

## Soil Contamination from Buried Pesticides

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The extensive application of pesticides creates an environmental risk due to the toxic pesticide residues, identified in air, water, soil, foods and human tissues. (Diskith, 1991). Their disposal especially by burial, a method widely applied in the past, apparently contributes to the soil contamination. The most important classes of pesticides are organophosphorus and organochlorine compounds. Generally, these compounds are degraded in soil by microorganisms to derive energy, carbon and other nutrients for their growth and metabolism, increasing their population and thus affecting the transformation of plant nutrients, in soil (Bollag 1982). Some pesticides (particularly organochlorine compounds) were banned after evidence of their toxicity, persistence and bioaccumulation in the environment and their ability to concentrate in the food chain. Organophosphorous compounds are considered to degrade, either biologically or chemically, in plants, animals and soils, more rapidly depending on their formulation, method of application, climate and soil types and conditions (Khan 1980). Data on the environmental fate of pesticides are required, in order to determine the potential of a pesticide to reach groundwater, including information on its hydrolysis, photolysis, aquatic metabolism, leaching and field dissipation. Since the fate of pesticide residues are of great importance, they are currently detected by determination in various environmental matrices. The chromatographic techniques used for pesticide analysis require efficient isolation and preconcentration procedures (Barcelo 1991, Miliadis 1994). Traditional extraction methods are often inconvenient (time consuming and expensive) for sample analysis and faster and more effective techniques such as solid phase extraction (SPE) are applied (Zief and Kiser, 1990).

In early seventies (1972) large quantities of pesticides were buried with large quantities of lime in various places in Greece as much as possible away from ground water. These pesticides were organochlorine pesticides banned from the Greek market or organophosphorus pesticides unsuitable for use. Today there has been an increased concern on the safety of the applied disposal method and on the soil contamination close to these places. The purpose of this study was to investigate the contamination of the soil from buried pesticides in two places in Greece, one in Attica and another in Messinia in South Greece.

## MATERIALS AND METHODS

Seven samples from two burial sites, one in Attica and one in Messinia were examined for pesticide residues. Four samples (At) were taken from the burial site itself in Attica, namely they were mixtures of pesticide residues and lime, one sample came from the soil exactly under the burial site (after digging) in Attica (A<sub>2</sub>) and consisted mainly of soil and lime and two samples were taken from the area close to the burial site in Messinia (M<sub>1</sub>, M<sub>2</sub>).

Based on our information related to at that time pesticide usage and discharge, the samples were examined for the presence of the most probable pesticide residues to be found. So, the samples from the first site in Attica (At) were analysed for the presence of dimethoate, dinocap, mevinphos, diazinon, and parathion E residues, while the samples from Messinia were analysed for aldrin, dieldrin, gamma-BHC (lindane), parathion E, parathion-M and p,p'-DDT residues.

The analytical method included an extraction procedure, a cleanup procedure and gas chromatographic analysis and it was a modification of the method described by Marble and Delfino (1989). For the extraction 50 g of soil were thoroughly mixed with 100 ml acetonitrile (extraction solvent) and 9 g sodium chloride (in an explosion-proof blender jar). After blending, the solvent and sample were transferred to a 500 ml conical flask and combined with small volumes of acetonitrile rinses of the blender jar. The sample was placed onto an horizontal flat-bed shaker and allowed to mix for 12 hr at 150 rpm. After shaking, the supernatant acetonitrile solution was filtered through 10 g anhydrous sodium sulphate. The soil sample was rinsed using 50 ml acetonitrile and filtered as above. The combined extracts were concentrated on a rotary evaporator to a volume of approximately 10 ml and stored at 4 °C until cleanup.

Cleanup procedure was the following: The Solid phase extraction C18 (pre-packed reversed-phase octadecyl-bonded silica) columns were preconditioned by passing through the column 3 ml methanol and then 3 ml HPLC grade water under vacuum, ensuring that the packing material remained wet. While cartridges were still wet, one ml aliquot of the above sample extract was mixed with one ml HPLC grade water and then loaded on the cartridge and pulled through under vacuum. The cartridges were, then, dried under vacuum for about 10- 15 min. The solvent phase was removed from the vacuum manifold. The analytes were eluted with 2 ml ethyl acetate. Fortified soil samples were prepared by adding to a 50 g soil sample standard mixture solution containing dimethoate, dinocap, mevinphos, diazinon and parathion E (2.5, 5.0 and 7.5 µg of each) for the Attica region samples and aldrin, dieldrin, gamma-BHC (lindane), parathion E, parathion-M and p,p'-DDT (1.25, 2.5 and 5.0 µg of each) for the Messinia region samples.

The chromatographic analysis of the aliquots from cleanup treatment was achieved using a Varian 3700 model gas chromatograph, equipped with two detectors, a Ni-63 electron capture detector (ECD) and a nitrogen-phosphorus

detector (NPD). A glass column (200 cm x 2 mm i.d.) was used, packed with 1 : 1 mixture of 10 % OV-101 plus 15 % OV-210 on Chromosorb WHP (80-100 mesh). The temperatures of injector, column and detector were maintained at 220 °C, 200 °C and 300°C, respectively. The flow rate of carrier gas (N<sub>2</sub>) was adjusted to 100 ml/min, the injection volume was always 21µl and two chromatograms were obtained for each sample. Quantification was achieved by use of a computer integrator. The average recovery was 90 % for the organochlorine compounds and 85 % for organophosphorus compounds.

## RESULTS AND DISCUSSION

Initially, some properties (pH, moisture content and appearance) of the collected soil samples were examined. The results are given in Table 1. It is obvious that the high pH value is due to the presence of lime.

**Table 1.** Characterization of soil samples

Name of sample	Moisture Content (%)	pH (1% in water)	Appearance
A <sub>1</sub> (Attica)	24	12	mud mixed with lime
A <sub>2</sub> (Attica)	24	12	mud mixed with lime
M <sub>1</sub> (Messinia)	14	9	mud
M <sub>2</sub> (Messinia)	14	9	mud

**Table 2.** Buried pesticide residues in soil (dry weight)

Pesticide Residue	Detection Limit ng	Attica (A <sub>1</sub> ) ppm	Attica (A <sub>2</sub> ) (ppm)	Messinia (M <sub>1</sub> ) (ppb)	Messinia (M <sub>2</sub> ) (ppb)
Aldrin	0.001			ND	ND
p,p'-DDT	0.002			ND	ND
Diazinon	0.01	15	ND		
Dieldrin	0.01			ND	ND
Dimethoate	0.02	30	ND		
Dinocap	0.50	ND	ND		
Lindane	0.0002			1.0	1.0
Mevinphos	0.5	30	ND		
Parathion-E	0.1	2	0.26	0.15	0.15
Parathion-M	0.1			ND	ND

ND not detected

The results of the determination of pesticide residues, based on the combination of SPE and chromatographic analysis, are presented in Table 2.

It is of great interest that organochlorine pesticides were not detected in any of the examined samples, since this group is considered persistent to biodegradation. The low content of A<sub>1</sub> samples in pesticides indicates that the buried pesticides have been significantly degraded and/or dissipated and their presence will continue to decline due to the high pH value and to the great amount of lime still remaining in the burial site. The detection of only one pesticide (parathion-E) in A<sub>2</sub> sample, below the burial area in Attica, at very low concentration (0.26 ppm) reveals that the soil contamination has been maintained at a very low level. The low traces of pesticides determined in Messinia samples (parathion-ethyl and lindane), which were close to the burial region, shows that it is extremely difficult to correlate these results to contamination caused by the buried pesticides in 1972.

From the results, it was concluded that there was no danger for soil contamination from the buried pesticides at least in the sites we investigated.

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