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Endosulfan in the atmosphere of South Florida: Transport to Everglades and Biscayne National Parks

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ABSTRACT

Nutrient inputs from urban encroachment and agricultural activities have been implicated in contributing to the environmental health decline and loss of organism diversity of South Florida ecosystems. Intensive agricultural pesticide use may also challenge these ecosystems. One possible mechanism is pesticide release to the atmosphere after application. The process is enhanced in this region due to the calcareous soils, frequent rainfall, and high humidity and temperatures. This study examined the atmospheric fate of the widely-used insecticide endosulfan. Air samples were collected over a five-year period (2001–2006) at a site within the agricultural community of Homestead, Florida and at sites located in nearby Biscayne and Everglades National Parks (NPs). Mean gas phase air concentrations of α-endosulfan were 17 $\pm$ 19 ng m^{-3} at Homestead, 2.3 $\pm$ 3.6 ng m^{-3} at Everglades NP, and 0.52 $\pm$ 0.69 ng m^{-3} at Biscayne NP. Endosulfan emissions from agricultural areas around Homestead appeared to influence air concentration observations at the NP sites. During an intensive sampling campaign, the highest total endosulfan concentrations at the NP sites were observed on days when air parcels were predicted to move from Homestead towards the sampling locations. The α-endosulfan fraction ($\alpha/(\alpha + \beta)$) was used to examine the contribution of pesticide drift versus volatilization to the overall residue level. The formulated product has an α fraction of approximately 0.7, whereas volatilization is predicted to have an α fraction of $\geq$0.9. The median α- fraction observed during periods of high agricultural activity at Homestead and Everglades NP was 0.84 and 0.88, respectively, and during periods of low agricultural activity the median at Homestead was 0.86, indicating contributions from drift. The median α fraction at Everglades NP was 1.0 during periods of low agricultural activity, while Biscayne NP was 1.0 year round indicating air concentrations are primarily influenced by regional volatilization.

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1. Introduction

The United States Environmental Protection Agency (US EPA) announced in June 2010 its plan to terminate all endosulfan uses due to risks to agricultural workers and to wildlife (US EPA, 2010). In 2011, the United Nations Stockholm Convention on Persistent Organic Pollutants added endosulfan to its list of Persistent Organic Pollutants to be eliminated worldwide (United Nations, 2011). A recent review of the global environmental fate of endosulfan indicates that α-endosulfan is persistent and undergoes long range atmospheric transport (Weber et al., 2010). However, no published studies exist examining the fate of endosulfan in the atmosphere in a region of frequent agricultural use.

One of the areas of the United States where endosulfan has been most heavily used is South Florida (Fig. 1). Monitoring data and ecological risk assessments based on water and biota measurements from canals draining agricultural areas of South Florida have shown that exposure to the insecticide endosulfan may be causing chronic toxic effects on aquatic invertebrates and shellfish (Key et al., 2003; Scott et al., 2002; SFWMD, 2011). In a two-year study

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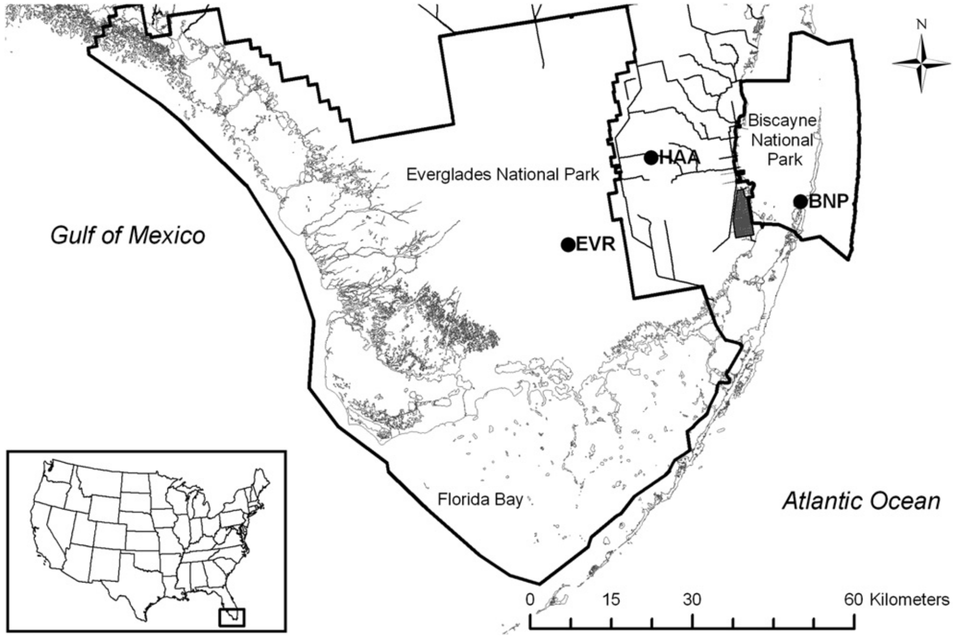


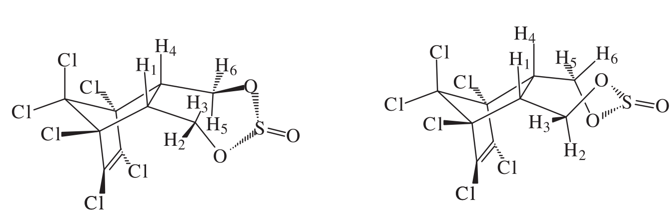
Fig. 1. Map of South Florida with major water bodies, air sampling stations, boundaries of Everglades and Biscayne National Parks, and locations of canal structures.

(2002–2004) of the currently-used pesticides in South Florida, atrazine, endosulfan, metolachlor, chlorpyrifos, and chlorothalonil were the most frequently detected in the canals and in Biscayne Bay. Concentration data were used to calculate an aquatic life hazard potential for the planting period (November) versus the harvest period (March). This analysis indicated that a higher hazard potential occurs from the use of endosulfan and primarily during harvest (Harman-Fetcho et al., 2005). More recently, an aquatic ecological risk assessment was conducted in South Florida (Rand et al., 2010), and the highest risk was found in agricultural areas just east of the Everglades National Park. However, the atmospheric contribution of endosulfan residues to these waterways and the surrounding ecosystem remains unknown.

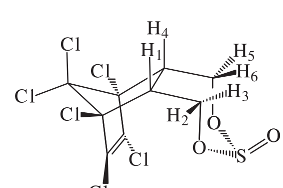
Climate and hydrologic conditions in South Florida are different from other major agricultural centers in the United States, thereby limiting the usefulness of previous pesticide fate research data. These conditions include: calcareous soils, frequent rainfall, high humidity, high temperatures, and a transmissive aquifer system. The soils in South Florida's Dade County range from peat and muck in the northwest to medium and fine sand in the central and southeast (Fish and Stewart, 1991). In some areas soils consist of porous limestone, and cultivated soils represent a thin layer of low moisture, naturally weathered or mechanically crushed limerock (Shinde et al., 2001). The low-water holding capacity of some South Florida soils and high temperatures also necessitate frequent irrigation of crops, which when coupled with the frequent prophylactic application of pesticides, enhances the probability of pesticide release to the atmosphere. The most recent agricultural census conducted by the US Department of Agriculture (USDA) indicated that an average 8000 kg of endosulfan active ingredient are applied to vegetable crops produced in the area annually (USDA, 2011). Therefore the transport processes related to atmospheric transport and deposition may be more important to the overall fate of endosulfan than in other agricultural regions. Further it appears that the associated human and ecological exposure risks will persist at least until the end of 2014 when all endosulfan uses in Florida will be terminated (US EPA, 2011).

Endosulfan is applied to crops as a 7:3 α:β isomeric mixture (Fig. 2). Despite the 7:3 isomeric ratio of the applied product, this ratio has rarely been observed in environmental samples. In addition, isomerization of the symmetrical β isomer to the asymmetrical α isomer has been observed to occur under environmentally relevant conditions (Rice et al., 1997a, 1997b; Schmidt et al., 1997, 2001). Previous studies have found α-endosulfan as the overwhelming predominant isomer in air and near equal amounts of α and β-endosulfan in rain samples (e.g., Burgoynes and Hites, 1993; Chan and Perkins, 1989). Endosulfan sulfate is the most frequently detected degradation product of endosulfan and is likely to be more persistent than the parent compounds (Weber et al., 2010).

Objectives of the present study were to investigate the atmospheric fate of endosulfan in South Florida as this regions ecosystems have undergone extensive detrimental effects and restoration efforts are underway (Perry, 2004; Porter and Meier, 1992; Thayer et al., 1999; WRDA, 2000). The approach was to collect air samples in a heavily agricultural area of South Florida (Homestead) and in two adjacent National Parks (Biscayne and Everglades



α-endosulfan (twist chair forms)



β-endosulfan (symmetrical)

Fig. 2. Molecular structures of α- and β-endosulfan.