steps, reported MDL's ranging from 0.1 to 0.002 μg/g (Balinova, 1978; Jarczyk, 1983). Recovery of the metribuzin analytes from samples fortified from 0.01 to 0.4 μg/g (n = 12) were acceptable

although the precision range was wide. Metribuzin (98 ± 9) and the DA metabolite (106 ± 13) were within quality assurance guidelines (65 to 135% recovery with ± 15% relative standard deviation) while the DK metabolite (89 ± 29) and DADK metabolite (118 ± 27) were outside the precision guidelines. This is not unusual for recoveries at the MDL and others have experienced poor precision of recoveries for the DADK and DK metabolites in soil (Balinova, 1978). Recoveries of chlorpyrifos (105 ± 7) were acceptable for both accuracy and precision.

The original GC/NPD analysis showed the presence of parent metribuzin in two samples at about 0.2 μg/g. Analysis of these samples by GC/MS did not confirm the presence of metribuzin. Control sediment samples fortified with 0.2 μg/g of metribuzin yielded an MS response similar to standard solutions in the same concentration range. Thus, none of the samples showed the presence of metribuzin or metabolites above the MDL's.

The GC/NPD analysis showed the presence of 1.1 μg/g of chlorpyrifos in one sediment sample near Black Rock. This sample had a high organic matter content. The presence of chlorpyrifos was confirmed by GC/FPD on a different stationary phase and also by GC/MS. The amount of chlorpyrifos injected (ca. 10 ng) was sufficient to obtain positive identification by a standard NBS mass spectral library search. The chlorpyrifos metabolites, chlorpyrifos oxon and 3,5,6-trichloro-2-pyridinol were not detected in these samples (MDL ca. 0.1 μg/g).

Pesticide use records from the associated golf course were not available although the golf course manager stated that chlorpyrifos was not used on this course. Because of the highly variable climatic conditions in Hawaii, there are no overall typical pesticide use patterns. Pesticide use records from two golf courses on the Kona coast of the island of Hawaii show an average herbicide use of 250 lbs a.i. (active ingredient)/acre, average insecticide use of about 550 lbs a.i./acre, and average fungicide use of 60 lbs a.i./acre (Brock and Kam, 1990). These records show high use of metribuzin along with MSMA and glyphosate herbicides as well. Chlorpyrifos was the most widely used insecticide.

Strong sorption of chlorpyrifos to soil organic matter contributes to a high surface loss potential and resulting potential to accumulate in sediments especially by drainage areas. Since chlordane has been banned as a termiticide, Hawaii homes and other buildings are often treated with chlorpyrifos and are treated more often than with chlordane (Brennan, 1990). In 1989, chlorpyrifos represented approximately 2/3 of Hawaii's termiticide use. In 1990, chlorpyrifos use has dropped to about 10% of the total with a corresponding increase in pyrethroid use (Brennan, 1990). Several buildings are in the drainage area where chlorpyrifos was detected.

Although chlorpyrifos and metribuzin have relatively high surface loss potentials, they usually are applied to golf courses in areas with a thick turf thatch. Absorption by the turfgrass, sorption to fixed soils, and degradation in this environment greatly reduce the surface loss potentials. It should be noted that the sediments were sampled during the relatively dry months of this area. A similar study performed during periods of high rainfall could result in significantly different results.

A short reflux followed by solvent evaporation before GC/NPD allowed sensitive determination of chlorpyrifos and metribuzin and metabolites in marine sediments. Selectivity was compromised on samples with high organic matter and a Florisil cleanup step could possibly remove these interferences. Mass spectrometry was necessary to confirm residues in sediments as the element specific detector gave false positives. Monitoring several drainage areas in several locations off-shore of a golf course on two occasions showed only one sample with chlorpyrifos residues. More monitoring near golf courses and better pesticide use records are needed to determine if pesticide leaching and runoff losses to marine ecosystems are significant.

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