ABSTRACT

Pesticides and Degradates (including Triazines) in Ground Water and Seepage Lakes in a Sand Aquifer: Implications for Persistence and Fate


Significant hydraulic exchange occurs between ground water and lakes on the Lake Wales Ridge (the "Ridge", in this paper), a 1,800-km² region in central Florida that contains more than 200 seepage lakes[4]. The Ridge is particularly vulnerable to leaching of agrichemicals as a result of seasonally high precipitation, extensive citrus agriculture, and highly permeable sandy soils containing minimal organic matter. Pesticide concentrations in ground water and lake samples on the Ridge are elevated compared to concentrations in ground water and streams in agricultural areas nationally in the United States, confirming this vulnerability. Nitrate concentrations are also elevated in the region where maximum nitrate (as N) concentrations ranged from 12 to 71 mg/L, among sampled wells and from 1.0 to 4.7 mg/l among most of the sampled lakes.

Sampling of eight Ridge lakes (surface area: 2 to 159 hectares) and ground water from 31 wells tapping the surficial aquifer (median depth to water table: 11 meters) yielded detections of 23 pesticides or degradates, some of which also occur relatively frequently in urban/suburban waters and in municipal water supplies nationally. Concentrations of simazine, norflurazon, diuron, and aldicarb, and their degradates are indicative of pesticide transport and degradation processes in Ridge ground water and lakes. Triazine pesticide degradates analyzed in the study included deisopropylatrazine (DIA; CEAT5), didealkylatrazine (DDA; CAAT5), deethylatrazine (DEA; CIAT5), deethylhydroxyatrazine (DEHA; OIAT5), deisopropylhydroxyatrazine (DIHA; OEAT5), hydroxyatrazine (HA; OIET5), and hydroxysimazine (HS; OEET5), with DIA, DDA, DEA, DEHA, HA, and HS detected in water samples. Simazine is the principal parent triazine pesticide; atrazine is not applied in Florida's citrus areas. Concentrations of pesticides and degradates were typically lower in samples from lakes compared to ground water, often by an order of magnitude or more. This pattern likely reflects chemical degradation and dilution as ground water moves through the subsurface into the lakes and the increased opportunity for biogeochemical degradation (including photolysis), sorption, and dilution of pesticides within the lakes compared to the ground-water system. Also, the ratios of pesticide degradate-to-parent concentrations typically were greater in lakes than in ground water, consistent with degradation along ground-water flow paths to the lakes and with further chemical breakdown within the lakes. Based on limited sampling in four study lakes, differences in pesticide and degradate concentrations between shallow and deep zones of the lake water column were notable only for norflurazon and its degradate. Norflurazon and demethyl norflurazon concentrations and parent-degradate ratios indicated more rapid degradation of norflurazon in shallow zones (1.5-meter sample depth) compared to deep zones near lake bottoms (6- to 14-meters), likely attributable in part to photodegradation by sunlight in these clear-water lakes (Secchi depths: 3.8 to 6.4 meters). Quarterly samples indicated that norflurazon concentrations were lowest during summer in nearly all sampled lakes. Detections of 20 pesticides or degradates in the lakes, including 12 compounds exceeding the 0.06-µg/l common reporting level and 11 compounds detected in more than half of the sampled lakes, indicate their persistence in the region's ground-water / lake systems and suggest relatively rapid ground-water transit times.

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[4] Lakes which are fed predominantly by ground-water inflow as opposed to surface-water inflow.
Pesticides & Degradates (including triazines) in Groundwater & Seepage Lakes in a Sand Aquifer: Implications for Persistence and Fate

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Summary

Current-use pesticides, some of which are known or suspected endocrine disruptors, are among the more frequently detected emerging contaminants in drinking-water sources. Groundwater & lakes in the citrus area of central Florida, a region particularly susceptible to pesticide leaching, provide a field reference of pesticide occurrence for ecosystem assessments, as well as insight into chemical mixtures & concentration changes that occur with transport of parent & degrade pesticides within a closely linked groundwater - surface water system. Sampling of the lakes & groundwater (surficial aquifer) during 1999-2008 yielded detections of 23 pesticides & degradates; some of which, in addition to agricultural areas, have been detected nationally in urban streams & municipal water supplies. The most frequently detected pesticides were norflurazon, bromacil, simazine, diuron, & aldicarb. Six triazine pesticide degradates were detected including DIA, CDIA, DIA, OHIA, hydroxytriazine, & hydroxynicotazine. Simazine is the primary parent triazine pesticide applied in the region.

Concentrations of pesticides & degradates were typically much lower in the lakes compared to groundwater. This pattern likely reflects chemical degradation & dilution as groundwater moves through the subsurface into the lakes, & increased opportunity for biocatalytic degradation, sorption, & dilution of pesticides within the lakes & the groundwater system. Spatial & temporal variability of parent-degrade concentrations within the groundwater - lake system provide further insights into pesticide transport & fate in this region.

Introduction

• This study was one of the first nationally to sample pesticides in small- to medium-sized lakes (<500 ha) to evaluate long-term seasonal changes in pesticides in groundwater regionally, & to analyze for hydroxytriazine.

• The lakes are typically shallow lakes with no surface water inflows.

• Citrus pesticide usage is high compared to other agricultural classes. It includes herbicides, insecticides, & fungicides; the long growing season includes multiple applications per year in this region.

Sampling

• Groundwater was generally sampled at depths near (~1 m) below the water table. Lake samples were collected near lake center at a depth of 1.5 m, with some samples evaluating changes in concentrations with lake depth.

• The lake study evaluated additional pesticides & lower reporting limits compared to the groundwater study.

• Pesticide samples of groundwater were analyzed by F. Dept. of Agric. Lab; Lake samples were analyzed by USGS labs.

Study Description

<table>
<thead>
<tr>
<th>Study Description</th>
<th>Groundwater</th>
<th>Lakes</th>
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<tr>
<td>Monitoring Site</td>
<td>Wells (1), Lake (1)</td>
<td>Wells (5), Lake (1)</td>
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<td>Sampling Frequency</td>
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<td>Weekly (groundwater), Monthly (lake)</td>
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<td>1989-2005</td>
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<tr>
<td>Lake Sampling</td>
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<td>1999-2003</td>
</tr>
</tbody>
</table>

[For additional information: http://es.er.usgs.gov/lake_Wake_Ridge/index.html]

Sampling

The Lakes are ground water-fed, & water flows through the lakes laterally & vertically into the groundwater system. Groundwater monitoring focused on the surficial aquifer system.

Results

Concentrations of norflurazon plus DM norflurazon generally were higher in groundwater than lakes, & ratios of degradate-to-parent concentrations in lakes vs groundwater reflects the influence of factors such as dilution & biocatalytic breakdown processes as water moves through the subsurface & into the lakes.

• The occurrence of pesticides & their degradates in the lakes indicates their propensity to persist over time in both groundwater & surface waters in this region, & often years after usage has terminated (e.g. bromacil).

• The typical lower concentrations of pesticides in lakes & higher ratio of degrade-to-parent concentrations in lakes vs groundwater reflect the influence of factors such as dilution & biocatalytic breakdown processes as water moves through the subsurface & into the lakes.

• Documentation of pesticide mixtures & measurement of pesticide cooccurrences are important for not only for assessing risks to human health & aquatic life, but also for understanding pesticide transport & fate.

• Pesticide concentrations in groundwater & lakes exhibited large spatial variability, in spite of relatively uniform surrounding landscape (citrus), soil properties, & agri-cultural practices. Groundwater flowpaths, additional in-lake sampling, & local-scale data on agricultural usage is needed to better understand the relative influence of factors controlling spatial variability & temporal patterns in concentrations.

Acknowledgements

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