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Endosulfan in Wind-Transported African Dust Depositions in Crete

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Abstract The presence of endosulfan in samples of African dust after a typical red dust storm in May 2007 was investigated. The samples were collected from a remote and mountainous area of Crete (Greece) where olive groves are cultivated. Endosulfan I, endosulfan II and endosulfan sulphate were detected at concentrations of 2.7, 1.4 and 1.1 ng/g, respectively, indicating that long range aeolian dust transport could be a possible source of contamination of olive cultivations.

Keywords Pesticides · Transport · Dust-storm · Endosulfan

Although rainfall is moderate over the Eastern Mediterranean Basin, it receives relatively high dust fluxes particularly from the adjacent Sahara Desert (Herut et al. 2005). For Crete in particular annual dust flux ranges from 10 to 100 g m^{-2}, most of the deposition taking place in a few annual dust events (Pye 1992).

Dust depositions from such an event that took place on May 28th 2007 were examined for the presence of endosulfan, as a possible source of endosulfan contamination of olive groves located in isolated, mountainous areas, away from any other cultivation. The Saharan origin of the collected dust was confirmed by meteorological data from the National Observatory of Athens, Institute of Environmental Research and Sustainable Development. Confirmation data was also retrieved from the NAAPS/SAT archive of the "NRL/Monterey Aerosol Page" for the area of Eastern Mediterranean (Fig. 1).

Following attempts by other investigators, our group is the first to report the detection and quantification of endosulfan in African-dust samples in Greece.

Materials and Methods

A CEM MARS microwave sample preparation system was used for sample preparation (CEM Corporation, Matthews, North Carolina, United States). The gas chromatographic system used was a Varian CP-3800 (Walnut Creek, CA, USA) equipped with a CTC CombiPal autosampler (Zwingen, Switzerland) a CP-1177 split/splitless injector and an electron capture detector. The GC column used was a Varian Factor-Four VF-5 ms (30 m × 0.25 mm × 0.25 μm). Carrier gas was He (1 mL/min flow).

Endosulfan I, II and endosulfan sulphate standards were purchased from Dr Ehrenstorfer (Augsburg, Germany). All solvents were of pestiscan purity (Labscan Ltd, Dublin, Ireland).

For dust sampling, a large flat panel with a sleek and clean surface of one square meter was placed one meter above the ground level, in a mountainous isolated area of Crete, in the prefecture of Iraklion. The panel was thoroughly cleaned on the 25th of May and the deposited dust (~35 g) was collected on the 30th of May, after an intense dust "event". Samples were also collected when dust air masses were not present, in order to control for sources of contaminants other than African dust.

In order to assess interference from random impurities from solvents or glassware, a method blank was prepared using an aliquot of a clean solid matrix such as quartz sand of the approximate weight of the samples.

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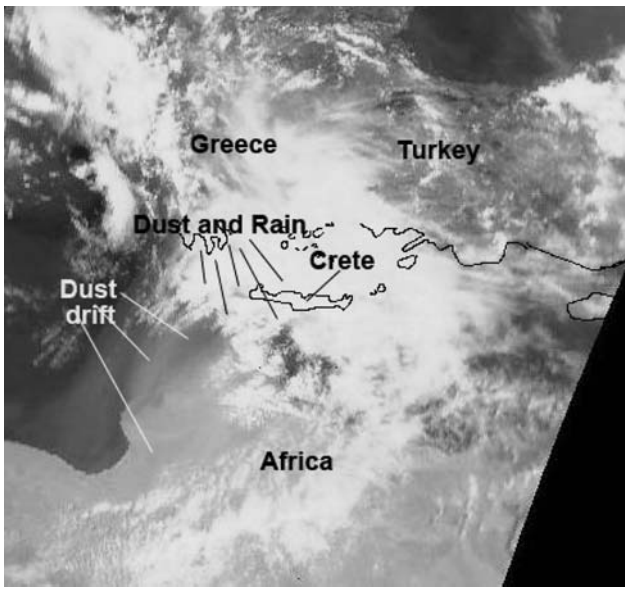

Fig. 1 Satellite picture of Eastern Mediterranean on 28th May 2007

Two aliquots of the sample were spiked at two different levels (Table 1). The spiked aliquots were left at room temperature overnight in a closed glass container before being subjected to the sample preparation procedure.

Sample preparation involved weighing 10 g of each sample directly in a Teflon® vessel appropriate for microwave assisted extraction (MWAE). 25 ml of acetone/hexane 1:1 mixture were added. The MWAE apparatus was operated at 800 W and samples were irradiated for 10 min at appropriate time intervals in order not to exceed 115°C. Next, the extracts were filtered, washed with another 25 ml acetone/hexane 1:1 mixture and evaporated until volume of 10 ml under a gentle stream of nitrogen.

Linearity of response of the detector was established at four different levels for each analyte, using the respective calibration solution mixtures.

The conditions of the GC-ECD chromatographic system used were: Injection port temperature 225°C, splitless (hold 4 min), column: VF-5 30 m × 0.25 mm id × 0.25 μm film thickness, column flow: 1 mL/min, oven temperature program: 100°C (2 min) then 15°C/min 160°C and then 6°C/min 270°C final temperature (5 min) Detector ECD: 300°C, make up gas N_2: 30 mL/min.

The presence of endosulfan I, II and sulphate was confirmed by analysis of samples and standards on a second (CP-Sil 5 Cb) and a third (DB-1701) columns of different polarity.

Results and Discussion

Dust transport and deposition has been implicated for many undesired effects i.e. radiation contamination of the environment (Prokopakis et al. 2007; Papastefanou et al. 2001), transport of bacteria, fungi and other microbes, as well as toxic chemicals to the Caribbean (Garrison et al. 2006, 2003; Griffin et al. 2002).

In a recent study (Tsatsakis et al. 2003) fenthion and dimethoate residues have been detected in organic olive oil at concentrations significantly different of those detected in olive oil from conventional cultivations. Such contamination could be related to contamination of the olive fruit from drift from neighbouring groves and from contamination in the olive mill during the extraction of the olive oil. However, in another study (Amvrazi and Albanis 2009) similar concentration levels of endosulfan were determined in olive oils from both organic and conventional cultivations. These detections cannot be attributed in such contamination.

During olive pre-harvest months-especially spring-rainfall combined with dust of African origin is a common phenomenon in Greece. It was thus decided to examine dust depositions from such dust storm events for the presence of endosulfan as a possible source of the abovementioned contamination.

Validation of the method included linearity of response of the ECD (r^2 for endosulfan I, II and sulphate were found 0.993, 0.996 and 0.999, respectively) and recovery at two levels of fortification for each analyte (>70%). The limit of detection and limit of determination was established by means of the concentration that gave a signal to noise ratio of 3 and 10, respectively, (Table 1). Lack of interference

Table 1 Linearity, recovery and limit of detection (LOD) and quantification (LOQ) of the method

Active ingredient	Linearity of response				Recovery				LOD (ng/g)	LOQ (ng/g)
					Level 1		Level 2			
	Level 1 (ng/g)	Level 2 (ng/g)	Level 3 (ng/g)	Level 4 (ng/g)	Fortification (ng/10 g dust)	Recovery (%)	Fortification (ng/10 g dust)	Recovery (%)		
Endosulfan I	10	5	2	1	50	80	100	71	0.06	0.15
Endosulfan II	4	2	0.8	0.4	20	110	40	76	0.08	0.18
Endosulfan sulphate	4	2	0.8	0.4	15	87	30	121	0.1	0.23

Table 2 Levels of endosulfan in sample

Active ingredient	Concentration in dust (ng/g)
Endosulfan I	2.7
Endosulfan II	1.4
Endosulfan sulphate	1.06

was established by analysis of laboratory blank samples. In field blank samples (i.e. dust samples collected during normal meteorological conditions) the analytes under study were found below limits of detection.

In the sample collected during the dust event, endosulfan I, II and sulphate were detected at 2.7, 1.4 and 1.06 ng/g, respectively, (Table 2). This is in complete accordance with the findings of a relative study (Garrison et al. 2006) where more than 100 analytes were screened in dust samples from African dust-source regions and downwind sites in the Caribbean. Endosulfan was detected in all samples.

Although endosulfan II is considered more stable to oxidative or photolytic degradation, the fact that endosulfan I is more abundant in our samples may be due to its strong adsorption on dust particles (Wadaskar et al. 2006).

Desorption of endosulfan from soil particles is favoured at either high or low pH in comparison to neutral pH (Kumar and Philip 2006). The low polarity waxy cover, the acidic cuticle and the increased fatty acid content of olives, present favourable conditions for selective endosulfan desorption from dust particles.

In conclusion, the method that has been developed in order to examine the presence of endosulfan I, II and sulphate in dust depositions of African origin, gave acceptable results for recovery and provided extracts without any interfering substances, an important advantage when extracting from dust or soil materials.

The analysed samples were found to contain endosulfan I, II and sulphate, in complete accordance to relevant studies. Thus, aeolian transport and deposition of African dust is a possible route of contamination of cultivations from endosulfan. The special characteristics of olives could favour the selective release of endosulfan from dust particles, explaining its presence in samples of organic olive oil produced in remote areas of Crete. Further investigation is in progress in order to confirm the above hypothesis.

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