Analytical Determination of Pesticide Metabolites and Carrier Chemicals in Wisconsin Wells

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BACKGROUND/NEED

Concern over groundwater contamination by the products of environmental degradation of agriculturally applied chemicals has begun to match the concern over contamination by the applied chemicals themselves. There is also concern over the effect on groundwater quality of carrier chemicals used in pesticides.

The metabolites of metribuzin have received very little attention as groundwater contaminants. Metribuzin is widely used as a pre- and post-emergent control for grassy and broadleaf weeds in soybeans and potatoes. About 78% of Wisconsin potato crop acreage is treated with metribuzin. Potatoes are commonly grown in the sandy soils of the Lower Wisconsin River Valley and the Central Sands area which are well known for their susceptibility to groundwater pollution by pesticides. Metribuzin has been detected in a number of wells in this area.

Limited research has been conducted on the environmental fate of metribuzin and metabolites in groundwater. Metribuzin is relatively soluble in water, and is not strongly bound to most soils. It is more mobile in light textured soils than is atrazine which is commonly detected in groundwater throughout the state. Monitoring of metribuzin and metabolites in water has been sparse. Although several investigators have reported methods to measure metribuzin metabolites, poor recoveries were obtained. Very little work has been done on the limit of detection for metribuzin and metabolites.

OBJECTIVES

The original purpose of the study was to measure metribuzin, alachlor, atrazine, cyanazine, their metabolites and carrier chemicals used in their formulation in Wisconsin groundwater susceptible to pesticide contamination. The focus of the study was narrowed to improve analytical methods for measuring metribuzin and its metabolites.

METHODS

Samples were collected from Wisconsin Department of Natural Resources monitoring wells using standard sampling procedures. Most of the groundwater sites were known to have metribuzin contamination.

A variety of analytical techniques were evaluated. A technique using solid phase extraction (SPE) and high performance liquid chromatography (HPLC) was optimized to allow measurement of metribuzin and its major metabolites- deaminated metribuzin (DA), diketometribuzin (DK) and deaminated diketometribuzin (DADK).

RESULTS

Metribuzin and metribuzin metabolites were found in all but 2 of the 20 wells sampled. The highest concentration for metribuzin was 10.2 μg/L. Maximum concentrations of DA, DK, and DADK were 1.56, 0.54 and 1.88 μg/L, respectively. The parent herbicide was found in 14 of the wells, while DA, DK and DADK were found in 18, 13 and 16 of the wells, respectively.

A technique utilizing SPE and HPLC, was found to provide the best overall results. The mean recoveries in Madison tap water and distilled water averaged about 111% for metribuzin, 93% for DA, 35% for DK and 63% for DADK. Recoveries from samples spiked in Madison tap water (300 mg/L as $CaCO_3$) and HPLC grade distilled water were essentially the same. Percent recoveries and precision of metribuzin and DA analyses were good. Recoveries of DADK and DK were about 65% and 35% respectively. Overall accuracy and precision were as good as, or better than, reported in the literature. The limit of detection (LOD) determined for the analytes were 0.19, 0.24, 0.14 and 0.28 μg/L for metribuzin, DA, DK and DADK, respectively.

A list of 15 inert carrier chemicals was obtained from Ciba-Geigy. None of the chemicals appeared to be an environmental hazard based on a literature assessment of the chemicals.

DISCUSSION/CONCLUSIONS

Very little data exists on metribuzin and metabolites in natural waters to allow comparison to the results of this study. The SPE/HPLC method described here was found to be useful for measuring metribuzin and metabolites, atrazine and metabolites, alachlor and metabolites and cyanazine and metabolites. The method was precise and recoveries were high for metribuzin and DA, and generally higher than reported in the literature for DADK and DK. Due to low recovery of DK, it can only be considered a qualitative or semi-quantitative test for DK. Similar recoveries from tap water and distilled water, as well as from recovery analyses performed on groundwater collected from the Central Sands and Wisconsin Valley regions, suggests the absence of groundwater interferences.

Recoveries were improved by adding NaCl to the sample prior to extraction. The use of two cartridges in series also improved the extraction efficiency. Another important variable was vacuum pressure. When the pressure was carefully controlled, the precision of the test was improved.

The ratio of parent to metabolites is higher when the total concentration is high. When total concentrations are less than about 2 μg/L, the metabolites comprise most or all of the total metribuzin concentration. Such a pattern suggests that those wells with high parent concentrations may have been influenced by recent field applications of metribuzin.

The limit of detection determined here is substantially lower than reported by the U.S. EPA in their 1990 national survey of pesticides in drinking water wells.

IMPLICATIONS/RECOMMENDATIONS

Due to the ratio of parent to metabolites it would be of interest to try to correlate metribuzin and metabolite ratios with dates of field application of the herbicide. Additionally, the loss of metribuzin compounds during filtration should be investigated although it appears unlikely since metribuzin does not strongly bind to particles especially when acidified prior to filtration.

RELATED PUBLICATIONS

Lawrence, J.R., Eldan M. and Sonzogni, W.C. (1993) Metribuzin and Metabolites in Wisconsin Well Water. Water Research 27:1263-1268.