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Identification of Free Organic Chemicals Found in Composted Municipal Refuse¹

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ABSTRACT

Composted municipal refuse can be considered as a low-grade fertilizer, but its use on land is limited by the level of contamination from heavy metals and toxic chemicals. In order to evaluate the qualitative composition of the organic fraction of these materials, three Spanish refuse composts were analyzed.

The samples were sequentially extracted with ether and ethanol, which constitute the total lipids extract. The nonsaponifiable fraction is made up of *n*-alkanes, in the range of C₁₄ to C₃₁, as well as olefins. The saponifiable fraction contains *n*-fatty acids from C₁₄ to C₂₄ and some branched fatty acids. The method used for separation and identification of specific organic compounds in sediments was adapted for municipal composts and the resulting methylene chloride extract subjected to gradient chromatography on alumina. The fractions eluted from the column with pentane, and pentane-methanol contained aliphatic hydrocarbons; the benzene fraction was made up of phthalate esters, and the benzene-methanol and methanol fractions contained a mixture of aliphatic hydrocarbons, phthalate esters, *n*-fatty acid methyl esters, and some individual compounds. The presence of aliphatic hydrocarbons and fatty acids in municipal composts suggested a microbial origin, while phthalate esters may arise from the debris of plastic packaging.

Additional Index Words: aliphatic hydrocarbons, fatty acids, fatty acid methyl esters, phthalate esters.

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In Spain, as in other countries, three main methods are used for disposal of municipal refuse. While incineration is employed in a few cities, composting accounts for about 10% of municipal refuse produced. The most common technique, and it is likely to continue to be so in the near future, is dumping.

In 1978 the Spanish production of composted municipal refuse was 438,800 metric tons, from which 51% was applied to vineyards, 24% to horticultures, 9% to citrus, 4% to cereals, 3% to beets, 3% to almond trees, and <1% to rice³. As supplies of farmyard manure

have fallen and the resources of other organic substrates are quite exhausted in Spain, composted municipal refuse has become more widely used on farm land and this practice is expected to become more popular in the future.

Compost contain >50% organic matter and almost all the nutrients needed by plants and, thus, seem to be of benefit for application in agriculture or horticulture. Field experiments have shown that addition of compost will improve soil physical properties (12), and the pH, organic matter, and some macro- and micronutrients levels were also increased (13). Therefore, compost can be considered as a low-grade fertilizer. Its potential use on land, however, will be limited by the level of contamination from heavy metals and toxic chemicals. Soil and plant tissues analyses indicated that potentially toxic compounds could accumulate in the soil if compost were applied at heavy rates (15), and that compost application may cause ground water pollution (7).

While considerable literature has been published about the effects of toxic inorganic compounds in soils, as far as we know no data are available on free noxious organic compounds present in composts. The only reference we found was related to sewage sludges, in which Boyd et al. (2) isolated phthalic acid esters and fatty acid methyl esters by Soxhlet extraction with hexane, benzene, acetone, and methanol.

In the present communication, we report the isolation and identification of free organic compounds in three different Spanish refuse composts, which represent about 30% of total Spanish compost production. It is expected that this study may contribute to a more complete knowledge of the characteristics of these materials.

MATERIALS AND METHODS

The raw refuse (mainly paper wastes and household garbage) were collected from the metropolitan areas of Sevilla, Puerto Real, and Granada. The mean composition of the refuse on a percent dry-weight basis were: paper, 15-20; metals, 3.5-5; glass, 2.5-6; plastics, 3-8; organic matter, 40-50; miscellaneous, 36-11; and moisture, 40-50. In the treatment plants several operations (picking, shredding, screening, etc.) were carried out before the fermentation stage.

The air-dry compost samples, with a minimum of 3 months of composting were classified in the laboratory by means of a grinding and screening apparatus. The fraction <2 mm (dark, well-decomposed state, and fine texture) represents between 54 and 62% of the total sample weight, and its chemical analysis is shown in Table 1.

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³Virgil, F. The compost in Spain. Present and future. (In Spanish.) Int. Conf. on Compost, Madrid, Spain. January 1980. Office of Environment, Ministry of Public Works and City Planning, Madrid.

Table 1—Chemical analyses of the three compost samples.

Content	Sevilla	Puerto Real	Granada
	%		
Moisture	32.5	29.0	32.9
Ash	51.0	61.2	56.0
Oxidizable C	15.1	9.9	13.6
Total organic matter	49.0	38.8	44.0
N	1.4	1.0	1.5
P	0.6	0.2	0.4
K	0.7	0.3	0.6
Ca	7.5	5.5	8.5
Mg	0.5	0.2	1.0
S	0.2	0.3	0.5
	ppm		
Micronutrients			
Fe	2,230	1,250	3,360
Mn	500	1,250	1,100
Cu	200	180	200
Zn	700	4,000	500
B	3	15	n.d.
Nonessential heavy metals			
Cd	0.04	0.09	0.09
Ni	0.76	1.08	0.81
Cr	1.52	2.07	1.80
Pb	8.69	12.35	10.78

Two different methods were followed for isolation of free organic compounds. One of them involved the extraction of samples (10 g) of composts sequentially with ether and ethanol for 18 hours each using a Soxhlet extractor. A combined sample of both extracts, which constituted the total lipid extract, was separated into saponifiable and nonsaponifiable fractions. The first fraction was methylated with diazomethane prior to gas chromatographic analysis.

The other method was that of Hites and Biemann (6), initially developed for identification of specific organic compounds in sediments from a highly polluted river. The method has been shown to separate aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, and phthalate esters in different fractions, and it was adopted for this study because most of the expected compounds in composts fall into these classes of organic compounds. The method consists of extraction of the samples (10 g) with methylene chloride for 18 hours in a Soxhlet extractor. The solvent was evaporated under vacuum at 25°C and the extract was weighed (Table 2). The extractable matter was dissolved in a small volume of methylene chloride and subjected to gradient chromatography on neutral alumina. Woelm alumina was washed with methylene chloride several times and then activated at about 95°C for several hours. A 26-ml column (9 mm i.d.) was prepared with a slurry of alumina in pentane, and five fractions were eluted with a succession of solvents as follow: pentane, pentane-benzene (1:1), benzene, benzene-methanol (1:1), and methanol. Each fraction was evaporated to dryness and redissolved in a small amount of methylene chloride.

Table 2—Quantitative distribution of compost organic fractions.

Fractions	Puerto			Major compounds
	Sevilla	Real	Granada	
	mg/10 g			
Ether extract	44	33	27	—
Alcoholic extract	36	41	35	—
Total lipid extract	80	74	62	—
Saponifiable fraction	28	31	42	Fatty acids
Nonsaponifiable fraction	40	24	8	Alkanes
Methylene chloride extract	37	21	26	—
Pentane fraction	7	6	6	Alkanes
Pentane-benzene fraction	4	2	3	Alkanes
Benzene fraction	6	4	5	Phthalate esters
Benzene-methanol fraction	5	3	4	Phthalate esters and fatty acid methyl esters
Methanol fraction	3	1	2	Phthalate esters and fatty acid methyl esters

The different fractions were analyzed by direct injection into a gas-chromatograph-mass-spectrometer computer system (Hewlett-Packard mod 5992 B). Separation of compounds was achieved using a 3,000 by 3 mm stainless steel column packed with 3% OV-17 on Chromosorb W HMDS 80-100 mesh, programmed from 100 to 270°C at a rate of 6°C/min, and then isothermal for 15 min.

Helium at a flow rate of 20 ml/min was used as carrier gas. Mass spectrometer conditions were: MS peak detect threshold 50 linear counts, scan speed 690 amu/sec, electron multiplier 1400 eV, electron energy 70 eV, and mass range 40-800.

RESULTS AND DISCUSSION

The nature of the municipal refuse is complex and heterogeneous. During the composting process, biological degradation of a variety of more-or-less readily decomposable compounds (sugars, starches, hemicelluloses, lignins, tannins, fats, celluloses, oils, proteins, etc.) results in formation of a relatively humified stable product. In this paper, only the nonhumified free organic compounds were studied.

The lipid fraction of Spanish composts consisted mainly of aliphatic and olefinic hydrocarbons (non-saponifiable fraction) and fatty acid methyl esters (saponifiable fraction). Since the latter fraction was methylated prior to the gas chromatographic separation it is likely that fatty acid methyl esters are present in this fraction largely as fatty acids rather than as esters.

Figure 1A shows the gas chromatogram of the non-saponifiable fraction of Sevilla compost which exhibits an evident *n*-alkane pattern in the range of C₁₈ to C₃₂ with maxima at C₂₇. In addition to *n*-alkanes, the corresponding series of olefins can also be found as minor compounds in the chromatogram. All the other composts studied had similar patterns and distributions of *n*-alkanes, but in the Puerto Real sample the predominant *n*-alkane was C₂₅.

The C preference ratio (ratio of C-odd to C-even compounds) of the nonsaponifiable fraction was 1.05. The range of alkanes from composts, its predominance, and C preference ratio was similar to those reported for microbial hydrocarbons (20). Stransky et al. (18) found that the ratio of odd to even C-numbered alkanes was approximately one in primitive plants, whereas in cuticular waxes of higher plants the odd-number homologues predominated. Furthermore, Jones (8), Fisher et al. (4), and Weete (20) reported an equal distribution of C-odd to C-even hydrocarbons for microorganisms including *Aspergillus* and *Penicillium*, two of the most frequent fungi in the composting process, as reported by Poincelot (14). These facts strongly suggest that the compost hydrocarbons are mainly of microbial origin.

The Puerto Real saponifiable fraction (Fig. 1B) showed a range of *n*-fatty acid methyl esters from C₁₄ to C₂₆, C₁₆ being the most abundant acid, followed by C₁₈. In addition to *n*-fatty acids, some branched-chain fatty acid methyl esters could be identified. The distribution of the *n*-fatty acids and the fact that a very high percentage of total *n*-fatty acids are C₁₆ and C₁₈ acids also indicates a microbial origin for the bulk of the fatty acids isolated (5). Therefore, the lipid fraction of compost is derived from microorganisms, inasmuch as dead and living microorganisms can be 25% of the weight of composts (14).

In general, the compounds that were identified in the composts using the method of Hites and Biemann (6)

could be divided into three groups. The first group (the pentane and pentane-benzene fractions from alumina chromatography) contained aliphatic and olefinic hydrocarbons. The second group (benzene fraction) contained mainly phthalate esters instead of the polycyclic aromatic hydrocarbons found in sediments. The third group (benzene-methanol and methanol fractions) contained a mixture of *n*-alkanes, phthalate esters, *n*-fatty acid methyl esters, and some individual compounds.

Fig. 1—(A) Gas chromatogram of the nonsaponifiable fraction of Sevilla compost; (B) Gas chromatogram of the saponifiable fraction of Puerto Real compost.

The gas-chromatography-mass-spectrometry analyses of the pentane and pentane-benzene fractions showed them to have the same composition of the non-saponifiable fraction previously studied, and therefore, they will not be discussed.

Figure 2A shows the Sevilla benzene fraction chromatogram indicating the presence of diisobutyl, di-*n*-butyl, dioctyl, dicyclohexyl, di-(2-ethylhexyl) phthalates, and di-(2-ethylhexyl) azelate. The Puerto Real and Granada composts had comparatively less phthalates, however, diisobutyl, di-*n*-butyl, and di-(2-ethylhexyl) phthalates were found in the former, and di-*n*-butyl and di-(2-ethylhexyl) phthalates in the latter. In all the three composts, phthalate esters represent between 80 and 87% of the benzene fraction, as estimated by gas chromatography.

Fig. 2—(A) Gas chromatogram of the benzene fraction of Sevilla compost; (B) Gas chromatogram of the benzene-methanol/methanol fraction of Sevilla compost.

Phthalates have been reported in a wide variety of substances (foods, milks, soils, plants, and animals) over a wide geographic area. They are used in industry as plasticizers, pesticide carriers, cosmetics, fragrances, oils, and insect repellents (13), and therefore are commonly present in municipal wastes. Berk et al. (1), examining the effects of 24 species of fungi, noted that phthalate esters do not serve as C sources for fungi. Klausmeier and Jones (9) studied the metabolism of phthalates in enrichment cultures, and found that di-*n*-octyl and diallyl phthalates did not support growth and that growth with dimethyl phthalate was scanty. Moderate microbial growth was noted with diethyl, dipropyl, dibutyl, butyl isodecyl, *n*-octyl, *n*-decyl, and isooctyl isodecyl phthalates. More recently, Engelhardt et al. (3) tested the ability of *Penicillium lilacinum* and three bacteria to degrade di-*n*-butyl, diisobutyl, di-*n*-octyl, and di-(2-ethylhexyl) phthalates. The corresponding monoesters were identified as degradation products. Therefore, the persistence of the phthalate esters after the composting process is not surprising.

The benzene-methanol and methanol fractions of each compost have the same composition, and therefore, were combined. Figure 2B shows the chromatogram of this fraction from Sevilla compost. The presence of *n*-C₁₄, *n*-C₁₆, *n*-C₁₈, and *n*-C₂₀ fatty acid methyl esters, di-(2-ethylhexyl) azelate, dicyclohexyl phthalate, di-(2-ethylhexyl) phthalate, diphenylsulfone, and caffeine was established.

The Puerto Real benzene-methanol-methanol fraction contains two isomers of tributyl phosphate, *n*-C₁₆, and *n*-C₁₈ fatty acid methyl esters, *n*-C₁₄ and *n*-C₁₆ alkanes, dibutyl phthalate, and di-(2-ethylhexyl) phthalate, while in the Granada fraction tributyl phosphate, nonylphenol, dibutyl phthalate, di-(2-ethylhexyl) phthalate, and *n*-C₁₈ fatty acid methyl ester were identified. The presence of methyl esters of fatty acids in these fractions not previously methylated in laboratory, indicated that these esters might be of biological origin. In fact, Laseter et al. (11) and Laseter and Weete (10) reported that in addition to free fatty acids, methyl and ethyl esters were present in abundance in fungi, C₁₆ being the predominant ester. Tributyl phosphates are used as plasticizers in industry (17), nonylphenol as detergent, and caffeine may arise from the residues of coffee infusions widely drank in Spain.

From the results reported here it is evident that application of municipal compost to land adds free organic chemicals, namely alkanes, fatty acids, and phthalate esters. The question arises whether these compounds may be toxic to plants and soils. Taking into account the maximum contents of total lipids and the mixture of compounds extracted by methylene chloride, the application of a normal rate of 30 metric tons/ha adds 0.05 and 0.025 ppm, respectively, of the above compounds to the 0- to 20-cm surface layer of soil. Obviously, the chemicals cannot be considered toxic at this low level, considering, furthermore, the detoxification that occurs in soil due to both the adsorption of these organic compounds on soil constituents (16) and to the biological decomposition process. It has been found (unpublished results) that oxidative degradation of humic acids isolated from these composts yields the same type of com-

pounds previously identified. This indicates that the amount of toxic organic chemicals present in compost would be higher than those determined by solvent extraction. Furthermore, as shown in Table 1, the excessive quantities of some micronutrients in these composts point out that repeated heavy applications would carry a risk of progressive contamination of the soil and lead to plant toxicity; however, the significance of pollution due to organic chemicals in composts is presently unknown.

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