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Pesticides in Golf Course Waters Associated with Golf Course Runoff

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Pesticides are widely used in golf courses to maintain the quality of the turfs. These pesticides include insecticides, fungicides, and herbicides. They may contaminate the environment through runoff and leaching, and may bring about adverse effects to nontarget organisms (Kendal et al. 1992; 1993). The adverse effects of golf courses on the environment have caused so much concern in recent years, that a World No-Golf Day has been declared by conservation groups (Allison et al. 1994). Some studies on the behavior of pesticides in golf courses have been reported in the past few years (Smith et al. 1993; Miles et al. 1992. Odanaka et al. 1994). Most of the studies were carried out in North America and Japan. The results may differ considerably under tropical conditions. In Singapore, a tropical country, the rainfall averages 2400 mm annually and distributes fairly evenly throughout the year. The relatively high rainfall level may cause more significant pesticide runoff in golf courses. The residue level of pesticides in golf course waters can be a very useful index for assessing the effect of pesticide runoff to nearby environment. In this work, a survey on pesticide residues in golf course waters (artificial lakes and ponds, and accumulated rain water) in Singapore was carried out. The present paper reports the results of the survey.

MATERIALS AND METHODS

Pesticides of purity higher than 98% were obtained from Supelco or ChemService. Acetonitrile, methanol, and ethyl acetate were HPLC-grade solvents. Dichloromethane was residue-grade reagent. Octadecyl-bonded silica cartridges for solid-phase extraction were obtained from Supelco (Envi-18, 3-mL tubes). A Shimadzu LC-6A liquid chromatograph or a Perkin Elmer binary pump liquid

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chromatograph was used for the analysis.

Ten water samples (2 litres each) were collected from nine golf courses around Singapore during the period of April and May, 1994. Six of the samples were from artificial ponds or lakes in the golf courses, and four were fresh rain water accumulated beside the fairways. They were transported to the laboratory immediately and extracted within 24 hours after sampling.

To obtain more reliable results, both solid-phase extraction and conventional liquid/liquid extraction were used for the enrichment of the water samples.The procedures of the solid-phase extraction have been described elsewhere (Wan et al. 1994a). The procedures of liquid/liquid extraction are as follows: An aliquot of a water sample (500 mL) was extracted with ethyl acetate + dichloromethane (5:l by volume, 3x60 mL) in a separating funnel. Sodium chloride (50 g) was added to water to improve the extraction efficiency. The combined extracts were dried over anhydrous sodium sulfate and concentrated to ca 1 mL using a rotary evaporator. To remove residual ethyl acetate, which would affect subsequent liquid chromatographic analysis, methanol (10 mL) and isobutanol (0.2 mL) were added to the concentrating flask. The liquid was further concentrated to 1 mL.

An UV-vis detector set at 215 nm wavelength was used for the detection. A LC-ABZ column (250 x 4.6 mm, 5 μm) obtained from Supelco was used for the separation. It is silica-based and reverse-phased column embedded with amino groups, and is suitable for analysis of acidic, basic, and neutral compounds. The mobile phase was acetonitrile + pH 2.6 phosphate buffer (47:53 by volume). The limit of determination, defined as five times the baseline noise, varied between 0.005 ng mL^{-1} and 0.2 ng mL^{-1} (Table 1). The development and optimization of this method has been described elsewhere(Wan et al. 199433). A cyano column obtained from Phenomenex (250 x 4.6 mm, 5 μm) was used for confirmation. The mobile phase was acetonitrile+water (30:70 by volume).

Recoveries were determined both with solid-phase extraction and liquid/liquid extraction. Thirty three pesticides were studied. In addition to those registered in Singapore for golf course use, pesticides used in other countries for golf course maintenance were also included, in case that some golf course maintainers in Singapore may also use them for their specific purpose. As it was very difficult to analyze so many compounds simultaneously on one chromatographic column, the pesticides were divided into three groups according to their distribution in the chromatogram, so that all pesticides within a group were well separated from each other. Pond water (500 mL) fortified with one group of the pesticides at 10 ng mL^{-1} concentration was extracted by solid-phase extraction or liquid/liquid extraction following the above described procedures and analyzed by liquid chromatography.

RESULTS AND DISCUSSION

The recoveries of 33 pesticides by the two extraction methods are given in Table 1. Generally speaking, the two methods gave similar recoveries. In solid-phase extraction, the recovery of simazine was above 150%. It could be due to the effects of some impurities or dedradative products of other pesticides with retention time similar to simazine. In liquid/liquid extraction, large amount of organic solvent used for the extraction was concentrated to 1 mL, causing a more complicated background in chromatographic analysis. The background noises sometimes prevented analysis of compounds with retention time shorter than 4 min, such as dichlorvos. In addition to large amount of organic solvents required, emulsification hindering phase separation has also been regarded as a disadvantage of liquid/liquid extraction. In the present analysis of the real samples, emulsification did not create a problem. Solid-phase extraction has the advantages of much less organic solvent required and lower background in chromatographic analysis. However, it also demonstrated a disadvantage over liquid/liquid extraction, in that the cartridge was easily clogged by the particles and humic substances in some real samples, leading to a much slower extraction. The extraction time of a 500-mL real sample was sometimes as long as 12 hours, five times longer than clean water samples. Prefiltration of the water samples could be helpful in overcomeing this problem. However, pesticides carried by the particles might also be lost.

When analyzed by the LC-ABZ column, seven samples gave one or two peaks with similar retention time as the standards. The subsequent confirmation analysis with a cyano column negatively identified most of the peaks. Among the 10 samples collected, only 2 were detected with trace amounts of pesticides. One sample contained pyridalphenthion at 1 ng mL^{-1}. The other contained deverino at 0.1 ng mL^{-1}. The results obtained by solid-phase extraction and liquid/liquid extraction were the same. It can be concluded that the pesticide runoff in golf courses in Singapore is not significant.

Similar survey for pesticide residues in golf courses in the tropical regions has scarcely been reported. Some studies modeling the leaching and runoff of pesticides in golf courses indicate that only

Table 1. Recoveries of pesticides from water at 20 ng mL^{-1} by solid-phase extraction and by conventional liquid/liquid extraction (duplicated results)

Pesticide	Detection limit (ng mL-1)	Recovery (%)	
		Solid-phase extraction	Liquid/liquid extraction
Simazine	0.01	159, 152	87, 70
Isoprocarb	0.02	106, 116	85, 93
Fenobucarb	0.02	103, 107	82, 70
Methyldymeron	0.02	105, 119	92, 76
Devrino	0.01	111, 108	97, 79
Isoprothiolane	0.05	112, 118	88, 101
Mepronil	0.01	111	120, 110
Flutolanil	0.01	105, 118	112, 150
Diazinon*	0.05	<5	50, 25
Thiobencarb	0.02	91, 104	94, 78
Iprodione*	0.02	102, 110	77, 97
Terbutol	0.05	99, 107	88, 72
Isofenphos	0.05	102, 112	89, 83
Pencycuron	0.05	99, 106	99, 82
Butamifos	0.1	111, 105	109, 109
EPN	0.05	80, 93	94, 97
Prowl	0.1	58, 68	91, 76
Dursban	0.2	55, 65	91, 73
Balan	0.1	48, 61	61, 57
Dichlorvos	0.2	4, 8	54, 58
Thiram*	0.01	<5	66, 33
Captan*	0.01	<5	<5
Pyridalphenthion	0.02	89, 96	93, 106
Chloroneb	0.01	89, 87	89, 88
Proamide	0.02	89, 96	95, 93
Chlorothalanil	0.02	83, 81	93, 96
Etridiazole	0.05	53, 21	11, 11
Bensulfite	0.1	105, 104	97, 98
Tolclofos	0.05	78, 79	97, 81
Isoxanthion	0.1	75, 83	79, 75
Carbaryl*	0.005	100, 100	97, 95
alpha-Naphthol**	0.005	80, 92	50, 74
Profenofos*	0.02	96, 100	94, 108

* Registered for golf course use in Singapore; ** A degradation product of carbaryl.

pesticides with relatively high water solubility can be washed away from the turf greens (Odanaka et al. 1994). Pesticides with low water solubility tend to be adsorbed by the turf greens and the soil or degraded on the spot (Miles et al. 1992). The very low residue level of pesticides in the golf course waters in Singapore may be ascribed to the hot and humid climate and strong sunlight, which accelerate the degradation and evaporation of the pesticides.

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