

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 $17 \pm 19 \text{ ng m}^{-3}$ at Homestead, $2.3 \pm 3.6 \text{ ng m}^{-3}$ at Everglades NP, and $0.52 \pm 0.69 \text{ ng m}^{-3}$ 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 ≥ 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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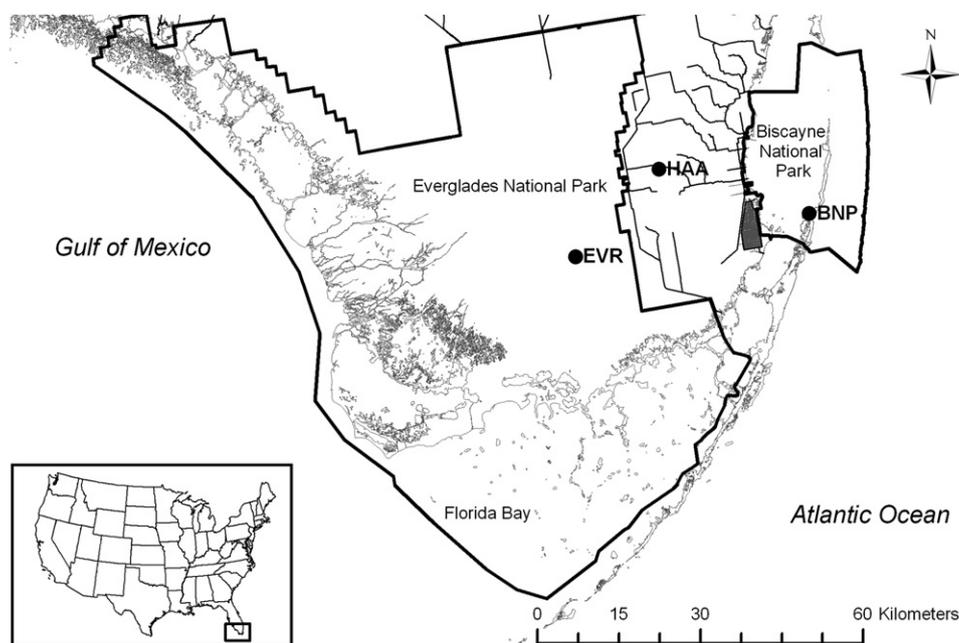


Fig. 1. Map of South Florida with major water bodies, air sampling stations, boundaries of Everglades and Biscayne National Parks, and locations of canal structures.

(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., Burgoyne 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

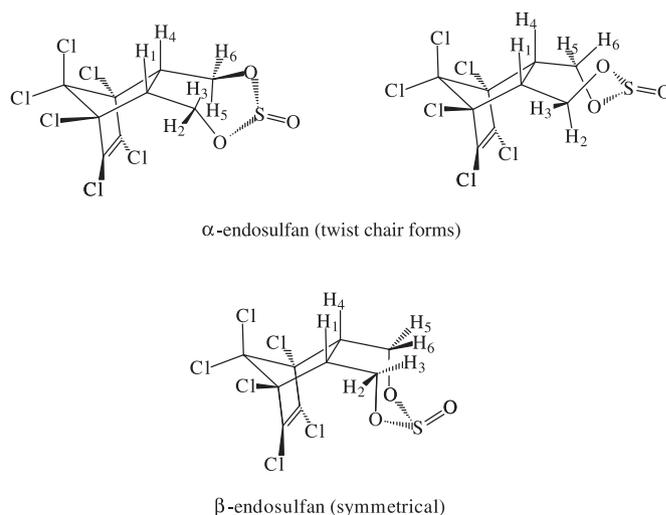


Fig. 2. Molecular structures of α - and β -endosulfan.

National Parks). Utilizing the unique properties of the two endosulfan isomers, the contributions of drift versus volatilization to air concentrations observed in the field are examined.

2. Methods and materials

2.1. Sampling sites and sample collection

Three air sampling sites were established in South Florida: 1) the Homestead agricultural area (HAA), (25.5087750°, –80.4987111°); 2) Everglades National Park (EVR), Daniel Beard Research Center (25.3903806°, –80.6799778°); and 3) Biscayne National Park (BNP), Adams Key, which is a remote island and part of the Emerald Keys (25.3975139°, –80.2346333°) (Fig. 1). EVR is approximately 10 km west south of agricultural fields and is surrounded by grasses, shrubs, and trees. BNP is small island surrounded by the Atlantic Ocean on the east and Biscayne Bay on the west and is more than 20 km east of agricultural activities. Each site was equipped with meteorological equipment to measure various parameters including temperature, rainfall, and wind speed; evapotranspiration was measured at HAA only.

Air samples were collected at HAA from October 2001–May 2006, at EVR from April 2004–August 2006; and at BNP from

October 2002–August 2006. Collection frequency was approximately biweekly from April through September and weekly during the growing season activity (October–March). In addition, near daily samples were collected at all three sites from mid February 23–March 14, 2005.

Air samples (integrated over 24 h, 10 AM–10 AM the next day) were collected simultaneously from all three sites using a high-volume sampler (Model GPNY 1123, Grasby General Metal Works, Village of Cleves, OH, USA). The sampling assembly consisted of a filter (for particulates) and a sorbent for the gaseous fraction. Air was pulled at ca. 0.5 m³ min⁻¹ (volume = 500–700 m³) through a 20.3 × 25.4 cm rectangular glass fiber filter (GFF) (Gelman A/E, Pall Corp., Ann Arbor, MI, USA) followed by two 7.6 × 7.6 cm cylindrical polyurethane foam (PUF) plugs held within a glass sleeve. Field blank samples were collected from each site on a monthly basis, and the flow rate of each sampler was calibrated regularly with a calibration orifice device.

2.2. Sample processing and analysis

PUFs and GFFs were pre-cleaned and prepared for sampling as described by Kuang et al. (2003). Sample PUFs and GFFs were returned to their individual containers after collection and were

Table 1

Summary of gas phase endosulfan air concentration results with statistical comparisons of sites; HAA (2001–2006), EVR (2004–2006), and BNP (2002–2006).

Compound	Site	Sample number ^a (n)	Detections (%)	Minimum ^b (ng m ⁻³)	Maximum (ng m ⁻³)	Median ^b (ng m ⁻³)	Mean ± SD2 (ng m ⁻³)	Statistical comparison ^{b,c}
<i>Comparison of sites including all samples</i>								
<i>α-endosulfan</i>								
	HAA	176	95	0.10	96	10	17 ± 19	A
	EVR	107	98	0.027	16	0.82	2.3 ± 3.6	B
	BNP	154	61	0.020	3.7	0.18	0.52 ± 0.69	C
<i>β-endosulfan</i>								
	HAA		94	0.054	27	1.9	3.7 ± 4.6	a
	EVR		74	0.024	1.9	0.19	0.39 ± 0.48	b
	BNP		28	0.024	0.44	0.12	0.14 ± 0.10	b
<i>Endosulfan sulfate</i>								
	HAA		95	0.011	1.8	0.19	0.32 ± 0.34	a
	EVR		93	0.0043	0.30	0.028	0.044 ± 0.046	b
	BNP		32	0.0029	0.089	0.012	0.017 ± 0.018	c
<i>Comparison of sites during high agricultural activity (October to May – all years)</i>								
<i>α-endosulfan</i>								
	HAA	123	96	0.50	96	15	22 ± 21	A
	EVR	70	99	0.081	16	1.5	3.2 ± 4.1	B
	BNP	117	68	0.020	3.7	0.19	0.57 ± 0.73	C
<i>β-endosulfan</i>								
	HAA		96	0.054	27	3.4	4.7 ± 5.0	a
	EVR		90	0.024	1.9	0.24	0.45 ± 0.52	b
	BNP		33	0.024	0.44	0.12	0.14 ± 0.10	b
<i>Endosulfan sulfate</i>								
	HAA		96	0.011	1.83	0.29	0.40 ± 0.37	a
	EVR		53	0.0040	0.30	0.038	0.054 ± 0.051	b
	BNP		38	0.0029	0.09	0.011	0.017 ± 0.017	c
<i>Comparison of sites during low agricultural activity (June to September – all years)</i>								
<i>α-endosulfan</i>								
	HAA	53	94	0.10	22	3.2	6.0 ± 6.4	a
	EVR	37	97	0.027	4.1	0.36	0.64 ± 0.088	b
	BNP	37	41	0.26	1.2	0.14	0.29 ± 0.35	b
<i>β-endosulfan</i>								
	HAA		91	0.10	5.1	0.67	1.1 ± 1.2	a
	EVR		43	0.047	0.55	0.094	0.16 ± 0.14	b
	BNP		11	0.051	0.13	0.081	0.085 ± 0.034	b
<i>Endosulfan sulfate</i>								
	HAA		94	0.016	0.67	0.091	0.13 ± 0.11	a
	EVR		92	0.0050	0.13	0.020	0.026 ± 0.024	b
	BNP		14	0.0071	0.61	0.014	0.021 ± 0.022	b

^a The number of samples for α-endosulfan is the same for the other two compounds within a comparison group.

^b Values below the limit of quantitation were not included.

^c Statistical analysis was a one-way analysis of variance using a Kruskal–Wallis test. Significant differences between the three sites ($p < 0.05$) are noted for each compound using the letters a, b, and c. Use of capital letters (A, B, C) indicates a high level of significant difference between all three sites ($p < 0.0001$). Sites with the same letter are not significantly different from each other.

kept frozen at $-20\text{ }^{\circ}\text{C}$ until processing. Sample PUFs and GFFs were fortified with diazinon- d_{10} and were extracted separately in batches of 15–20 via Soxhlet extraction with ethyl acetate or dichloromethane, respectively, for 12 h. Extracts were reduced to 5–10 mL *in vacuo* and reduced to 1.0 mL using a gentle stream of high purity (99.9%) nitrogen gas. A laboratory blank and a fortified spike sample were processed with each batch of samples to observe any matrix interference or contamination and to determine extraction efficiency, respectively.

Samples were analyzed for the three endosulfan compounds using an Agilent (Santa Clara, CA, USA) 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC–MS). The system was operated in selected-ion monitoring mode using electron capture negative ion mass spectrometry. The ions 406, 408 and 410; 406, 404, and 408; 386, 384, and 388 were used as quantifying and qualifying ions for α -endosulfan, β -endosulfan and endosulfan sulfate, respectively, with the quantifying ion listed first. The chromatographic conditions were as follows: column, DB-17MS (Agilent J&W, Santa Clara, CA, USA), 30 m, 0.25 mm i.d., 0.25- μm thickness; flow rate through the column, 1.4 mL min^{-1} ; temperature program, 130 $^{\circ}\text{C}$, raised at 6 $^{\circ}\text{C min}^{-1}$ to 205 $^{\circ}\text{C}$, held for 4.5 min, raised at 6 $^{\circ}\text{C min}^{-1}$ to 300 $^{\circ}\text{C}$, and held for 5.5 min; interface, 300 $^{\circ}\text{C}$; quadrupole, 150 $^{\circ}\text{C}$; source, 200 $^{\circ}\text{C}$; injector, 290 $^{\circ}\text{C}$. The ionization gas was ultra high purity methane supplied at 2 mL min^{-1} . Eighty ng of 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB-204) were added to all extracts just before analysis and used as an internal standard. A five-point calibration curve was utilized for sample extract quantitation.

2.3. Quality assurance and quality control

For the gaseous and particulate phase air samples, the method detection limits (MDLs) were determined by spiking 5 ng of each compound onto pre-cleaned PUFs or GFFs (8 replicates) and extracting and processing as above. Standard deviations of measured replicate concentrations from these low-level spike experiments were used to calculate the MDL for each compound according to the US EPA (2004) standard methods. MDLs were 0.002 ng m^{-3} per compound for both gas and particulate phase samples assuming a sample volume of 500 m^3 . Limits of quantitation (LOQ) were based on extraction efficiency and instrument performance and were three times the MDL or 0.006 ng m^{-3} . Laboratory blanks did not contain any peaks which exceeded the LOQ for either PUFs or GFFs. PUF field blank samples did occasionally contain small quantities of α - and β -endosulfan which did exceed the limits of quantitation, especially those collected at the HAA site where air concentrations were highest. Therefore, the average field blank value of 7.7 ng and 8.4 ng for α -endosulfan and β -endosulfan, respectively, was subtracted from the mass detected in all sample extracts prior to calculating air concentration values. An adjusted LOQ value was calculated for α - and β -endosulfan as three times the average field blank value of 0.033 ng m^{-3} and 0.046 ng m^{-3} , respectively, based on a 500 m^3 sample volume. For endosulfan sulfate, PUF field blanks did not contain any peaks which exceeded the LOQ. GFF field blanks did not contain any interfering peaks.

Recovery of the extraction surrogate averaged $107 \pm 38\%$ ($n = 988$ including both front and back PUFs) for PUF and $115 \pm 39\%$ ($n = 198$) for GFF. Only selected GFFs were extracted to assess particulate phase contributions to total air concentrations including samples from HAA and BNP from 2002 to 2004. Recovery of the three endosulfan compounds, α -endosulfan, β -endosulfan and endosulfan sulfate, averaged $98 \pm 23\%$, $95 \pm 21\%$, and $85 \pm 22\%$ ($n = 23$) for PUF, and $117 \pm 32\%$; $128 \pm 31\%$, and $117 \pm 30\%$ for GFF, respectively. Concentration values were not corrected for spike recoveries results.

Gas phase concentration values were calculated from mass of the analytes on the front PUF plug. Breakthrough to the second PUF plug was observed most frequently at the HAA site (14% of samples) where concentrations were the highest, but the percent breakthrough was minimal for the most volatile compound, α -endosulfan, averaging only 2%.

2.4. Dispersion modeling

Dispersion modeling of the South Florida region was carried out using the Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler and Rolph, 2011). The location of the HAA site was used as the emission point and the appropriate

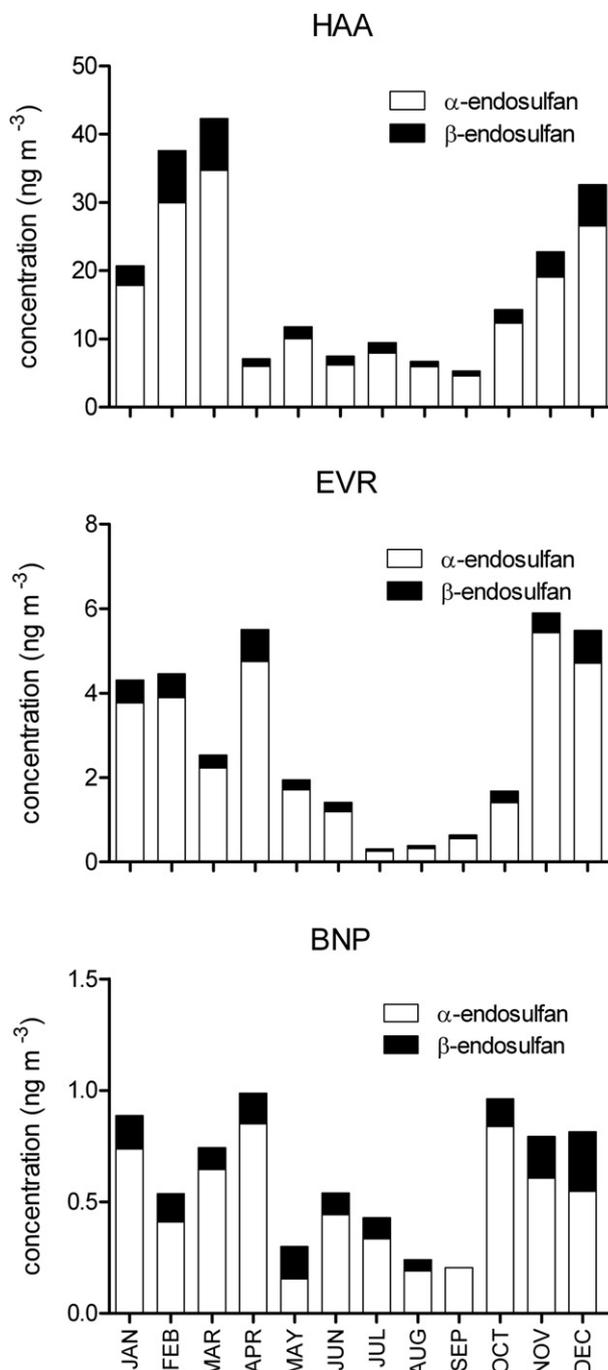


Fig. 3. Average monthly endosulfan concentrations of α - and β -endosulfan at each site.

meteorological inputs were run without regard to absolute concentration (release quality = 1) over a period coinciding with sample collection at EVR and BNP sites on selected dates. Default parameters were used except for the following: no deposition, release top = 10 m, release bottom = 0 m, release duration = 4 h, and model run duration = 4 h.

2.5. Calculations and statistical analysis

Concentration values below the LOQ were not estimated and were not included in any calculations or statistical analyses. Histograms, box-plots, one-way analysis of variance using a Kruskal–Wallis test (a nonparametric test that does not assume Gaussian distribution) and unpaired *t*-tests were conducted using GraphPad Prism® (GraphPad Software, La Jolla, CA, USA).

3. Results and discussion

3.1. Gas phase concentrations and spatial comparison

Air samples were collected at HAA from May 2002 through June 2006, at EVR from April 2004 through June 2006, and at BNP from December 2002 through August 2006 (Fig. 1). The α isomer of endosulfan was detected in nearly all samples (95–98%) at HAA and

EVR and in 61% of the samples at BNP (Table 1). The overall mean gas phase air concentration of α -endosulfan at HAA ($17 \pm 19 \text{ ng m}^{-3}$), which is located within the agricultural production area, was an order of magnitude greater than the mean concentration at EVR ($2.3 \pm 3.6 \text{ ng m}^{-3}$) and two orders of magnitude larger than the mean concentration at BNP ($0.52 \pm 0.69 \text{ ng m}^{-3}$). The differences between median concentrations at each of these sites were highly significant ($p < 0.0001$) reflecting the differences in proximity to pesticide application activities. β -endosulfan and endosulfan sulfate were also frequently detected in the gas phase at HAA (94–95%) (Table 1). β -endosulfan was detected less frequently than endosulfan sulfate at EVR (74% and 93%, respectively). Both compounds were infrequently detected at BNP ($\leq 32\%$). Mean air concentrations of β -endosulfan were approximately 3–5 times lower than α -endosulfan at each station, and endosulfan sulfate averaged 8–11 times lower than β -endosulfan. Therefore, while all three compounds were detected at all three stations, α -endosulfan was the compound detected most often and at the highest concentrations.

The gas phase concentrations of endosulfan observed in South Florida were much greater than the values found at other locations and appear to reflect frequent local usage. For example, in Bloomington, Indiana, α -endosulfan values ranged from 1.3 to 887 pg m^{-3} and β -endosulfan was observed in only one sample

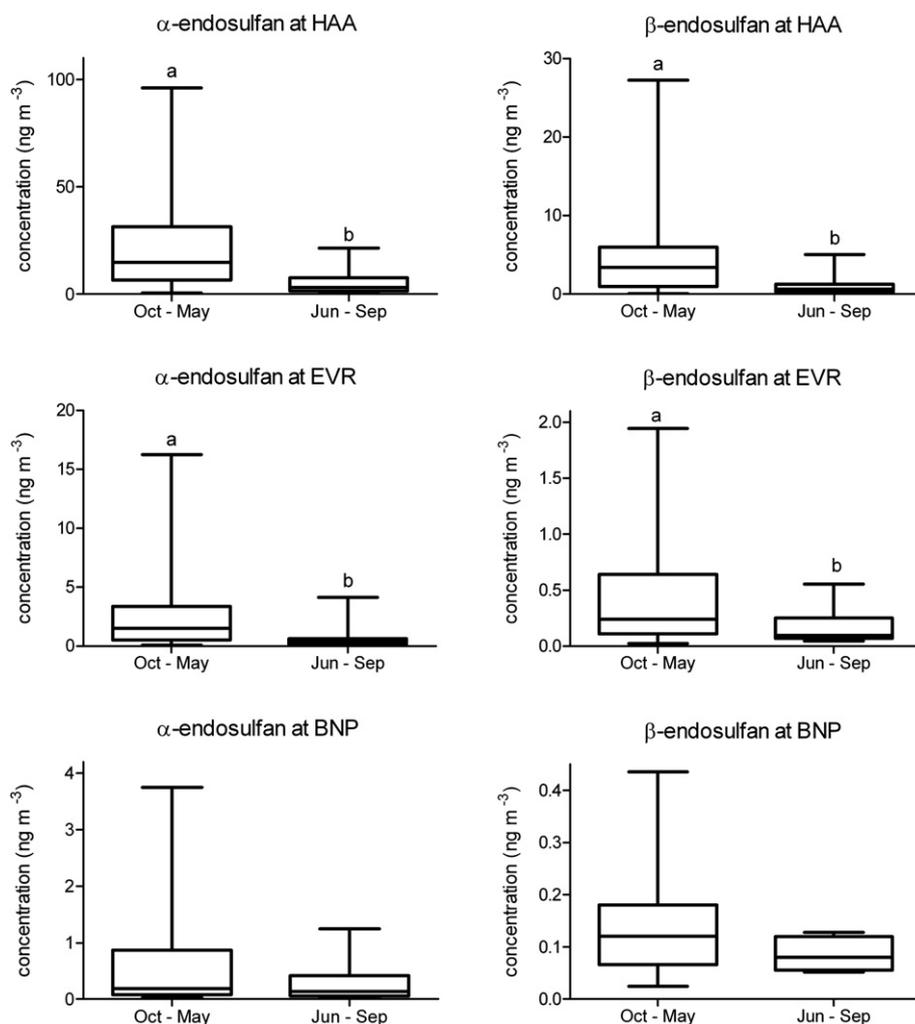


Fig. 4. Box plot of endosulfan isomer concentrations during high and low agricultural activity at each site. Significant differences in average concentrations between high and low agricultural activity at a site for each isomer are noted using letters a and b ($p < 0.05$ using unpaired *t*-test). Whiskers represent minimum and maximum values, the box encloses the interquartile range and the line within the box represents the median.

(Burgoynes and Hites, 1993). The highest values of α -endosulfan were attributed to endosulfan usage in neighboring states (Hafner and Hites, 2003). Further north at Eagle Harbor, Lake Superior, the annual average concentrations of the α - and β -endosulfan were 20 and 1.5 pg m^{-3} , respectively (Tuduri et al., 2006). At the Alert arctic air monitoring station in Canada, the annual arithmetic mean values (1993–2005) ranged from 3.2 to 6.5 pg m^{-3} for α -endosulfan (Hung et al., 2010), and no values were reported for β -endosulfan.

3.2. Effects of agricultural activity

Although some vegetable production in South Florida takes place during the hot, rainy summer months of June to September, most vegetables are planted beginning in October with harvest generally occurring in March through May. Nursery crop production, which is increasing in this region, occurs year round (USDA, 2011). Thus, the highest atmospheric concentrations of endosulfan residues are expected during the winter vegetable growing season, but could also be observed during the summer months.

Average monthly gas phase concentrations were calculated to examine the temporal changes in endosulfan concentrations of each isomer at each site (Fig. 3). In general, lower monthly mean concentrations were observed for each isomer during June to September, while higher monthly mean concentrations of each isomer occurred during fall/winter/spring months. These temporal patterns suggest that air concentrations at all three sites are influenced to some extent by local agricultural activity.

This argument is further strengthened by comparing the average gas phase concentration for each compound at each site for all samples collected during high agricultural activity (October through May) with the average concentration during low agricultural activity (Fig. 4). The average concentrations of α -endosulfan for high versus low agricultural activity periods were significantly different ($p < 0.0001$) at both HAA and EVR. While higher α -endosulfan concentrations were also observed during high agricultural activity at BNP, the average concentration was not significantly different from the average concentration for low agricultural activity. Concentrations of β -endosulfan were also significantly higher during high agricultural activity at both HAA and EVR, but not at BNP.

Average concentrations of each isomer during high and during low agricultural activity were also compared between sites (Table 1). The average concentrations of α -endosulfan at HAA, EVR, and BNP during high agricultural activity were all significantly different from one another ($p < 0.0001$). However, while the average concentration of β -endosulfan at HAA was significantly greater ($p < 0.05$) than the values at BNP and at EVR, the average concentrations at BNP and at EVR were not significantly different from one another. This is likely due to a lower frequency of β -endosulfan detection at BNP and fewer samples were collected overall at EVR. For the low agricultural activity period, the average concentrations of both endosulfan isomers at HAA were significantly greater ($p < 0.05$) than their respective average concentrations at BNP and EVR. Again, the average concentrations at BNP and EVR which were not significantly different from one another. These data also indicate that air concentrations at all three sites are strongly influenced by magnitude of local emissions and proximity to the source and *a priori* by wind direction.

Results of particle phase sample analysis from HAA and BNP in samples collected from 2002 to 2004 revealed differences in the distribution between the gas and particle phases in the source (HAA) and receptor (BNP) region. At HAA α -endosulfan was detected in 60% of samples while β -endosulfan and endosulfan sulfate were detected more frequently at 79 and 80% of samples, respectively ($n = 125$). At BNP, the site most distant from

agricultural production, α -endosulfan was detected in only 3% of samples, and β -endosulfan and endosulfan sulfate were detected in 12% and 6% of samples respectively ($n = 63$).

The overall mean particle phase concentration at HAA for β -endosulfan ($0.28 \pm 0.54 \text{ ng m}^{-3}$) was higher than for α -endosulfan ($0.055 \pm 0.12 \text{ ng m}^{-3}$) reflecting an opposite trend from gas phase concentrations. This observation can be explained by differences between the octanol-air partition coefficients for the two isomers. The log octanol-air partition coefficient ($\log K_{oa}$) for β -endosulfan (9.53) is 10 times greater than for α -endosulfan (8.49) (Shoeb and Harner, 2002). Considering the total gas plus particle phase concentrations for each compound in individual air samples, the average percent particle concentration was $0.54 \pm 1.1\%$ for α -endosulfan, $11 \pm 16\%$ for β -endosulfan (a $10 \times$ greater fraction), and $17 \pm 18\%$ for the less volatile endosulfan sulfate.

A comparison of gas and particle phase concentrations for both isomers and endosulfan sulfate in individual air samples for a representative period in 2002 and 2003 (Fig. 5) indicated that both gas and particle phase concentrations were greater during the period of agricultural activity. Separating results by high and low agricultural activity, the mean particle phase concentrations for samples for both β -endosulfan and endosulfan sulfate were significantly higher during high agricultural activity ($p < 0.05$ based on unpaired two-tailed *t*-test). However, no significant difference

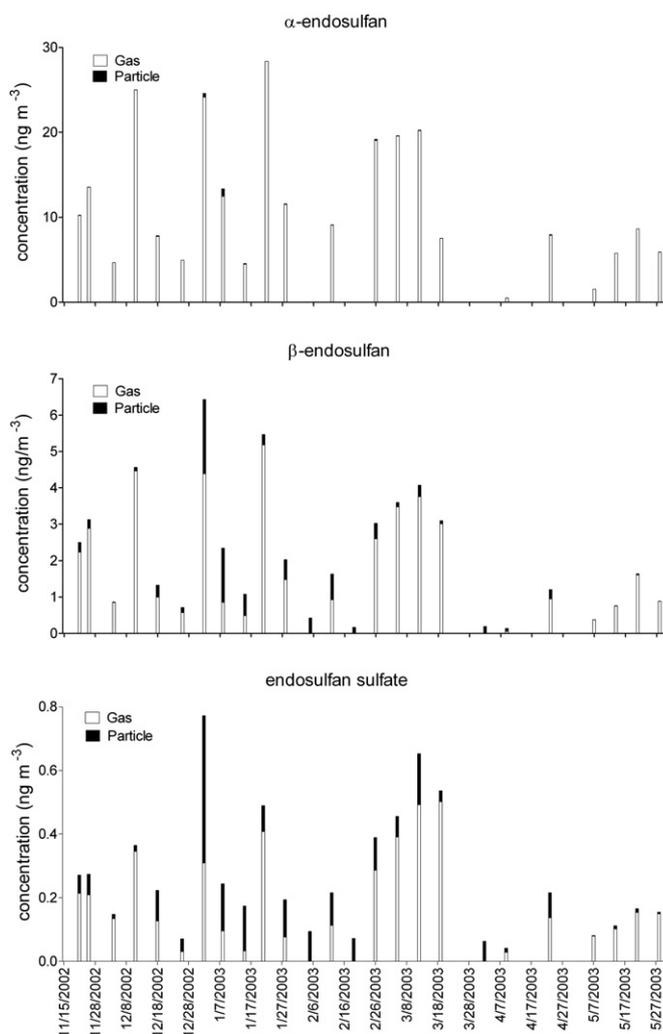


Fig. 5. Gas and particle phase concentrations of α - and β -endosulfan and endosulfan sulfate at the HAA site from November 2002 to June 2003.

was found for α -endosulfan. Particle phase concentrations of all three compounds were infrequently detected at the more distant BNP site. This is consistent with particle bound residues being more quickly removed from the atmosphere through dry deposition and rainfall scavenging.

3.3. Intensive sampling to examine transport

To characterize the potential transport of endosulfan from the agricultural region around HAA to the sites in the National Parks more fully, daily air samples were collected from all three sites during a high endosulfan use period for three weeks from late February to mid-March 2005. Concentrations at BNP (average α : $0.76 \pm 0.75 \text{ ng m}^{-3}$; average β : $0.12 \pm 0.086 \text{ ng m}^{-3}$) and EVR (average α : $2.4 \pm 3.9 \text{ ng m}^{-3}$; average β : $0.34 \pm 0.49 \text{ ng m}^{-3}$) were

highly variable indicating atmospheric transport of endosulfan to these areas was episodic (Fig. 6). Comparing the paired sets ($n = 13$), when the concentration values at BNP were greater than the average concentration ($n = 7$), the concentration values at EVR were less than the concentrations observed at BNP. The highest concentrations of α - and β -endosulfan were observed on February 25 and March 3 at BNP and EVR, respectively, and exceeded the average concentration of both compounds during this period by at least two standard deviations.

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Draxler and Rolph, 2011) was used to evaluate the potential movement of endosulfan from the HAA site during the period of 10 AM to 10 PM on these two days corresponding to the period when pesticide application and release was most likely to occur (Fig. 6) (Fry et al., 2011). The modeled 4-h dispersion plumes

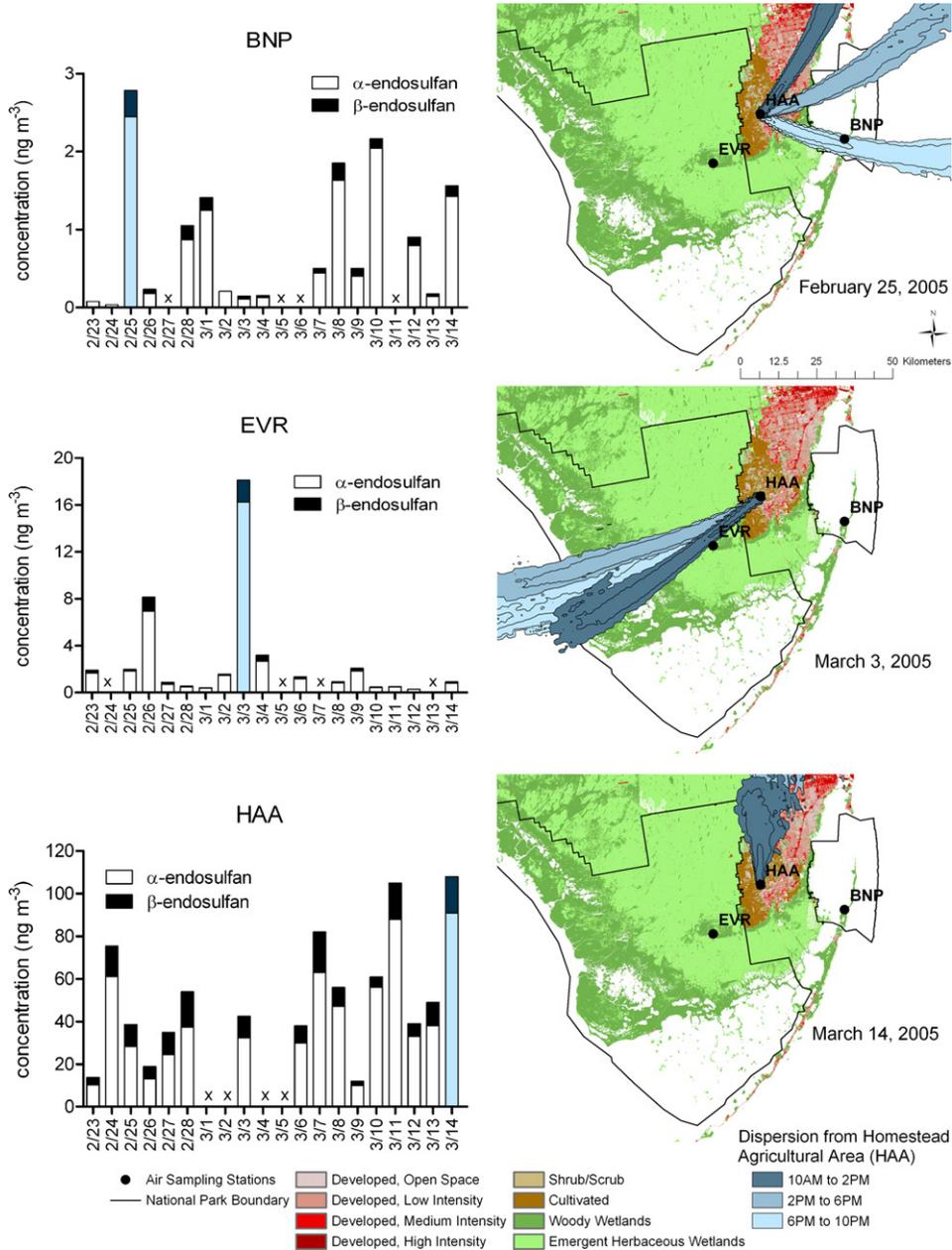


Fig. 6. Concentrations of endosulfan isomers at all three sites from February 23–March 14, 2005 and Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) modeled dispersion plumes from HAA on February 25, March 3, and March 14, 2005. The “x” shown on the stacked bar graphs indicates no data are available for those dates. Land use data provided in the maps represent conditions in 2006 (Fry et al., 2011).

from HAA on February 25 were transported to the east towards BNP, whereas on March 3, the plumes were carried in a westerly direction towards EVR. The model results along with measurements at BNP and EVR indicate that the agricultural area around HAA was a significant source of endosulfan to the surrounding region. The highest α -endosulfan and second highest β -endosulfan concentration at HAA were observed on March 14. Dispersion plumes modeled for this date indicated a northern pathway, but the plume was somewhat more localized at HAA, likely leading to higher concentrations in this area.

3.4. Contribution of drift versus isomerization and volatilization

Volatilization is governed by temperature and humidity of the environment and by the vapor pressure, the aqueous solubility, and various partitioning coefficients of the compound. For volatilization from soil to the air, soil sorption (K_{oc}) is also important, while Henry's Law constants (HLCs) are critical for volatilization from water to the air (Woodrow et al., 2001). Although their vapor pressures are similar, the HLCs of α -endosulfan ($0.70 \text{ Pa m}^3 \text{ mol}^{-1}$) and β -endosulfan ($0.045 \text{ Pa m}^3 \text{ mol}^{-1}$) are greater than an order of

magnitude different due to the greater aqueous solubility of β -endosulfan (Shen and Wania, 2005). The HLCs predict that α -endosulfan would partition nearly ten times more to the atmosphere, whereas β -endosulfan would be much more likely to partition to the aqueous phase (Weber et al., 2010). Whereas, formulated endosulfan is applied to crops in a 7:3 ratio of α : β , many long range transport studies have demonstrated that α -endosulfan is the more predominant isomer observed in air and that the β isomer was often not found above detection limits (Weber et al., 2010 and references therein). Reinforcing the concept that α -endosulfan is the overwhelmingly predominant isomer in the gas phase is a controlled field application study where ten times as much α -endosulfan compared to β -endosulfan volatilized from soil over a several week period after endosulfan application (Rice et al., 2002).

Isomerization of β - to α -endosulfan has also been documented. In studies measuring the air–water partitioning of pure β -endosulfan using a wetted-wall column, a 99:1 ratio of α : β isomers was found in the air and a 9:91 ratio in the aqueous phase indicating that isomerization readily occurs (Rice et al., 1997a, 1997b). This study strongly suggested that β -endosulfan is much more likely to

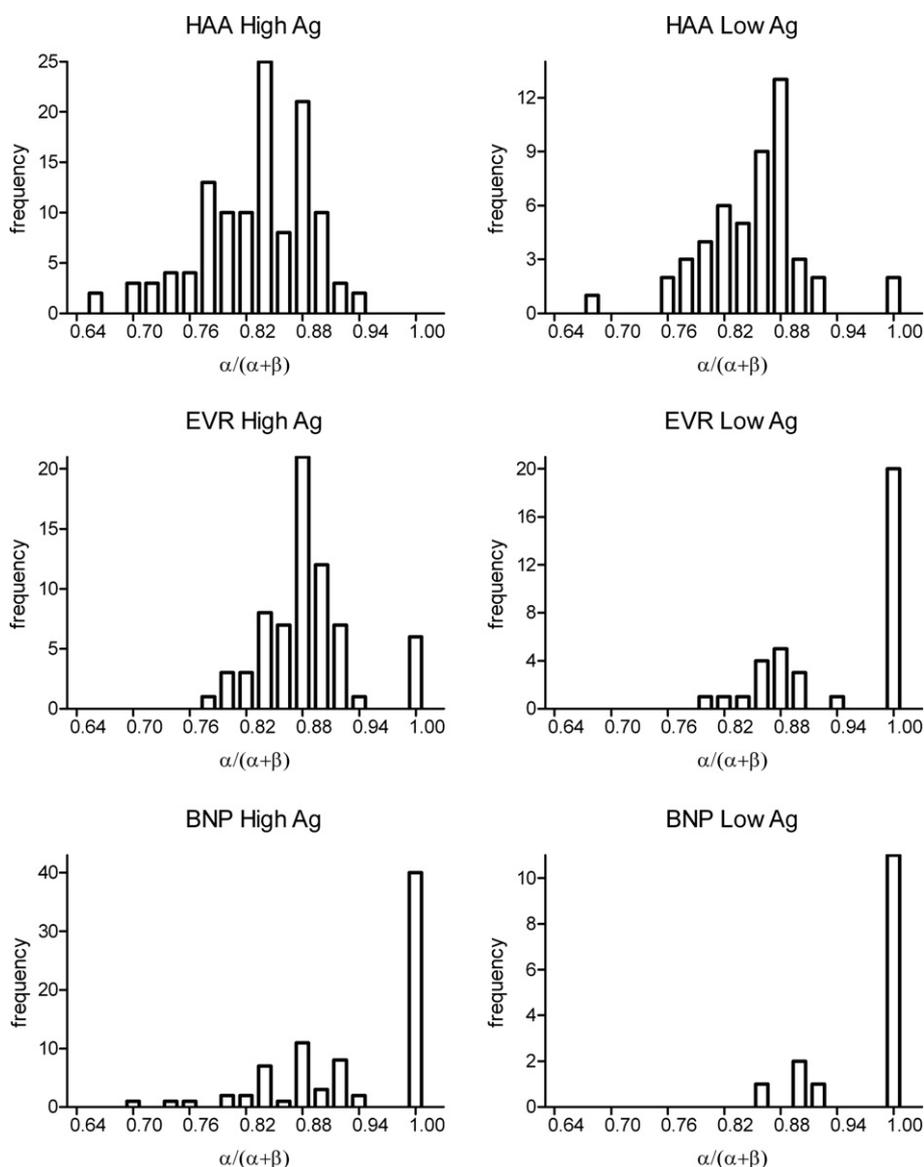


Fig. 7. Histogram of α -endosulfan fraction of the total of amount of α - and β -endosulfan [$\alpha/(\alpha + \beta)$] for each sample; bin = 0.02.

undergo isomerization to α -endosulfan than to volatilize especially in an aqueous environment. Interestingly, this isomerization has also been observed in the solid phase (Walse et al., 2002). Previous work using molecular modeling postulated a mechanism for isomerization whereby the seven member ring of β -endosulfan twists slightly to cause asymmetry and subsequent isomerization to α -endosulfan (Schmidt et al., 2001). This process provides even more α -endosulfan to be formed and to be available for volatilization to the atmosphere.

Spray drift is defined as downwind movement of airborne spray droplets beyond the intended area of application originating from aerial or ground-based spraying operations. (Stephenson et al., 2006; Felsot et al., 2011). Endosulfan is applied to the plant canopy to protect the crop from insect infestation; therefore, some spray drift is likely to occur depending on weather conditions. In contrast to volatilization, an air concentration ratio near 7:3 of α : β is most likely due to spray drift.

To examine the contribution of drift versus volatilization, the α -endosulfan fraction of the total of amount of α - and β -endosulfan [$\alpha/(\alpha + \beta)$] was calculated for each sampling event at each site during high and low agricultural activity and the frequency distribution of these values are shown in Fig. 7. This approach is more useful than the simple ratio of α/β since β -endosulfan was not observed in greater than 50% of the samples at BNP and EVR. Assuming a 15% propagated sampling and analysis error in this study, α -endosulfan fraction values at $0.7 \pm 15\%$ (0.66–0.75) were most likely due to drift with very little contribution from volatilization and isomerization processes. Thus, values of 0.95–1.0 have very little drift contribution. Conversely, volatilization or the two step process of isomerization followed by volatilization are the primary emission processes when the amount of α -endosulfan fraction [$\alpha/(\alpha + \beta)$] is close to 1.

In fourteen HAA and two BNP samples, α -endosulfan fraction values were found to be less than or equal to 0.75, that is, drift was the most likely residue source. The total endosulfan concentrations in the two BNP samples were low. α -Endosulfan fraction values of 1.0 were found at 1%, 24%, and 54% of all the HAA, EVR, and BNP samples and were most likely due to volatilization and possibly isomerization. The median α -endosulfan fraction during high agricultural activity at HAA and EVR were 0.84 and 0.88, respectively, and during low agricultural activity the median at HAA was 0.86. As expected, at EVR at low agricultural activity and for BNP at high and low agricultural activity, the median was 1.0, indicating that emissions transported to these sites are due to volatilization and isomerization processes.

Finally, isomerization could also occur in atmospheric droplets due to drift. As above, this would cause more α -endosulfan to be formed which, again due to its HLC would volatilize to the gas phase more than β -endosulfan. Thus, a value of 1.0 for [$\alpha/(\alpha + \beta)$] does not necessarily preclude some contribution of drift followed by isomerization in the atmosphere.

4. Conclusions

This work provides an important contribution to the overall understanding of the environmental fate of endosulfan in regions of agricultural production. Results indicate that agricultural activity in the South Florida region led to frequent and significant release of endosulfan to the atmosphere during the 2001 to 2006 sampling period. Gas phase concentrations at all three sites were dominated by the most volatile isomer, α -endosulfan, with concentrations in the HAA agricultural production area ten times greater than observed at the EVR site and a hundred times greater than at the BNP site. Concentrations of both α - and β -endosulfan were significantly higher at HAA and EVR during the high agricultural activity

period between October and May when compared to the rest of the year, but concentrations were not significantly different at BNP. Throughout the year, concentrations of α -, β -, and endosulfan sulfate were significantly higher at HAA than at either of the other two sites. Particle phase concentrations at HAA were highest on average for β -endosulfan reflecting a higher log K_{oa} value. However, detections of particle phase endosulfan were infrequent at BNP indicating these residues were quickly removed from the atmosphere.

Changes in the daily air concentration values at EVR and BNP were linked to modeled dispersion of air parcels originating from the region around HAA, indicating efficient transport to the surrounding region. The novel aspect of endosulfan isomerization combined with its physical and chemical properties allowed for concomitant analysis of drift from application and emission following application. Examination of the α -endosulfan fraction at the three sites indicates that a combination of both drift and volatilization (and possibly in combination with isomerization) processes influenced the atmospheric concentrations of endosulfan at HAA and EVR while volatilization (and possibly in combination with isomerization) was the primary emission process affecting endosulfan levels at BNP.

Results of this work strongly suggests that heavy agricultural use of endosulfan can lead to locally-high atmospheric concentrations with greater α -endosulfan emissions from the aqueous phase due to its higher HLC and the potential isomerization of β -endosulfan to α -endosulfan followed by volatilization. The model predictions and measurements carried out at EVR and BNP also indicated that residues were transported into ecologically sensitive areas, although the magnitude of deposition is unknown. Infrequent detections of β -endosulfan and endosulfan sulfate at the BNP site indicated these compounds were likely deposited in the local area while α -endosulfan remained in the atmosphere and was available for long range transport.

Disclaimer

Mention of specific products is for identification and does not imply endorsement by the US Department of Agriculture or the US National Park Service to the exclusion of other suitable products or suppliers.

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Abbreviations

ARS	Agricultural Research Service
BNP	Biscayne National Park
EVR	Everglades National Park
GC–MS	gas chromatograph–mass spectrometer
GFF	glass fiber filter
HAA	Homestead agricultural area
HLC	Henry's Law Constant
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory
LOQ	limit of quantitation
MDL	method detection limits

NP	National Park
K_{oa}	octanol-air partition coefficient
K_{oc}	soil organic carbon-water partition coefficient
PUF	polyurethane foam
SFWMD	South Florida Water Management District Water
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency; WRDA, Water Resources Development Act of 2000.

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