PERSISTENT ENDOSULFAN SULFATE IS FOUND WITH HIGHEST ABUNDANCE AMONG ENDOSULFAN I, II, AND SULFATE IN GERMAN FOREST SOILS

Bussian BM[1]*, Lehnik-Habrink P[2], Aichner B[2], Henkelmann B[3], Pandelova M[3], Schramm K-W[3,4]

[1] Federal Environment Agency, Section Soil Quality and Soil Monitoring, Am Wörlitzer Platz, 06844 Dessau-Roßlau, Germany; [2] BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany; [3] Helmholtz Zentrum München-German Research Center for Environmental Health, Molecular EXposomics, Ingolstädter Landstrasse 1, 85764 Neuherberg, Germany; [4] Department für Biowissenschaftliche Grundlagen, Technische Universität München, Weihenstephaner Steig 23, 85350 Freising, Germany

Introduction

Endosulfan is a synthetic organochlorine compound which is used globally as an agricultural insecticide. Technical endosulfan is produced as a 2:1 to 7:3 mixture of isomers I and II. It has been introduced as a broad spectrum insecticide in 1954 by Farbwerke Hoechst / Germany and has soon reached a global production of about 10.000 tonnes per year. It is estimated that the current production is significantly higher than in the mid 1980s although endosulfan is banned in more than 60 countries since a couple of years. Detailed figures about its production, environmental exposure and fate are given in the literature[1,2].

It has been proven experimentally as well as by model calculations that endosulfan has a long range transport (LRT) potential and can therefore be detected globally. Due to its persistency, its bioaccumulative and toxic potential and the LRT properties in line with the global use endsulfan has been classified as a Persistent Organic Pollutant (POP) and has been identified as priority hazardous substance under European Quality Standards Directive (2008/105/EC).

Endosulfan is transformed under aerobic conditions via biologically mediated oxidation to endosulfan sulfate, which again is slowly degraded to the more polar metabolites endosulfan diol, endosulfan lactone, endosulfan ether. Since endosulfan sulfate also poses unacceptable risks, or causes unacceptable harm, to human health and the environment and is even more persistent than its parent molecule reliable monitoring data are needed for the I- and II-isomers in conjunction with the main degradation product endosulfan sulfate to assess them in a joint approach.

This paper presents the data of a monitoring study of German forest soils which have been analyzed to get data specifically for POPs and PAHs. This study proves that endosulfan is abundant in all samples, where the main metabolite endosulfan sulfate is found with even higher abundance than the parent molecules.

Materials and methods

Sampling strategy

As part of the second forest soil status report in Germany (BZE II) at about 450 plots (16 km x 16 km) top soil samples (humic layer) and the first levels (0-5 cm and 5-10 cm) of the mineral layer have been taken. The sampling campaign was performed from 2007 to 2008 by the forest authorities of the German states with technical assistance of the experts of the German states forest research facilities. For this POP-monitoring study a subset of 80 top soil (humic layer) samples (representing a 64 km x 64 km grid) has been selected.

Directly after sampling the soil material was stored in cooled brown glass bottles and kept at about 0 °C for some hours until they were transferred to a freezer for intermediate storage and kept at – 20 °C. Subsequently, the samples were sieved by a 4 mm cross diameter stainless steel sieve and homogenized by a Tyler divider and bottled for further analytical treatment. The pretreatment of the samples was performed at about – 10 °C. The laboratory samples were stored at – 20 °C until use.

Drying of the samples was not performed to avoid loss of volatile contaminants. In turn, extraction of the analytes was done with field wet samples and the water has been removed after extraction.

ASE extraction

The soil extraction was carried out on Accelerated Solvent Extractor (ASE 300, Dionex GmbH, Idstein, Germany). 20 g of wet soil was mixed with diatomaceous earth (Hydromatrix, Agilent), spiked with a mixture labeled internal and extracted with n-hexane:acetone (75:25, v/v) at 120°C and pressure of 12 MPa. Two static cycles of 10 min were applied for a complete extraction. The extract was passed over anhydrous sodium sulfate to remove water.

Preparation of the sample for measurement

The clean-up with silica gel and Alumina B with 3% water for OCP-analysis and the clean-up with C18 is carried out following the procedure published previously[3].

Finally, the reduced eluate (0.5 mL) was transferred to a 2 mL autosampler vial with micro-insert and further evaporated by a gentle stream of nitrogen to a final volume of 20 µL. Into the vial a recovery standard (Pentachlorotoluene, 1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin $^{13}C_{12}$) was spiked before.

Measurement and Reporting

The measurement is carried out with GC/MS. The parameters used for the isomer specific detection of organochlorine pesticides are given in Table 1. The quantification criteria included confirmation of retention times and isotope ratios of the labeled standards and respective analytes. Routinely, the mass fragment with the highest intensity of the molecular or fragment ion cluster was used for quantification. Concentrations were calculated by comparison of the signal heights of the analyte with its respective labeled analogue.

Table 1: GC/MS parameter for the isomer specific detection of organochlorine pesticides

GC	Type	Agilent 6890
	Column	Rtx-Dioxin2, 40 m, 0.18 mm ID, 0.18 µm film thickness (Restek)
	Temperature program	60 C, 1.5 min, 25 C min^{-1}, 140 C, 8 C min^{-1}, 300 C, 20 min
	Carrier gas	helium, constant flow: 1.3 mL/min
	Injector	Cold injection system CIS 4 (Gerstel)
	Temperature program injector	120 C, 12 C s^{-1}, 280 C, 5 min
	Temperature transferline	300 C
	Autosampler	A200S (CTC)
	Injection volume	0.5 µL pulsed spitless
MS	Type	MAT 95S (Thermo)
	Ionisation mode	EI, 50 eV, 260 C
	Resolution	> 9000
	Detection	SIM mode

Results and discussion

In order to get a first overview of the contamination of German forest soils by endosulfan about 20 samples of a subset of 80 samples (representing a 64 km x 64 km grid) have been analyzed (see Table 2).

Table 2: contents of Endosulfan I, II and Endosulfan sulfate of top soil (humic layer) samples of forest soils

values in pg/g dry weight	Min	Mean	Median	90th Percentile	Max
Endosulfan I	24.4	189.9	135.9	373.2	1,225.4
Endosulfan II	122.8	550.6	369.8	948.5	5,904.1
Endosulfan sulfate	1,867	17,803	13,071	34,662	130,358

At a first glance these results coincide with the fact that the sulfate is the predominant metabolite of endosulfan and more stable than the parent molecule[4]. A ratio similar with our result between endosulfan I and II was found in a study on pesticides in western Canadian mountains[5] and does coincide with model calculations[6]. Several studies prove that significant conversion from II to I has been observed and that isomer I is the more stable one[7]. However, this does not generally result in higher concentrations of isomer I. The higher abundance of isomer II can be explained by the fact that the isomer I is converted more readily under aerobic conditions to the sulfate than isomer II[4,8].

Our data indicate that soils act as s sink, where biotic and abiotic metabolism under aerobic conditions causes an accumulation of the – compared to the parent molecules – even more persistent compound endosulfan sulfate.

This points to the dilemma that the technical endosulfan represented by isomer I and II is banned and monitored, however the more abundant metabolite endosulfan sulfate is neither monitored nor banned. Monitoring data in Germany in accordance with the European directive on environmental quality standards in the field of water policy prove that the maximum allowable concentration for endosulfane I and II is occasionally exceeded in surface waters. Such monitoring indicates that endosulfan is still an environmental problem.

The study argues for a systematic monitoring of endosulfan I, II, and sulfate and underlines the need for further research, specifically on the fate of endosulfan including biomagnifications and bioaccumulation in soil.

Acknowledgements
The forest soil samples have been taken by the forest authorities of the federal states of Germany. Financial support from the environmental research fund of the federal minister of environment and nuclear safety / Germany (UFOPLAN FKZ 3707 71 201) is gratefully acknowledged.

References

1. UNEP, Stockholm Convention on Persistent Organic Pollutants, Report of the Persistent Organic Pollutants Review Committee on the Work of its Fifth Meeting (Addendum), Risk profile on endosulfan, 13 December 2009
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: 2966–2984
3. Wang J, Bi Y, Pfister G, Henkelmann B, Zhu K, Schramm K-W (2009) *Chemosphere* 75:1119-1127
4. Kathpal TS, Singh A, Dhankhar JS, Singh G. (1997) *Pestic Sci* 50:21–7
5. Daly G L, Lei Y D, Teixeira C, Muir D, Wania F (2007) *Environ Sci Technol* 41: 6020–6025
6. Becker L, Scheringer M, Schenker U, Hungerbühler K (2011) *Environ Poll* 159, 1737-1743
7. Rice C P, Chernyak S M, Hapeman C J, Biboulian S. (1997) *J Environ Qual* 26:1101–6
8. Leonard A W, Hyne R V, Lim R P, Leigh K A, Le J, Beckett R. (2001) *J Environ Qual* 30:750–759