# LEVEL, DISTRIBUTION, AND HUMAN HEALTH RISK ASSESSMENT ON THE EMISSION OF ENDOSULFAN FROM A MANUFACTURING FACILITY IN CHINA

Wang DG[1], Alaee M[2], Guo MX, Pei W

[1] Dalian Maritime University, Dalian, Liaoning, PR China; [2] Water Science and Technology Directorate, Environment Canada, 867 Lakeshore Road, Burlington, OntarioL7R 4A6

## Introduction

Endosulfan is an organochlorine (OC) pesticide which acts as a contact poison in a wide variety of insects and mites primarily on crops such as tea, fruits, vegetables, grains, and cotton. Endosulfan and sulfate are generally considered to be toxic and classified by the World Health Organization and the U.S. Environmental Protection Agency as priority pollutants and the Persistent Organic Pollutants (POPs) treaty (http://chm.pops.int/) [1]. Endosulfan has been manufactured and used for about five decades across the globe [2]. It has been frequently reported in various environmental matrices, including air, water, soil, sediment, and biota. As a current use pesticide, it is reasonable to expect that the level of endosulfan in global environment will continue to increase.
Obviously, the emission from a manufacturing facility is another source to the environment. However, no information on the environmental levels of endosulfan in the vicinity of the manufacturing facility is available. In this paper, we describe spatial soil endosulfan concentrations near and far field of an endosulfan manufacturing plant as well as several air, sediment, fish and crop samples taken close to the facility. In addition, endosulfan sulfate, a degradation product, was also analyzed in samples around the facility. We performed preliminary human health risk assessment for the people working and living in the surrounding region.

## Materials and methods

Three air, 18 soil and 2 sediment samples were collected concurrently from a manufacturing facility in Jiangsu province of China in October 2009. Eight species of vegetation and five fish species were concurrently collected from this facility in May, 2010. Samples were extracted and analyzed according to previous methods [3, 4]. All samples were quantified with GC/MS (PolarisQ, Thermo) equipped with a 30 m × 0.25 mm × 0.25 μm DB-5 MS capillary column (J&W Scientific, Folsom, CA).
To evaluate human exposure to endosulfan via dietary intake, dermal contact, and inhalation from the manufacturing facility, estimated exposure doses (EED) for workers, residents, and children were calculated using methods described previously[2]. A comparison was made for risk assessment between the reference dose (RfD) and the EED via three exposure routes. The health risk for individual exposure pathways was evaluated using the hazard quotient (HQ), the ratio of estimated exposure dose to reference dose. A HQ value >1 indicates that a human is likely to consume a dose amount at which adverse health effects are likely to occur, and vice versa.

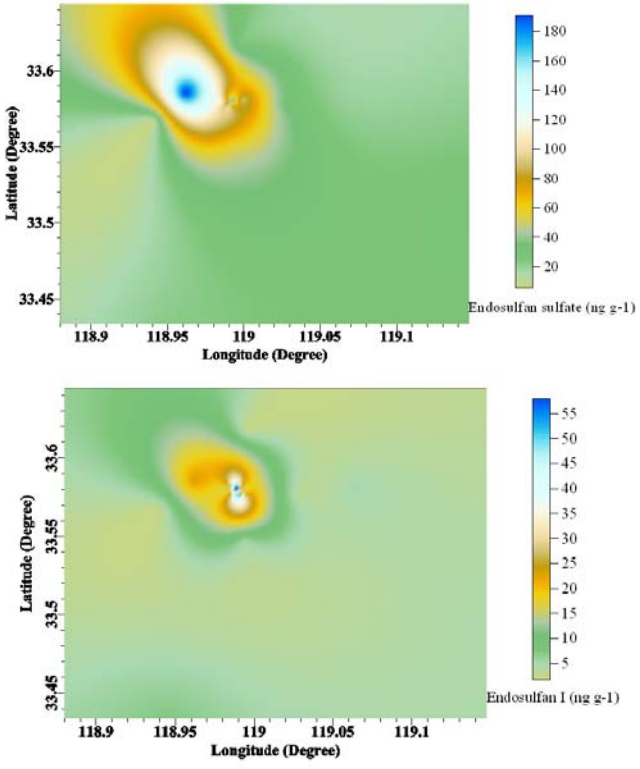
## Results and discussion

Endosulfan I, endosulfan Π, and endosulfan sulfate were detected in air, sediment, soil, fish and crop and the concentrations are summarized in Table 1. Air concentration for endosulfan I, endosulfan Π and endosulfan sulfate were several orders of magnitude greater than those reported to date. Liu et al. [5] reported that mean concentration for endosulfan I and endosulfan Π in 37 Chinese cities were 31.4 pg $m^{-3}$ and 13.9 pg $m^{-3}$, respectively. Our comparative maximum air concentration was approximately 9 and 26 times greater than mean level in 37 Chinese cities, respectively. Surficial soil concentration ranges of endosulfan I, endosulfan II, and endosulfan sulfate were greater than those in sediment samples. The concentration of endosulfan II was highest in both surface sediment and soil followed endosulfan sulfate and edusulfan I. However, a different concentration profile was observed in fish and crop samples, with endodulfan sulfate having the highest concentration followed by endosulfan I and endusulfan II .

Table 1. Concentration (mean ± standard error) of endosulfan in air (pg $m^{-3}$), soil (ng $g^{-1}$ dw) and sediment (ng $g^{-1}$ dw), grain (ng $g^{-1}$ dw), vegetable (ng $g^{-1}$ ww), and fish (ng $g^{-1}$ ww)samples.

| Sample | endosulfan I | endosulfan II | endosulfan sulfate |
|---|---|---|---|
| Gas phase, Air | 231 ± 84.9 | 182 ± 42.4 | 125 ± 30.0 |
| Particle phase, Air | 39.5 ± 16.9 | 116 ± 19.4 | 98.1 ± 55.4 |
| Gas + particle, Air | 270 ± 101 | 299 ± 43.5 | 223 ± 51.5 |
| Surficial soil | 17.0 ± 21.0 | 68.6 ± 71.4 | 61.2 ± 51.5 |
| Surficial sediment | 5.80 ± 4.35 | 23.5 ± 14.0 | 14.4 ± 9.10 |
| Grains | 1.63±0.46 | 1.12±0.28 | 5.22±3.18 |
| Vegetables | 2.12±0.96 | 1.29±0.82 | 5.34±2.89 |
| Fish | 2.62±2.03 | 1.29±0.79 | 6.03±3.56 |

Spatial distribution in soil of endosulfan I, endosulfan II and endosulfan sulfate around the facility is presented in Figure 1. The apex concentrations for all three compounds are located in the same spot, indicating a common source within the studies geographical grid, corresponding to the manufacturing facility. This scenario was confirmed by the Pearson correlation analysis. A significant positive correlation ($p < 0.01$) was found between the pairs of endosulfan I and II and endosulfan II and endosulfan sulfate. Unique, sharp profiles for both endosulfans I and II would be consistent with recent exposure of these compounds to the soil. The more diffuse pattern given by endosulfan sulfate would suggest a possible secondary source more than a diffuse source from the facility. Interestingly, the highest intense apex for endosulfan sulfate was observed in the soil profile at one rural site with a distance of 2.6 km from the facility suggesting an older source. The spatial distribution of concentrations showed that relatively higher concentration occurred in the northwest of the facility, where was the rural area. The other directions from the facility were the urban areas so that less usage of endosulfan in these areas.



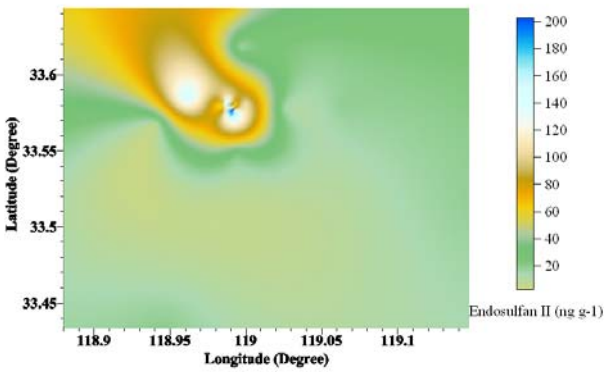



Figure 1. The concentrations of endosulfan I, endosulfan II and endosulfan sulfate in soil surrounding manufacturing facility.

The Pearson's correlation coefficient between the logarithm of endosulfan concentration and the logarithm of distance from the facility showed a negative relationship ($p$<0.01). It has been shown in Figure 2 that the concentrations of endosulfan in soil decreased rapidly with increasing distance from the facility by a factor of 10 within 45 km. This finding suggested that the facility has influenced the distribution of endosulfan in surficial soil and is an important source to the immediate surrounding environment.

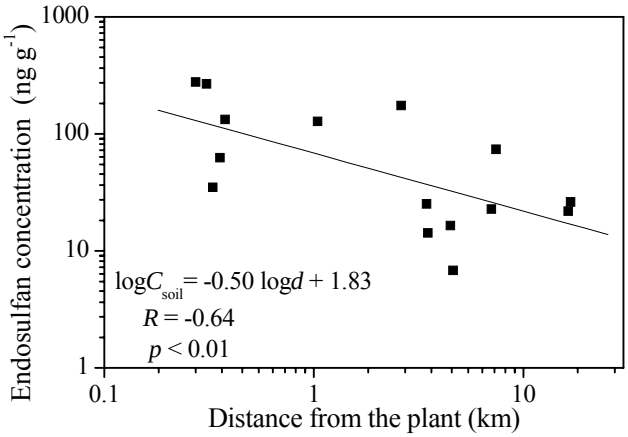



Figure 2. Endosulfan concentration in soil ($C_{soil}$) as a function of distance ($d$) from the manufacturing facility.

Table 2. Hazard quotient (HQ), estimated exposure dose (EED, mg $kg^{-1}$, $d^{-1}$) and reference dose (RfD, mg $kg^{-1}$, $d^{-1}$) of endosulfan for worker, resident, and children via dietary, dermal contact, and inhalation at study sites in manufacturing facility in China.

| Exposure route | [a]HQ | | | EED | | | [b]RfD | [c]NOAEL | [d]UF | | | | MF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | worker | resident | children | worker | resident | children | | | H | S | A | L | |
| dietary | $6.3\times10^{-3}$ | $6.3\times10^{-3}$ | $6.4\times10^{-3}$ | $3.6\times10^{-5}$ | $3.6\times10^{-5}$ | $3.6\times10^{-5}$ | $5.7\times10^{-3}$ | 0.57 | 10 | 1 | 10 | 1 | 1 |
| dermal | $1.6\times10^{-8}$ | $5.3\times10^{-9}$ | $5.8\times10^{-9}$ | $9.7\times10^{-11}$ | $3.2\times10^{-11}$ | $3.5\times10^{-11}$ | $6.0\times10^{-3}$ | 0.60 | 10 | 1 | 10 | 1 | 1 |
| inhalation | $5.4\times10^{-5}$ | $3.2\times10^{-5}$ | $4.9\times10^{-5}$ | $1.0\times10^{-7}$ | $6.3\times10^{-8}$ | $9.6\times10^{-8}$ | $1.9\times10^{-3}$ | 0.19 | 10 | 1 | 10 | 1 | 1 |

[a] HQ = EED/RfD.

[b] RfD = NOAEL (experimental dose)/(UF×MF), UF is standard uncertainty factor and MF is modifying factor.

[c] No observed adverse effect levels (NOAEL, mg $kg^{-1}$, $d^{-1}$) via oral, dermal, and inhalation obtained from the repeated dose toxicity.

[d] UF = A×H×S×L, A = animal-to-human (interspecies); H = inter-individual (intraspecies); S = subchronic-to-chronic duration; L = LOAEL-to-NOAEL.

In this study, we performed a screening level risk assessment for this contaminated sites based on the worst-case scenario. These assessments provided a high level of confidence in determination a low probability of adverse risk and did not intend to provide definitive estimates of actual risk. Accordingly, we assumed all of the people living in this region consume local food only because these foods have the highest levels of endosulfan. In this study, we assumed that all endosulfan in air can be absorption via inhalation.

The oral, dermal, and inhalation RfDs were calculated to be 5.7, 6.0, and 1. $2\times10^{-3}$ mg $kg^{-1}$ $d^{-1}$, respectively, based on the EPA's method. Compared to the EEDs, we can calculate the HQs for workers, residents, and children in the manufacturing facility region and these values are shown in Table 2. Overall, the maximum HQ values were at least 3 orders of magnitude less than 1, indicating no adverse health effects were likely to occur at any present exposure dose, and that health risk was generally acceptable.

**Acknowledgements**

This study was funded by the National Natural Science Foundation Program of China (Grants 21077015), and the Fundamental Research Funds for the Central Universities.

**References**

1. UNEP, Proposal for listing endosulfan in the Stockholm Convention on Persistent Organic Pollutants, 2008.
2 Weber, J., Halsall, C. J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., Bidleman, T., (2010), *Sci Total Environ.* 408(15): 2966-2984.
3. Wang, D.-G., Alaee, M., Byer, J. D., Brimble, S., Pacepavicius, G. (2013) *Sci Total Environ.* (445-446) 329-336.
4. Wang, D.-G., Yang, M., Qi, H., Sverko, E., Ma, W.-L., Li, Y.-F., Alaee, M., Reiner, E. J., Shen, L. (2010), *Environ Sci Tech.* 44(17): 6608-6613.
5. Liu, X., Zhang, G., Li, J., Yu, L.-L., Xu, Y., Li, X.-D., Kobara, Y., Jones, K. C. (2009); *Environ Sci Tech.*43(5): 1316-1321.