Bull. Environ. Contam. Toxicol. (1997) 58:348--355

Environmental Contamination and Toxicology

Identification of Mixed O-Phenyl Alkyl Phthalate Esters in an Agricultural Land

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Received: 6 January 1996/Accepted: 15 November 1996

We report the identification of several series of asymmetric O-phenyl alkyl phthalates in agricultural lands in the center and south of the Israeli Coastal Plain. These substances have been observed at both soil surface and soil depth, at concentrations up to 6000 ppb.

Symmetric phthalate esters (I, $R_x = R_y$) are among the most common industrial chemicals. They are produced in large amounts and are used as plasticizers, in particular for PVC. Among these esters, diisooctyl phthalate (DIOP) is one of the most widely used (Bemis, 1982). Non-plasticizer applications of phthalates include a broad spectrum of uses, such as insect repellent preparations, pesticide carriers, cosmetics, liquid soaps, detergents, and industrial and lubricating oils.

While some environmental studies have reported fast biodegradation of phthalates (Kurane 1986), many reports indicate the occurence of phthalates in environmental samples of water and sediments, in fish, and in various aquatic organisms (Sheldon and Hites 1978, Thuren 1986, Fatoki and Vernon 1990), in significant amounts, extending to the ppm range. Significant levels of phthalates have also been observed in Israel, in samples from the soil surface, in soil profiles and also in groundwater (Muszkat et al. 1993). Phthalates enter the water phase through several mechanisms: aqueous leaching of plastic and wastes, incineration of plastic wastes and also wet deposition out of the atmosphere. They are also introduced into the atmosphere by direct volatilization from resin matrices. Due to their hydrophobic nature they tend to be absorbed to suspended particles and accumulate finally in sediments and in the food chain. Their spread in the environment is highly enhanced by absorption to various surface active components as well as to the soil macroparticulate matter and particulate

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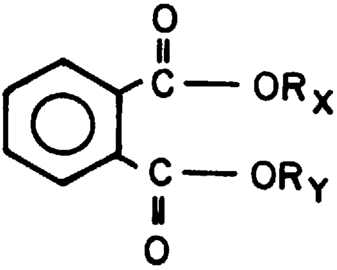


Figure 1. Structure of phthalate esters

organic matter (Giam and Atlas 1980). While the acute toxicity of phthalates to mammals is known to be low, there is suggestive information on their carcinogenicity (Giam et al. 1984). The direct degradation of phthalate esters in soil and the environmental effects of these substances seem to be poorly understood (Parkman and Remberger 1995). The existing information refers mainly to the symmetric phthalates and does not cover the asymmetric phthalate esters (I, R_x R_y), with different groups in the side chains, in particular mixed aromatic-aliphatic esters . Some of the asymmetric phthalates are known to be of high practical importance as plasticizers (Maksimenko et al. 1973).

In this paper we discuss the identification of asymmetric phenyl phthalate esters, (i.e., I, R_x R_y, $R_x = C_6H_5$, R_y being an aliphatic chain). These substances have been observed at relatively high levels in soil samples of several agricultural areas, both at soil surface, at depths of 2.0 and 4.5 m and also at a depth of 8.50 m, close to the water table level.

Table 1. Total phenoxy alkyl phthalates (ppb) in the unsaturated zone

Site	Depth (m)	ppb
Herzlia	soil surface	6000
Kfar Menachem	2.00	75
Ashdod	3.30-4.00	400
	8.00-8.60	260

MATERIALS and METHODS

The study of the phenyl phthalates was conducted in three cultivated areas (Table 1): **S1.** Near Herzlia, north of Tel Aviv, at the soil surface of a citrus grove, where irrigation was by groundwater. Soil surface at this site was composed of loamy clay, with DOC of about 20 mg/kg and field moisture 11% . **S2.** Near Kfar-Menachem (south eastern part of the Coastal Plain), where cotton is the main crop, at a depth of 2 m. Soil at this site was composed of mixed alluvial clay loam, rich of water content (40% field moisture) and with relatively high (33%) clay content. **S3.** An agricultural site close to Ashdod, in the vicinity of a polluted drinking water well (Muszkat et al. 1993) . Sampling was conducted at two depths: at a depth of 3.30-4.00 m yielding soil rich in clay (DOC 10 mg/kg), and at a depth of 8.00-8.60 m, close to the water table level. At 8m depth, the soil was composed of loamy sand, and DOC was 15 mg/kg. TOC values in Nir-Galim are relatively high (5%-7%), with high values up to 8% in the clay rich layers. TOC is known to correlate well with the clay content (Muszkat et al. 1992). Sampling procedures are described elsewhere (Muskat et al 1993).

Glassware was heated to 400°C to eliminate trace organic substances. The extraction solvents, methylene chloride and acetone, were of analytical grade, and, in addition, were double-distilled in our laboratory. Each soil analysis was repeated twice and was accompanied by blank analyses (solvents + reagents) and background GC/MS measurements. Concentrations were calculated against deuterated internal standards, added prior to the extraction step.
Analytical procedures are detailed elsewhere (Muszkat et al. 1993) .

RESULTS and DISCUSSION

The levels of the O-phenyl phthalates identified are summarized in Table 1, while Fig. 3 shows the reconstructed ion chromatogram (RIC) from soil samples at site **S1.** 26 components (total amount above 6000ppb), with a base peak of m/z=94 are shown. These GC/MS results were also observed in soil samples from sites **S2** and **S3.** They represent four series of phthalate esters as detailed in Scheme 1. This complex mixture of isomers is presumably due to the possibility of having isomers in the aliphatic chain and in the benzene part. These components emerged from the column at isothermal conditions (260°C), for about 12 minutes. Typical EI and isobutane-CI mass spectra are given in Fig. 2. The existence of two main groups of molecules is clearly seen: 1. molecular weight 354, main fragments 94 and

196, and 2. molecular weight 368, main fragments 94 and 210. The data rule out the nonionic surfactants alkyl phenol ethoxylates (APE). These are important pollutants of river water and of treated municipal wastewater but show different mass spectrometric patterns (Ventura et al. 1988, Shirashi et al 1985). The fragment m/z 94 is highly suggestive of phenoxy compounds . Thus the EI/MS of diphenyl phthalate (MW 318) reveals a base peak of m/z= 94 and a strong signal due to the complementary fragment, m/z 225 (40%). The common ion m/z 149 observed in many phthalates is missing here, (as well as the presently studied phenyl alkyl phthalates). This feature helped in interpreting the spectra, resolving the difficulty posed by the absence of the m/z 149 signal (McLafferty and Stauffer 1989). These results, supported fully by data of isobutane chemical ionization MS (CI/MS), point towards the isomeric series of O-phenyl alkyl mixed esters of phthalic acids (ortho and possibly meta and para). Two important mass spectrometric fragmentation products of O-phenyl phthalates **(Ia)** were observed (Scheme 1):
A. Phenoxyl ion, observed as the m/z= 94 base peak.
B. Ions of m/z=196 and m/z=210 (in CI the quasimolecular ions 197 and 211 were observed), assigned to the xanthone and the methyl xanthone (B) structure. This cleavage would occur via the abstraction of $^{\bullet}COOR_1$, followed by rearrangement of the complementary group described in scheme 1. In addition to this principal fragmentation pattern several minor patterns were observed, leading to the ions given in Scheme 2. This scheme includes the following paths: formation of **C** (ions 205, 219 and 233, at intensities of 2%-10%), by abstraction of the group $\bullet C_6H_5COO$; formation of **D** (ion 149, 1%-3%); formation of ions from group **E** (310 and 325, 2%-3%), the latter resulting in decarboxylation of the parent compound. The mechanisms of some of these cleavage patterns have been well documented in the mass spectrometric literature (McLafferty and Gohlke 1959). It should be noted that phthalate esters have been used as agrochemicals during the last several decades, both as insect repellents (dibutyl and dimethyl phthalate) and as major components of pesticide formulations (diisooctyl phthalate). The asymmetric phthalates described above may originate either from a deliberate agricultural treatment or from impurities during the application of other phthalate agrochemicals. Another possible source of these phthalates may be a leakage from an industrial dump, especially in the case of site **2** close to a pesticide plant.

It seems that the O-phenyl phthalates were deposited at the mentioned sites several years ago. Be that as it may, their presence at these sites suggests the lack of efficient natural mechanisms for their degradation.

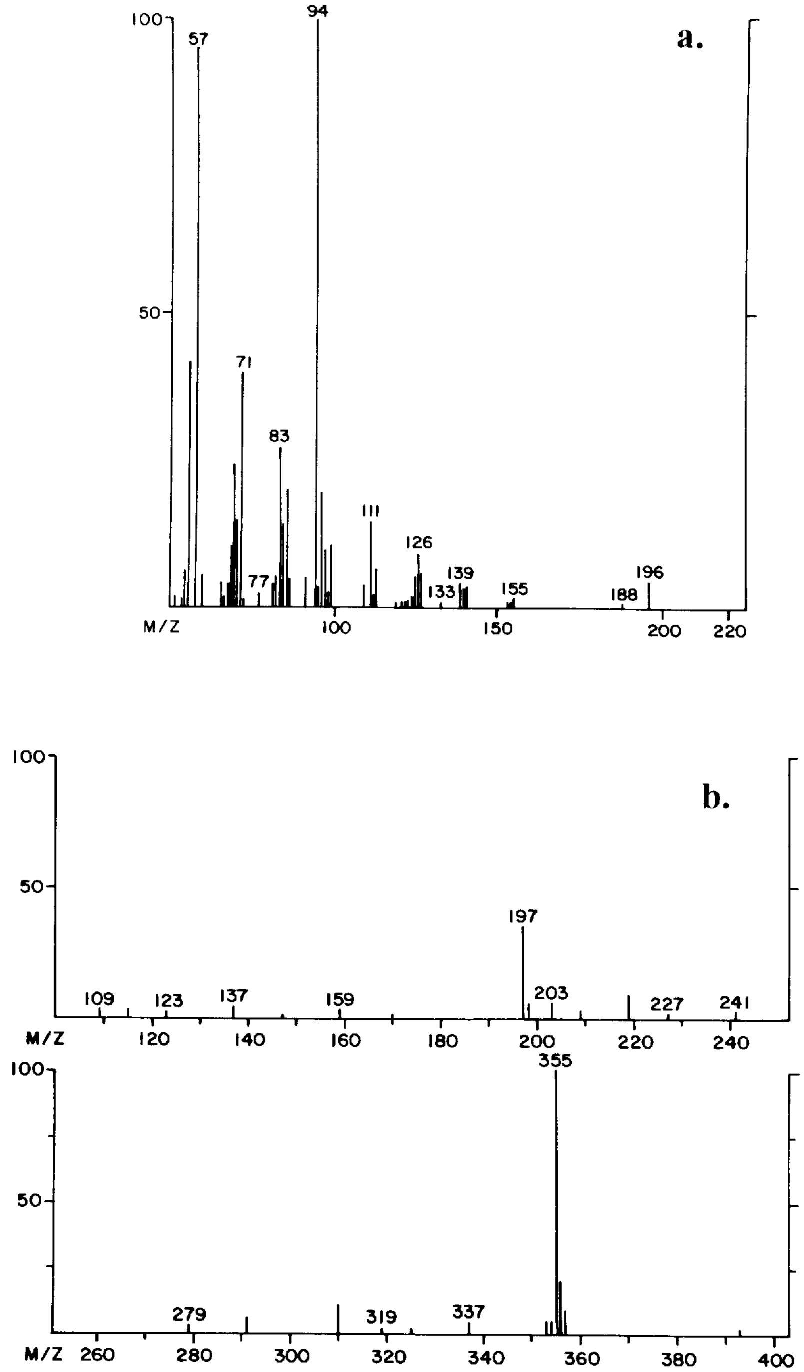
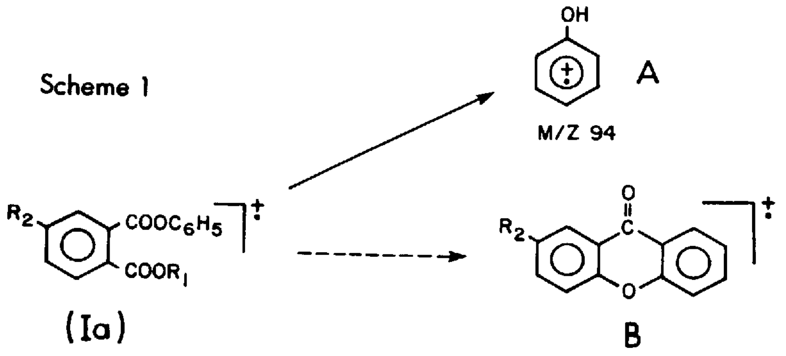


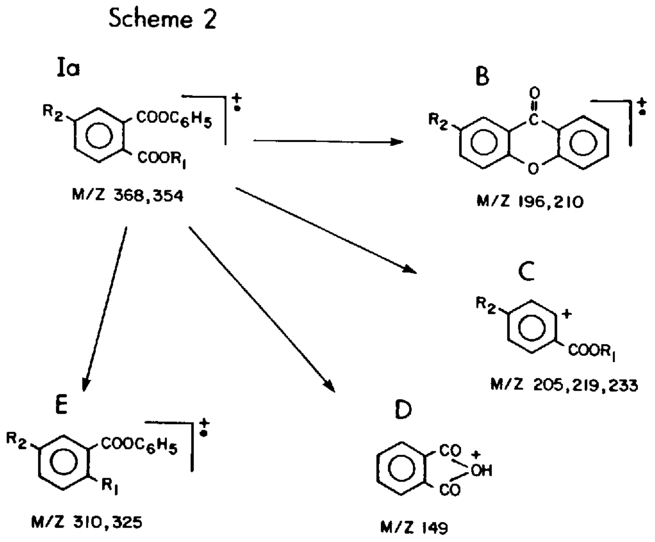
Figure 2. a. EI and b. Isobutane-CI mass specta of series with molecular weight 354.



R_1	R_2	M	M+1
C_8H_{17}	H	368	369
C_7H_{15}	H	354	355
C_7H_{15}	CH_3	368	369
C_6H_{13}	CH_3	354	355

R_2	M	M+1
H	196	197
CH_3	210	211

Scheme 1 Observed Main Fragmentation Patterns of O-Phenyl Alkyl Phthalates.



Scheme 2 Observed Minor Fragmentation Products of O-Phenyl Alkyl Phthalates.

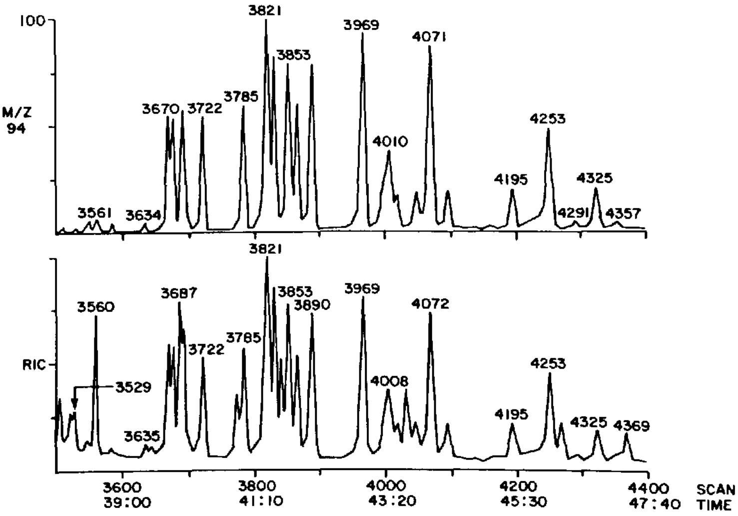


Figure 3. m\z 94 Reconstructed ion chromatogram (RIC), Obtained from soil samples close to Herzlia.

The ability of phthalates,both symmetric and asymmetric, of wide dissemination in the environment, by-passing the natural biodegradation processes and even penetrating deep into the soil, is of special interest, for it is to determine the groundwater quality of the specific area. The use of sewage sludge as soil fertilizer is becoming an accepted policy in many parts of the world, and is generally preferable to combustion or deposition of sewage sludge in landfills. Since phthalates are common contaminants of municipal effluents, their presence has to be considered in this context.

Acknowledgments. Soil samples examined in this report were collected within the framework of the German Israeli Foundation (G.I.F.) project on “The Fate of Organic Contaminants in Water and Sediments”, Principal Investigators L. Muszkat and I. Schuphan; Cooperating Investigators W. Ebing, M. Frost, D. Ronen and the Late M. Magaritz. The support of G.I.F. is gratefully acknowledged.

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