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Pesticides related to land use in watersheds of the Great Lakes basin

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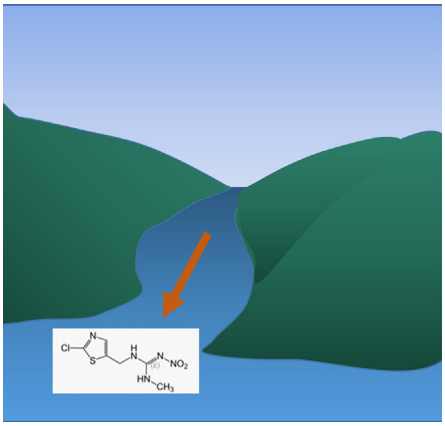
HIGHLIGHTS

- Neonicotinoid insecticides in some watersheds in Ontario, Canada exceeded the Canadian Water Quality Guideline.
- The new generation insecticides, flonicamid and flupyradifurone were detected in some watersheds.
- The pharmaceutical, fluconazole may be transported to watersheds from applications of biosolids to fields.
- A high proportion of watersheds could be classified by patterns of land use and the pesticides in surface waters.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we evaluated the distribution and concentrations of a range of neonicotinoid insecticides (NNIs) and other insecticides, fungicides, biocides and selected herbicides in watersheds that drain into the lower Great Lakes in Ontario, Canada. Polar Organic Chemical Integrative Samplers (POCIS) were deployed in 18 watersheds during late May to late June of 2016. Grab samples were also collected in 7 of these watersheds. There was generally good agreement between the time-weighted average concentrations of pesticides estimated from the POCIS and the concentrations detected in grab samples. The NNIs, thiamethoxam, clothianidin and imidacloprid, were present in several watersheds at concentrations that exceeded the Canadian Water Quality Guideline for imidacloprid of 0.23 μg/L. The new generation insecticides, flonicamid and flupyradifurone were also detected in some watersheds, which is the first report of these pesticides in the peer-reviewed literature. Atrazine, 2,4-D, dicamba, carbendazim, thiophanate methyl and several azole-based fungicides were also widely detected. Discriminant Function Analysis (DFA) indicated that a high proportion (i.e. >80%) of the watersheds could be discriminated from each other on the basis of the pattern of pesticides detected in surface waters, and the proportion of field crops in the watershed.

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1. Introduction

The Laurentian Great Lakes in North America are impacted by a range of chemical contaminants due to direct and indirect inputs from industrial, municipal and agricultural sources (Muir et al., 2009; Blair et al., 2013; Hull et al., 2015). While there is an extensive data base for many current-use pesticides in the Great Lakes basin, there are data gaps related to several classes of pesticides, including current use fungicides, new generation insecticides and biocides. Our previous work showed that fungicides used as pharmaceuticals or as personal care products are present in the Great Lakes basin from discharges of municipal wastewater (Metcalfe et al., 2016). Several herbicides and fungicides have been detected in urban storm water because of their use as biocides in building materials and paints, and we previously reported some of these biocides in urban watersheds in the Great Lakes basin (Metcalfe et al., 2016). Neonicotinoid insecticides (NNIs) are widely used in the Great Lakes Basin in areas where there is intensive agriculture (Struger et al., 2017; Hladik et al., 2018).

The objective of this study was to evaluate the distribution and concentrations of a range of insecticides, fungicides and biocides in 18 watersheds located in southern Ontario, Canada and to determine if the patterns of occurrence of the pesticides could be related to land use parameters. In addition to a high degree of urban development in the region, close to half of all pesticides used in the province for agriculture are applied in southern Ontario (Farm and Food Care Ontario, 2015). This study provides data on the levels of selected fungicides of agricultural and urban origin, biocides of urban origin and NNIs and selected other insecticides in surface waters that discharge into Lake Ontario, Lake Erie, Lake St. Clair and Lake Huron. Also monitored for comparative purposes were selected current use herbicides.

The primary monitoring technique for this study was passive sampling using the Polar Organic Chemical Integrative Sampler (POCIS). To correct for environmental factors that affect the rates of uptake of the target analytes into POCIS deployed in the field, selected POCIS were spiked with Performance Reference Compounds (PRCs) prior to deployment. In seven watersheds, grab samples of water were also collected at the time of POCIS deployments and retrievals. All samples were analyzed by liquid chromatography with tandem mass spectrometry (LC-MS/MS). The data on the distribution and concentrations of these compounds are interpreted with respect to agricultural and urban land uses, and in cases where regulatory limits are in place, the potential for exceedances of current water quality guidelines.

2. Methods and materials

2.1. Sampling

Monitoring was done in 18 watersheds within the Great Lakes basin in the province of Ontario, Canada (Fig. 1). These sites are part of the pesticide monitoring network jointly administered by the Ontario Ministry of the Environment and Climate Change and Ontario Ministry of Agriculture, Food and Rural Affairs. Most of these watersheds are located in areas of intensive agriculture of soybeans, corn and winter wheat. At one site (i.e. Four Mile Creek) located in the Niagara peninsula, there is intensive viniculture and production of fruit crops. Several watersheds are also highly urbanized.

Two POCIS purchased from EST Labs (St. Joseph, MO, USA) were deployed at each of the monitoring sites. A single POCIS spiked with Performance Reference Compounds (PRCs) was also deployed at each site. All three samplers were placed together in a stainless-steel cage for

Fig. 1. Pesticide monitoring sites in watersheds within the lower Great Lakes Basin located in Ontario, Canada. The green lines show the boundaries of the watersheds upstream of the monitoring sites.