Poster Presented at the "2ND International Conference on the Occurrence, Fate, Effects, and Analysis of Emerging Contaminants in the Environment", August 4-7, 2009, Ft. Collins, CO.

Poster Title: "*Pesticides and Degradates (including Triazines) in Ground Water and Seepage Lakes in a Sand Aquifer: Implications for Persistence and Fate", By Choquette, Kraft, Daiker, Kroening, Lucas, Meyer, Schroeder, and Hicks.*

ABSTRACT

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

Anne F. Choquette[1], U.S. Geological Survey, Carol L. Kraft, Southwest Florida Water Management District, Davis H. Daiker, Florida Department of Agriculture, Sharon E. Kroening[2], U.S. Geological Survey, Patricia A. Lucas, Florida Department of Agriculture, Michael T. Meyer, U.S. Geological Survey, Michael P. Schroeder[3], U.S. Geological Survey, and Richard W. Hicks, Florida Department of Environmental Protection

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; CEAT[5]), didealkylatrazine (DDA; CAAT[5]), deethylatrazine (DEA; CIAT[5]), deethylhydroxyatrazine (DEHA; OIAT[5]), deisopropylhydroxyatrazine (DIHA; OEAT[5]), hydroxyatrazine (HA; OIET[5]), and hydroxysimazine (HS; OEET[5]), with DIA, DDA, DEA, DIHA, HS, and HA 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.

[1] USGS, 640 Grassmere Park Dr., Nashville, TN. 37211, tele. 615.837-4774, email: achoq@usgs.gov.

[2] Current affiliation: Minnesota Pollution Control Agency, St. Paul, MN.

[3] Retired.

[4] Lakes which are fed predominantly by ground-water inflow as opposed to surface-water inflow.

[5] Refers to nomenclature recommended by the International Union of Pure and Applied Chemistry (IUPAC), at http://www.acdlabs.com/iupac/nomenclature/ .

Pesticides & Degradates (including triazines) in Groundwater & Seepage Lakes in a Sand Aquifer: Implications for Persistence and Fate

Anne F. Choquette[1], C.L. Kraft[2], D.H. Daiker[3], S.E. Kroening[1], P.A. Lucas[3], M.T. Meyer[1], M.P. Schroeder[1], and R.W. Hicks[4]

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 ecorisk assessments, as well as insight into chemical mixes & concentration changes that occur with transport of parent & degradate pesticides within a closely linked groundwater – surface water system.

Sampling of the lakes & groundwater (surficial aquifer) between 1999-2008 yielded detections of 23 pesticides & degradates–some of which, in addition to agricultural areas, have been detected nationally in urban streams & in municipal water supplies. The most frequently detected pesticides were norflurazon, bromacil, simazine, diuron, & aldicarb, &/or their degradates. Six triazine pesticide degradates were detected including DIA, DDA, DEA, DIHA, hydroxysimazine, & hydroxyatrazine. Simazine is the primary parent triazine pesticide applied in the region.

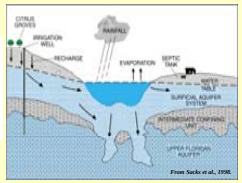
Concentrations of pesticides & degradates were typically much lower in the lakes compared to groundwater. This pattern likely reflects chemical degradation & dilution as groundwater moves through the subsurface into the lakes, & increased opportunity for biogeochemical degradation, sorption, & dilution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

[For additional information: http://fisc.er.usgs.gov/Lake_Wales_Ridge/index.html]

Introduction

- This study was one of the first nationally to sample pesticides in small- to medium-sized lakes (< 200 ha); to evaluate long-term seasonal changes in pesticides in groundwater regionally; & to analyze for hydroxysimazine.
- The lakes are typically seepage lakes with no surface-water inflows.
- Citrus pesticide usage is high compared to other agricultural classes, & includes herbicides, insecticides, & fungicides; the long growing season includes multiple applications per year in this region.

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



From Sacks et al., 1998.

Sampling

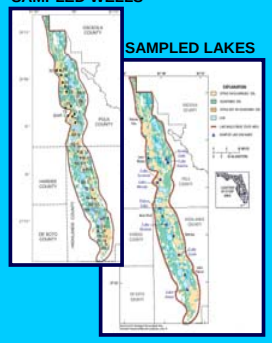
- Groundwater was generally sampled at depths near (< 7 m below) the water table; Lake samples were collected near lake center at a depth of 1.5 m, with some sampling to evaluate changes in concentrations with lake depth.
- The lake study evaluated additional pesticides & lower lab reporting limits, compared to the groundwater study.
- Pesticide samples of groundwater were analyzed by Fl. Dept. of Agric. Lab; Lake samples were analyzed by USGS labs.

Summary of Groundwater and Lake Sampling

Study Description	Groundwater	Lakes
Monitoring Sites	31 wells (in citrus)	7 citrus lakes; 1 control lake
Sampling Period	1999-2008	2003-2005
Sampling Frequency	Quarterly (long-term)	Each Lake Sampled Quarterly for 1 yr
# of Pesticides Analyzed	34	86
Lab Reporting Levels	0.2 to 0.5 µg/L	0.007 to 0.06 µg/L
Site Characteristics	**Depth to Water Table**: 1.2 – 31m **Well-Screen Length**: 3 – 6 m	**Lake Area**: 2 – 158 ha **Max. Depth**: 6 – 20 m

SAMPLED WELLS

SAMPLED LAKES

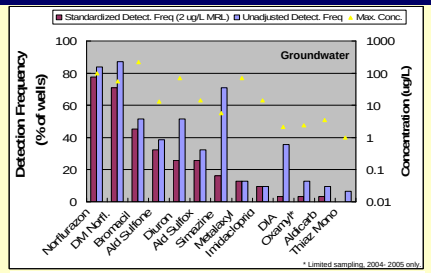


The Lake Wales Ridge, a relict paleoisland, is underlain by marine sands. Citrus covers about 25% of the 1,800-km² study area. Most of the soils of the Ridge have been classified as vulnerable to leaching of agricultural chemicals. About 40% of Florida's citrus is grown in the ridge areas.

Satellite photograph showing density of lakes on the Lake Wales Ridge. More than 200 lakes occur on the Ridge, covering 10% of the area.

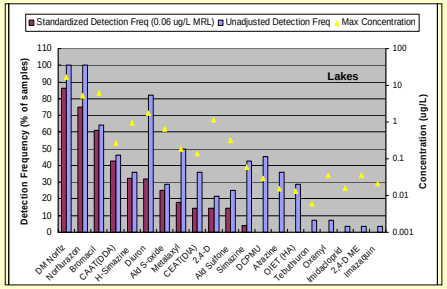
Lake Moody and nearby citrus. The Ridge lakes are typically "seepage lakes" with no surface water inflow or outflow. About 70% of Florida's lakes are seepage lakes.

Results



Detections of pesticides in samples from the 31 network wells, sampled quarterly 1999 to 2005. Graph excludes reconnaissance sampling for triazine degradates in subset of 5 wells (see graph of simazine & degs below). [MRL, minimum reporting level]

***Bromacil usage** was prohibited in Ridge citrus in 1994; but continues to be detected.*



Detections of pesticides in the samples from the 7 lakes surrounded by citrus agriculture. Each lake was sampled quarterly over a period of one year. [MRL, minimum reporting level]

PESTICIDE MIXTURES

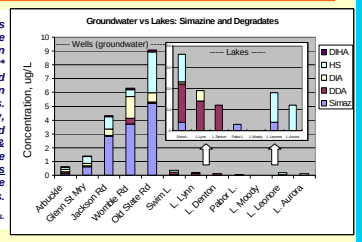
[Note: Lab Reporting Levels (RL) for the lakes were lower than for groundwater]

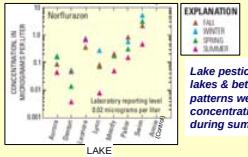
Lakes: **9 to 14 Pesticides & Degs Detected per Lake** (RL ~0.06 µg/L)
[1 to 3 Pesticides & Degs per Lake at RL 0.5 µg/L]

Groundwater: **0 to 13 Pesticides & Degs Detected per Well** (RL ~0.5 µg/L)
[median = 6 Pesticides & Degs per Well]

The simazine plus degradate concentrations in groundwater* exceeded concentrations in the lakes. Proportionally, simazine dominated in groundwater, & the simazine degradates dominated in the lakes.

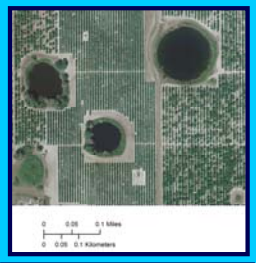
** Reconnaissance of 5 wells.*





Lake pesticide concentrations varied among lakes & between seasons. Consistent seasonal patterns were only evident for norflurazon concentrations which typically were lowest during summer months.

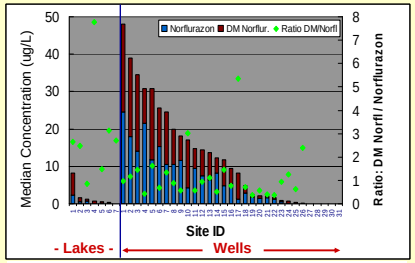
Citrus pesticides include herbicides, insecticides, & fungicides (50, 29, & 21% of total active ingredient, respectively, excluding petroleum distillate), many of which are applied multiple times per year due to the warm climate & long growing season.



Satellite photograph of Swim Lake (top right) & vicinity. Citrus is the dominant agriculture in the region & is commonly in close proximity to the lakes.

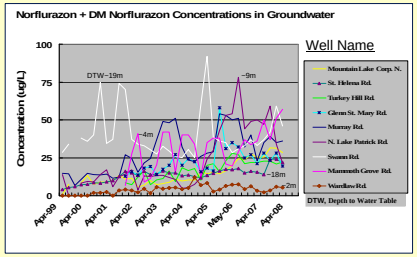
All wells are surrounded by citrus groves, and typically are located on road right-of-ways. Depth to water table ranged from 1.2 to 31 m in the well network (median: 11 m).

The typical soils consist of >97% sand-sized particles, <0.5% organic carbon in profile, with high permeability (>50 cm/hr).



Concentrations of norflurazon plus DM norflurazon generally were higher in groundwater than lakes, & ratios of degradate-to-parent pesticide typically were greater in lakes than groundwater.
[Medians: n=4 samples per lake, n=14 samples per well (Oct2001-Jan2005)]

Reconnaissance sampling with depth in 4 of the lakes indicated higher degradation rates for norflurazon & DM norflurazon in shallow vs deep depths, likely due to photolysis.



Temporal patterns in groundwater pesticide concentrations indicates both short-term (quarterly) changes & long-term trends, & patterns differed by site.

Conclusions

- Elevated pesticide concentrations in the Ridge lakes & groundwater (among the highest observed for these compounds in national networks) are likely related to agchemical usage, high rainfall, well-drained soils with minimal organic matter, low pH of GW, & rapid transport of water into & through the groundwater system. This region differs from many other regions in U.S., where often the pesticide concentrations in surface water are greater than in groundwater.
- The occurrence of pesticides & their degradates in the lakes indicates their propensity to persist over time in both groundwater & surface waters in this region, sometimes years after usage has terminated (e.g. bromacil).
- The typically lower concentrations of pesticides in lakes & higher ratio of degradate-to-parent concentrations in lakes vs groundwater reflects the influence of factors such as dilution & biogeochemicial breakdown processes as water moves through the subsurface & into the lakes.
- Documentation of pesticide mixtures & measurement of pesticide degradates 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 landuse (citrus), soil properties, & aquifer characteristics. Groundwater flowpath studies, additional in-lake sampling, & local-scale data on agchemical usage is needed to better understand the relative influence of factors controlling spatial variability & temporal patterns in concentrations

Acknowledgements

We thank Ed German[1] & the SWFWMD field staff for assistance with lake & groundwater sampling, & Roberta Starks[2], Catherine Wolden[2], James McNeill[4], & Eric DeHaven[2] for administrative support. Lake access was granted by Archbold Biological Research Station & private landowners; permission to drill & access wells was provided by Polk County & Highlands County Highway Departments.

[1] U.S. Geological Survey (Choquette: achoq@usgs.gov); [2] Southwest Florida Water Management District.; [3] FL. Dept. of Agriculture and Consumer Services; [4] Florida Dept. of Environmental Protection.