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# Spatial distribution of and seasonal variations in endosulfan concentrations in soil, air, and biota around a contaminated site

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ABSTRACT

Soil, air, tree bark, rice, wheat, invertebrates, and chicken tissues around a typical endosulfan-contaminated site were analyzed in each season in each of two years. The total endosulfan (the sum of α-, β-endosulfan and endosulfan sulfate) were significantly different in soil and air samples collected in the four seasons ($P < 0.01$) and the mean concentrations were 6.53 ng/g dry weight (d.w.) and 2.40 ng/m$^3$, respectively, in autumn, 3.32 ng/g d.w. and 2.48 ng/m$^3$, respectively, in winter, 2.10 ng/g d.w. and 0.93 ng/m$^3$, respectively, in spring, and 1.03 ng/g d.w. and 0.83 ng/m$^3$, respectively, in summer. The total endosulfan concentrations in tree bark, rice, wheat, and invertebrates were 23.0–278 (mean 95.5) ng/g d.w., 7.36–35.5 (mean 17.4) ng/g d.w., 34.3–158 (mean 83.1) ng/g d.w., and 401–4354 (mean 2125) ng/g lipid weight, respectively. The total endosulfan concentrations in the chicken gizzard, heart, liver, and meat samples were 552, 212, 699, and 221 ng/g lipid weight, respectively. The endosulfan concentrations in soil, air, and biota around the site were strongly influenced by endosulfan emissions from the site, and the concentrations had decreased to half the initial concentrations six months after endosulfan production stopped. The invertebrate and chicken bioconcentration and biomagnification factors indicated that endosulfan accumulated in the invertebrates and chicken tissues was slightly biomagnified by chickens.

## 1. Introduction

Endosulfan, a broad spectrum cyclodiene organochlorine pesticide, has been widely produced and used in China and many other countries, including Australia, Brazil, Canada, European Union countries, India, Indonesia, Mexico, and the USA (Weber et al., 2010). Technical endosulfan is dominated by two biologically active isomers, α-endosulfan and β-endosulfan, at approximate ratios of between 2:1 and 7:3, with impurities and degradation products such as endosulfan sulfate, which is as toxic as α-endosulfan and β-endosulfan. The chemical properties of endosulfan are shown in Table S1. Endosulfan poses risks to various organisms because it affects physiological functions, especially neurological functions (Preud'Homme et al., 2015; Wilson et al., 2014). Endosulfan is less persistent than other organochlorine pesticides in the environment, the half-lives of the toxic components of endosulfan (α-endosulfan, β-endosulfan, and endosulfan sulfate) being between nine months and 6 y (EPA, 2002; Fenner et al., 2003). Endosulfan was added to the Stockholm Convention list of controlled persistent organic pollutants in 2011, and endosulfan production and use was stopped in more than 60 countries. Endosulfan production and use stopped in March 2014 in China, although it can still be used to control budworms in cotton and tobacco fields.

Endosulfan has been found in various environmental compartments, including air, soil, vegetation, and water. Endosulfan often enters environment at the locations it was directly applied. Endosulfan is one of the most commonly detected pesticides in surface water in the USA and is one of the most abundant organochlorine pesticides in air (Weber et al., 2010). Endosulfan production sites are important sources of endosulfan, and environment near endosulfan production sites have been found to be seriously polluted with endosulfan (Fang et al., 2016). However, little attention has been paid to the transmission of endosulfan from contaminated sites to the surrounding environment, particularly in terms of seasonal variations. The demolition of abandoned endosulfan production facilities can aggravate the pollution of the nearby environment. Endosulfan will be produced and used in some countries for specific applications until appropriate alternatives are developed, so it is important that the spatial distributions and seasonal variations in endosulfan concentrations around endosulfan production

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plants are studied to allow endosulfan pollution to be controlled.

In this study, topsoil and ambient air samples were collected in each season around a typical endosulfan production site. The aim was to investigate seasonal variations in and spatial distributions of endosulfan concentrations in the environment around the contaminated site. Endosulfan concentrations in locally grown rice and wheat collected at harvest-time were also determined. Tree bark samples collected at the same times as the air samples were also analyzed. Invertebrates (budworms, butterflies, earthworms, grasshoppers, snails, and spiders) and free-range chickens from within 200 m of the site were also collected and analyzed. The objectives of the study were: (1) to determine the endosulfan concentrations in air, soil, and biota near a typical source of endosulfan pollution; (2) to study the seasonal variations in and spatial distributions of endosulfan concentrations around the pollution source; (3) to measure endosulfan concentrations in tree bark near the contaminated site and the relationship between these concentrations and the concentrations in passive air samples; and (4) to assess the health risks posed by endosulfan to people living near the contaminated site and to determine the endosulfan bioconcentration and biomagnification capacities of invertebrates and chickens living near the site.

## 2. Materials and methods

### 2.1. Sample collection

Soil samples were collected following the environmental soil monitoring protocol HJ/T166-2004 and the environmental quality monitoring of farmland soil protocol NY/T395-2000. A total of 108 soil samples were collected in all four seasons in each of two years. The soil samples were collected in circles centered on the contaminated site with radii of 0.5, 1.0, 2.0, 5.0, 10.0, and 30.0 km (control samples), as shown in Fig. 1. Each soil sample was collected using the five-point method with a stainless-steel shovel and was mixed with five subsamples, wrapped in foil, and sealed in a bag. The soil samples were then transported to the laboratory and stored at − 20 °C until they were analyzed.

Passive air samples were collected using polyurethane foam samplers following the draft standard for air quality monitoring in the environment (no. 4, announced by the Chinese State Environmental Protection Administration). Wind in the study area mainly comes from the southeast, so the air samplers were mainly placed northwest (downwind) of the site (see Fig. 1). The polyurethane foam samplers were Soxhlet extracted with dichloromethane for 24 h before use and deployed for three months before being returned to the laboratory for analysis. Some air samplers were lost or damaged, and 53 air samples were analyzed.

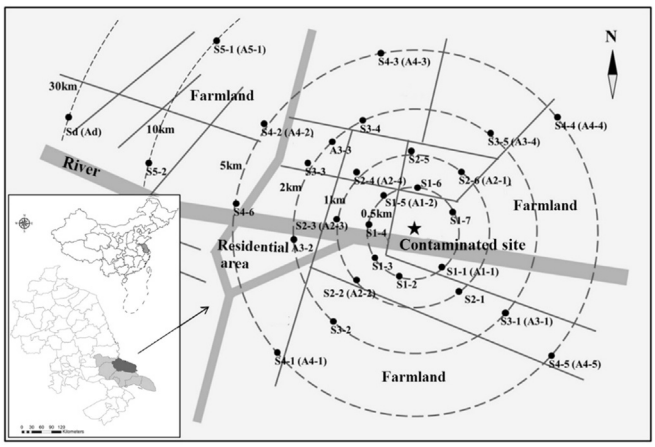


**Fig. 1.** Map showing the location of the sampling site and the locations at which the soil and air samples were collected.

Tree bark samples were collected at each air sampling point in each season. A total of 76 tree bark samples (19 per season) were collected. Each sample was taken from five metasequoia trees each 20–30 cm in diameter. Bark was collected 1.5 m from the ground. Pieces of bark 2 mm thick were collected from four directions around each tree. Rice samples (n = 21) and wheat samples (n = 25) were collected at harvest time (autumn and spring, respectively). Endosulfan bioconcentration from soil was investigated by analyzing rice and wheat samples collected at the same points as the soil samples were collected in autumn and spring. Invertebrates (budworms, butterflies, earthworms, grasshoppers, snails, and spiders) were collected from farmland 200 m around the study site in autumn. Free-range chickens were obtained from nearby farmers in each season. Each chicken was killed and tissue samples were collected at the farm the chicken was collected from. Samples of the gizzard, heart, liver, and meat were collected. Each biota sample was wrapped in foil and sealed in a bag, then transported to the laboratory in a portable refrigerator.

### 2.2. Extraction and pretreatment

Each soil sample was freeze-dried, ground, and passed through a 200 mesh sieve. A 5.0 g aliquot of each soil sample was Soxhlet extracted with 220 mL of a 1:1 (v/v) mixture of acetone and hexane for 24 h. Each extract was concentrated, then passed through a column filled with anhydrous sodium sulfate (2 cm) and activated Florisil (10 g), eluted with 50 mL of a 4:1 (v/v) mixture of hexane and dichloromethane. The clean extract was evaporated to about 2 mL and then to dryness under a gentle stream of nitrogen, then the residue was redissolved in 1 mL of *n*-hexane. The air samples were extracted in the same way as the soil samples as soon as they had been brought to the laboratory. Each biota sample was cleaned, chopped, and homogenized using a pulp refiner. Each homogenized invertebrate or chicken tissue sample was extracted without pre-treatment, whereas each tree bark, rice, or wheat sample was freeze dried and ground before being extracted. The biota samples were extracted and purified using the method used for the soil samples.

### 2.3. Instrumental analysis

α-Endosulfan, β-endosulfan, and endosulfan sulfate were identified by gas chromatography mass spectrometry (using an Agilent 7890A instrument; Agilent Technologies, Santa Clara, CA, USA) and quantified by gas chromatography with electron capture detection (using an Agilent 7890 instrument; Agilent Technologies). The gas chromatographs had split/splitless injectors and were fitted with HP-5 chromatographic columns (30 m long, 0.32 mm i.d., 0.25 μm film thickness; Agilent Technologies). A 1.0 μL aliquot of each sample extract was analyzed using splitless injection mode. The injector and detector temperatures were 250 and 315 °C, respectively. The carrier gas was high purity nitrogen, and the flow rate was 1.0 mL/min. The oven temperature program started at 60 °C, which was held for 2 min, increased at 20 °C/min to 160 °C, which was held for 1.5 min, increased at 5 °C/min to 210 °C, which was held for 2 min, and then increased at 5 °C/min to 270 °C, which was held for 3 min. The target analytes (α-endosulfan, β-endosulfan, and endosulfan sulfate) were separated well.

### 2.4. Quality assurance and quality control

The soil, air, and biota samples were subjected to strict quality control and quality assurance procedures similar to the procedures we used in a previous study. A laboratory blank was analyzed with every batch of 10 soil, air, and biota samples, and the endosulfan concentrations in all the blank samples (including the field blank samples for the air samples) were lower than the quantification limits, indicating that the sample transport, storage, and analysis procedures were reliable. The α-endosulfan, β-endosulfan, and endosulfan sulfate