Atmospheric Concentrations of Atrazine, Dieldrin, and *trans*-Nonachlor

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Abstract

Considerable effort has been put into investigating the atmospheric transport and deposition of environmentally persistent organochlorines in the Great Lakes region, yet little has been done to investigate those compounds which are currently being applied agriculturally. In this paper, we report on the results for an herbicide which is used currently, atrazine, and compare the results to those obtained for two highly chlorinated compounds, dieldrin and *trans*-nonachlor, which have been banned for a decade or more. Data are presented for the period August 1994 through October 1995. Air samples were taken on the shore of Lake Michigan, at Sleeping Bear Dunes, Michigan. Gas-phase and particle-phase samples were collected for 24 hours every 12 days. Precipitation samples were composited for 28 days. Dieldrin and atrazine were found in all samples. In most cases, dieldrin was the compound found in highest concentration, though atrazine in gas and particle-phases was highest subsequent to agricultural application. *Trans*-nonachlor was found in all gas-phase samples, and in most of the particle and precipitation samples. It was generally present in the lowest concentration of the three compounds. Though atrazine was found predominantly in the precipitation phase, with concentrations of nearly 350 ng/L occurring in the summer, low levels were found in all phases throughout the year. Thus, atmospheric transport and deposition should be considered when analyzing the environmental fate of the triazines.

Introduction

Rapid advances in organic synthesis in the 1940s enabled man to eradicate many disease vectors. Seemingly safe, these organochlorine compounds proved to be chronically detrimental -- to aquatic species, to avian wildlife, and ultimately to man. Typically, monitoring atmospheric concentrations of anthropogenic contaminants has focused on these persistent and ubiquitous organochlorine compounds, many of which have now been banned. In this study, we concentrate on an herbicide which is currently in wide use, atrazine, a mono-chlorinated compound representative of the triazines. For comparison, we also look at two compounds, dieldrin and *trans*-nonachlor, which are representative of organochlorine pesticides which previously enjoyed wide usage. Dieldrin is a persistent, stable insecticide containing 6 chlorines. It was used extensively in both agricultural and household applications, and it is the principle metabolite of another hexachlorinated insecticide, aldrin. These compounds have been banned since the mid-1970s. *Trans*-nonachlor, containing 9 chlorines and highly bioaccumulative, is a major constituent of technical chlordane, a widely used termiticide. Use of chlordane was severely restricted in 1978 and banned entirely in 1988.

Atrazine is moderately water soluble (30 mg/L at 20 °C), and it has a low vapor pressure (0.04 mPa at 20 °C).[1] By contrast, dieldrin and *trans*-nonachlor have lower water solubilities and higher vapor pressures (0.186 mg/L and 0.4 mPa for dieldrin).[1] In terms of usage, atrazine is the major herbicide in the United States. In 1992, nearly 70 million pounds of this triazine were applied, largely across the midwestern Corn Belt.[2]

Given its low vapor pressure, atrazine is not expected to be significantly volatilized.[3] In those geographic regions where it is used, it has been detected in ground water and surface runoff.[3,4] It has also been found in lakes remote from application sites and in precipitation,[5] thus implicating the atmosphere as a transport medium. Atmospheric transport of triazines in Europe has been investigated by several groups.[6-10] Glotfelty *et al.*[11] have looked at atrazine near the Chesapeake Bay. Eisenreich and Strachan[12] presented preliminary estimates for atrazine deposition to the Great Lakes in 1992, but little atmospheric work has been presented since then.

This study looks at the concentrations of *trans*-nonachlor, dieldrin, and atrazine in the gas, particle and precipitation phases in air at Sleeping Bear Dunes, on the northeastern shore of Lake Michigan. Sampling began in August 1994 and continued through October 1995. This work was done as part of the Lake Michigan Mass Balance Study, designed to determine trends in pollution levels.

Experimental Methods

Sampling protocol. Briefly, air samples were collected using high-volume samplers fitted with automatic filter covers to prevent passive loading. Samples were collected every 12 days for a period of 24 hours. Total air flow through the high-volume sampler was approximately 800 m^3. A quartz fiber filter was installed for the collection of particulates, and gas-phase organics were collected on XAD-2 resin. Precipitation was collected cumulatively for 28 day intervals in a wet-only sampler. All precipitation was funneled through a column containing approximately 7 g of XAD-2 resin. Each site was equipped with a 10 m tower for the collection of meteorological data, which were recorded automatically every six seconds using a data-logger and output as mean hourly values.

Analytical. Compounds were removed from the adsorbent material by 24 hour Soxhlet extraction using a 1:1 mixture of acetone and hexane. Silica gel was used to fractionate the concentrated Soxhlet extract, with atrazine eluting in the methanol fraction. Chromatographic separation was performed on a Hewlett Packard (HP) 5890 gas chromatograph (GC), using a 30 m × 250 µm i.d. (d_f= 0.25 µm) DB-5 column (J&W Scientific), and analytes were detected with an HP 5989 mass spectrometer operated in the electron ionization mode with selected ion monitoring. Injection of 1 µL was performed in the splitless mode.

Results and Discussion

All three compounds were present in the gas-phase throughout the year. Dieldrin was generally present in the highest concentration with a mean of 30 pg/m^3. The mean concentration for atrazine was 11 pg/m^3, followed by *trans*-nonachlor with a mean of 5 pg/m^3. Concentrations ranged from 0.2 to 255 pg/m^3 for dieldrin, from 0.4 to 71 pg/m^3 for atrazine, and from 0.2 to 19 pg/m^3 for *trans*-nonachlor. A similar temporal pattern was seen for all three compounds in the gas-phase (see Figure 1). Overall, there was remarkable similarity in the exhibited behavior, with the exception of a large increase in the concentration of dieldrin in May, 1995, and a smaller increase in both dieldrin and atrazine in November, 1994.

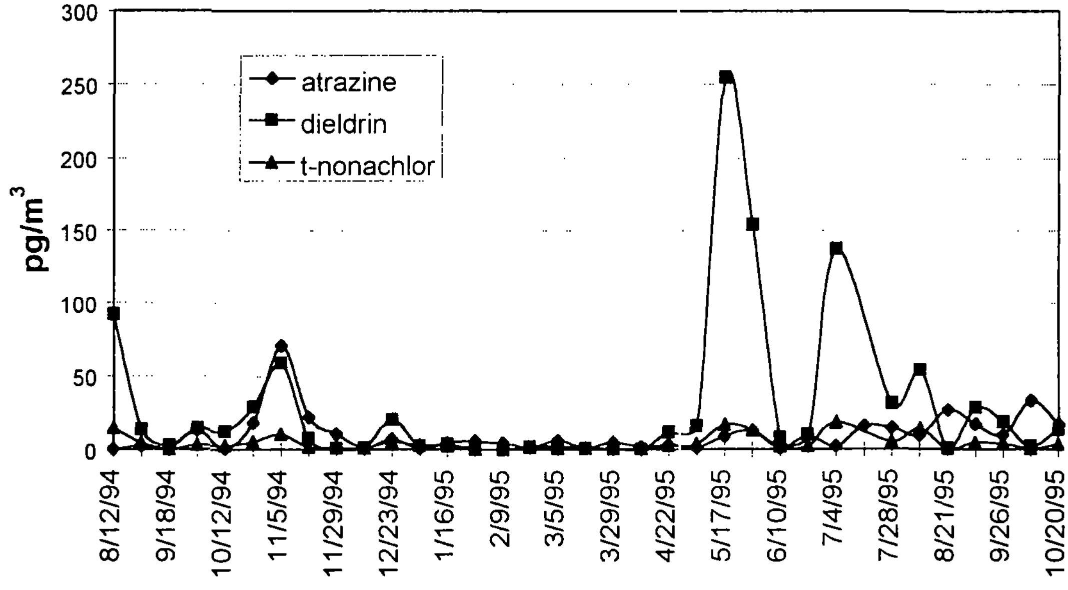

Figure 1. Gas-phase concentrations of three compounds at Sleeping Bear Dunes.

Both dieldrin and atrazine were present in all of the filter and precipitation samples, though *trans*-nonachlor was occasionally undetected. Concentrations for these compounds in the particle phase are shown in Figure 2. Values for dieldrin remained fairly constant, with a range of 0.3 to 10 pg/m^3. For much of the year it was present in the highest concentration of the three compounds. This changed suddenly in April, when particle-phase atrazine concentrations suddenly increased by 1-2 orders of magnitude, giving a range of 0.6 to 90 pg/m^3. Atrazine is used primarily as a pre-emergent broadleaf herbicide for corn, and in the Midwest, corn is generally planted in late April or early May. Thus, increases in atmospheric concentrations correlate with agricultural application of the compound. Values for *trans*-nonachlor in the particle phase remained below 0.6 pg/m^3. The temporal pattern in precipitation (see Figure 3) is similar to that for the particle-phase, with dieldrin and atrazine both present throughout the year, and atrazine increasing substantially in the late spring and early summer, reaching a high of about 350 ng/L. Values for dieldrin ranged from 0.2 to 3 ng/L, and *trans*-nonachlor remained below 1 ng/L

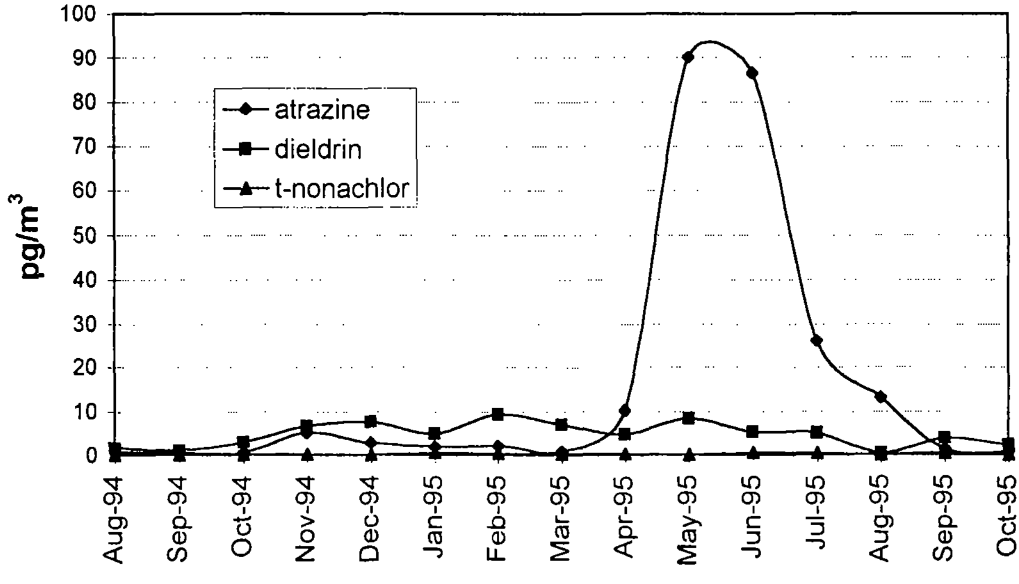

Figure 2. Particle-phase concentrations of three compounds at Sleeping Bear Dunes.

Recent work in our laboratory has determined the atmospheric half-life of *trans*-nonachlor at Sleeping Bear Dunes to be approximately 4 years, and of dieldrin to be about 2 years.[13] This information, combined with the more recent use of chlordane, makes it somewhat surprising that levels of *trans*-nonachlor should remain lower than dieldrin in all atmospheric phases. We did not account for partitioning into other environmental compartments, which obviously would effect the fate of anthropogenic contaminants. In spite of the low levels of *trans*-nonachlor present in the atmosphere, lower than atrazine, this compound has been found in remote regions of the globe.[14] It is remarkable that a pesticide, dieldrin, which has not been in commercial use for 20 years should be present in the atmosphere at levels close to, and at times surpassing, those of a compound in current agricultural use, atrazine. While most of the atrazine applied to soil is degraded or washed into local water systems, some remains available for transport through the atmosphere to remote regions. More research is needed to determine the extent to which this transport occurs.

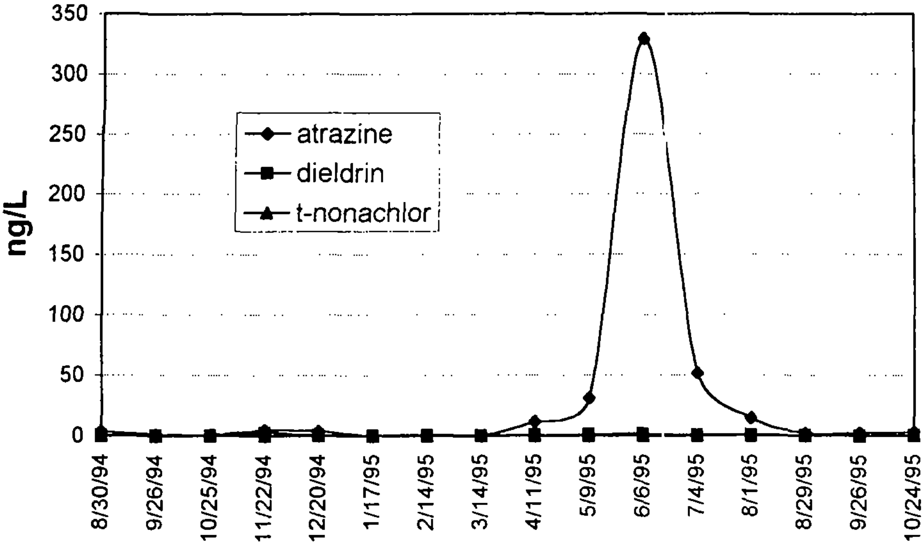

Figure 3. Concentration of three compounds in precipitation at Sleeping Bear Dunes.

Acknowledgments

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