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Degradation and Adsorption of Pesticides in Compost-Based Biomixtures as Potential Substrates for Biobeds in Southern Europe

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Biobeds have been used in northern Europe for minimizing point source contamination of water resources by pesticides. However, little is known regarding their use in southern Europe where edaphoclimatic conditions and agriculture practices significantly differ. A first step toward their adaptation in southern Europe is the use of low-cost and easily available substrates as biomixture components. This study investigated the possibility of replacing peat with agricultural composts in the biomixture. Five composts from local substrates including olive leaves, cotton crop residues, cotton seeds, spent mushroom substrate, and commercial sea wrack were mixed with topsoil and straw (1:1:2). Degradation of a mixture of pesticides (dimethoate, indoxacarb, buprofezin, terbuthylazine, metribuzin, metalaxyl-M, iprodione, azoxystrobin) at two dose rates was tested in the compost biomixtures (BX), in corresponding peat biomixtures (OBX), and in soil. Adsorption−desorption of selected pesticides were also studied. Pesticide residues were determined by gas chromatography with nitrogen−phosphorus detector, except indoxacarb, which was determined with a microelectron capture detector. Overall, BX degraded the studied pesticides at rates markedly higher than those observed in soil and OBX, in which the slowest degradation rates were evident. Overall, the olive leaf compost biomixture showed the highest degradation capacity. Adsorption studies showed that OBX and BX had higher adsorption affinity compared to soil. Desorption experiments revealed that pesticide adsorption in biomixtures was not entirely reversible. The results suggest that substitution of peat with local composts will lead to optimization of the biobed system for use in Mediterranean countries.

KEYWORDS: Pesticide degradation; adsorption; biobeds; biomixtures; compost; peat

INTRODUCTION

Point source pollution has been identified as a major factor contributing to the contamination of groundwater (GW) resources with pesticides (*1*−*3*). This is usually caused by pesticide mishandling such as inadequate control of spray leftovers, accidental spillage or leakage during pesticide loading, or spray tank washdown after application or as an accident during pesticide storage (*4*). In these cases, high pesticide loads are released into restricted areas with the potential to leach to GW. Therefore, in an effort to minimize the risk for point source contamination, biofiltration systems were developed (*5*).

The most commonly used on-farm pesticide biofiltration system is called a biobed. It is a simple to operate and cost-effective multilayered construction in the ground in the form of a pit filled with a mixture of bioorganic substrates (*6*, *7*). Their efficacy is based on their increasing capacity to adsorb pesticides or stimulate their rapid biodegradation by offering favorable physicochemical and biological conditions for maximum microbial activity. Biobeds were first proposed by Torstensson and Castillo in 1993, and now more than 1500 biobeds are currently operative in Sweden. Studies on full-scale systems showed that they manage to dissipate from 95 to 99% of the applied pesticides (*8*). Over the years there have been several modifications of the original design to adapt to the specific climatic conditions and requirements of other countries including the United Kingdom (*9*−*11*), Italy (*12*, *13*), Belgium (*14*), and Denmark (*15*).

The main component of a biobed, the biomixture, has been identified as a major factor controlling the efficacy of the biobed (*4*). An efficient biomixture favors pesticide sorption and supports an active microbial community able to degrade pesticides at high concentrations. In its typical form the biomixture consists of peat, straw, and topsoil at volumetric proportions of 1:2:1. Each of these components has a key role in biobed

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function: (i) soil offers sites for sorption and an active microbial community for pesticide degradation; (ii) lignocellulosic material in the form of straw (*6*), vine branches, and citrus peels (*16*), chitin (*17*), coconut byproduct (*18*), or sugar cane residues (*19*) acts as a carbon and nutrient source; and (iii) peat shows a higher sorption capacity, improves porosity, and sustains optimum water conditions. Nevertheless, the use of peat has been criticized due to its relatively high cost and limited availability, especially in southern Europe (*16*). In addition, its extensive use is not considered plausible with sustainable agricultural practice (*9*), stressing the need for its replacement by novel substrates characterized by high availability and low cost in the local agricultural market. Recent studies have proposed the replacement of peat with agricultural composts, the extensive use of which is considered to be an environmentally sound practice (*16*).

Composts and peat differ substantially in physicochemical characteristics, nutrient availability, and biological activity (*20*). Although the characteristics of individual composts are largely dependent on composting practices and its components (*21*), they are generally characterized by lower C content, higher levels of macronutrients such as N, P, and K, and neutral to basic pH compared to peat, which has a higher water-holding capacity, a significantly lower density, and an acidic pH. These large differences in the characteristics of peat and compost may reflect differences in the efficacy and robustness of the pesticide-degrading microflora and the overall dissipation capability of the biomixture. Peat-containing biomixtures (OBX) generally promote cometabolic pesticide degradation by offering an ideal environment for the growth of white rot fungi and consequent production of lignolytic enzymes able to catalyze the degradation of a wide range of compounds (*4*). On the contrary, the neutral to basic pH and high N availability of compost-based biomixtures (BX) promote metabolic pesticide degradation by bacteria (*4*).

So far, there are only limited and contradictory data regarding the relative and comparative performance of BX or OBX for the degradation and adsorption of pesticides. In a previous study, a composted manure-containing biomixture showed better degradation efficiency than the corresponding OBX (*22*). On the other hand, substitution of peat with green waste compost in the biomixture resulted in a reduction of the pesticide degradation rate (*23*). In another similar study, garden compost was proven to be more efficient than urban waste compost for the degradation of chlorpyrifos and its main metabolite, trichloropyridinyl (*16*). Thus, the main aim of this study was to assess different composts, relevant to local agriculture in southern Europe, as potential alternatives for peat in the traditional biomixture used in biobeds.

MATERIALS AND METHODS

Chemicals. Analytical standards of metribuzin (MTR, 99% purity), buprofezin (BUP, 99.3%), metalaxyl-M (MTX, 99.1%), azoxystrobin (AZX, 99%), iprodione (IPR, 99%), and dimethoate (DIM, 99%) were purchased from Chem Service (West Chester, PA), whereas indoxacarb (IND, 99.6%) and terbuthylazine (TRB, 99.4%) were donated from DuPont and Syngenta, respectively. Individual stock solution standards (1000 μg mL^{-1}) from the above analytical standards were prepared in acetone and stored at −18 °C. A mixture standard stock solution (containing all compounds) and working solutions were prepared in acetone. Calibration standard solutions for the degradation experiments were prepared in studied biomixtures and soil extracts, whereas those for the adsorption−desorption experiments were prepared in the appropriate extracts.

Composts and Preparation of the Biomixtures. A sandy clay loam soil (sand 54%, silt 26%, clay 20%) was collected from the upper soil layer (0−20 cm) of a peach orchard in Ampelies, Edessa, northern Greece. It was sieved through a 2 mm sieve and stored at 4 °C until further use. The soil had never been treated with any of the studied pesticides. Dry wheat straw was cut into small pieces (1−3 cm) able to pass through a 4.75 mm sieve.

The five composts tested differed in the composting method utilized for their preparation and also in the origin of the raw material used. The olive leaves (C2) and cottonseed (C5) composts were prepared in laboratory-scale composting buckets (75 cm × 75 cm × 70 cm). Olive leaves and cottonseeds (after oil extraction) were collected from a local olive mill and a cotton ginning house in Thessaly, respectively. The produced composts were left to mature for several months prior to subsequent use. The *Agaricus bisporous* spent mushroom substrate compost (C1) was collected from a mushroom-producing unit (Lazarina, Karditsa) and composted with horse manure and straw with the addition of small amounts of sand and limestone. It was kept in storage under temperate conditions to ensure complete maturation. Cotton residues (stems, cotton fibers) (C4) were composted in uncovered heaps with the addition of external N in the form of NH_4NO_3 (23 g kg^{-1}) at the beginning of the composting process. *Posidonia oceanica* sea wrack compost (C3) is a commercial product used in flower gardening. Two commercially available peat mixes (Maxiflori, Agroflora S.A., P1; and Univeralsubstrat, Klasmann-Deilmann GmBH, P2) were also included in the study for comparison purposes. All of the above materials were passed through a 3.15 mm sieve to exclude extraneous material and constituents exceeding the mean particle size.

Biomixtures were prepared by mixing manually soil, wheat straw, and one of the composts or peat types at volumetric proportions of 1:2:1. The biomixtures were kept in storage at room temperature to stabilize prior to their use. Previous studies have shown that a stabilization period maximizes the adsorption and degradation capacity of the biomixture (*14*). The main physicochemical characteristics of the soil, peat, and composts used in the experiment as well as those of the biomixtures prepared are presented in **Table 1**. Water-holding capacity (WHC) was measured gravimetrically following saturation of the substrate (30 g) with distilled water in a funnel with Whatman no. 1 filter paper and allowed to drain for 24 h. The pH was measured in a mixture of air-dried substrate and deionized water (1:5 w/v). Organic C content was measured by using the Walkey and Black oxidation method (*24*), and total N was determined after digestion with H_2SO_4 according to AOAC Official Methods of Analysis, method 976.06. Dissolved organic carbon (DOC) was estimated after extraction of 6 g of substrate dry weight (dw) with 20 mL of deionized water for 12 h, followed by centrifugation (10 min, 6000*g*) and filtration (0.45 μm). Lignin content was estimated using the acetyl bromide technique as proposed by Hatfield et al. (*25*). Total phenolics were extracted according to the method of Erhart et al. (*26*) and measured according to the method of Swain and Hillis (*27*) using gallic acid for standard curve preparation.

Degradation Studies. Mixed spiking solutions of eight pesticides were prepared using formulated products of dimethoate (Dimethoate 40 EC, DIM), indoxacarb (Steward 30 WG, IND), buprofezin (Applaud 25 WP, BUP), terbuthylazine (Action puro 50 SC, TRB), metribuzin (Sencor 70 WG, MTB), metalaxyl-M (Ridomil gold 48 SL, MTX), iprodione (Rovral 50 SC, IPR), and azoxystrobin (Quadris 25 SC, AZX). Pesticide selection was based on the range of their physicochemical characteristics and their frequent use in Greece in a substantial number of crops. All pesticides were applied in the different substrates at two dose rates. For the low application rate, DIM, IND, BUP, TRB, MTB, MTX, IPR, and AZX concentrations in the substrate were 3.3, 0.4, 1.6, 7.3, 4.4, 4.0, 5.2, and 3.1 μg of active ingredient (ai) g^{-1} of biomixture dw, respectively. The high application rate corresponded to 10 times the low dose, and it was applied in a second batch of all biomixtures.

The choice of application doses was based on a hypothetical scenario of eight 500 L spray tanks containing the pesticides after field application. Each pesticide remaining in the tank corresponds to 1% (low dose) and 10% (high dose) of the initial quantity of pesticides loaded in the tank. The sprayers were washed over the biobed, and the sum of pesticides end up in the biobed. For the estimation of pesticide concentration contained per mass of biomixture the following assumptions were made: (i) pesticide concentration in the sprayer corresponds to the mean recommended dose rate; (ii) the biomixture had a density of 600 g L^{-1}; and (iii) the pesticides were limited in the upper 10 cm layer of the biomixture and were uniformly spread over a 10 m^2 area.

Table 1. Physicochemical and Biological Characteristics of the Substrates and Biomixtures Used in the Experiment

substrate	density (mg mL^{-1})	WHC (%)	pH	organic C (%)	DOC[a] (%)	total N (%)	lignin (%)	total phenolics (μg g^{-1})	TCMB[b] (mg of C kg^{-1} of soil)	C/N
soil (S)	1.189	nd	6.57	1.8	0.01	0.19	nd[c]	nd	22.04	9.47
straw (Str)	0.112	nd	7.30	42.9	nd	0.56	17.7	1566.8	nd	76.61
peat 1 (P1)	0.282	nd	4.62	45.7	0.37	1.10	30.1	491.3	nd	41.55
peat 2 (P2)	0.274	nd	5.62	43.1	0.41	1.11	19.7	nd	nd	38.82
spent mushroom substrate compost (C1)	0.214	nd	6.74	25.9	1.01	2.49	22.6	94.1	nd	10.40
olive leaf compost (C2)	0.498	nd	7.51	24.4	0.70	3.15	14.2	132.0	nd	7.75
sea wrack compost (C3)	0.794	nd	8.68	7.3	0.12	0.46	6.4	11.4	nd	15.87
cotton residue compost (C4)	0.561	nd	6.76	10.6	0.11	1.52	9.8	64.7	nd	6.97
cottonseed compost (C5)	0.423	nd	7.37	30.1	2.10	6.21	9.4	312.8	nd	4.85
BX1 (C1 + Str + S)	nd	132.1	6.69	10.6	nd	0.81	nd	nd	82.4	13.09
BX2 (C2 + Str + S)	nd	149.4	7.36	10.8	nd	0.98	nd	nd	133.1	11.02
BX3 (C3 + Str + S)	nd	123.6	7.88	6.5	nd	0.28	nd	nd	65.5	23.21
BX4 (C4 + Str + S)	nd	141.1	6.74	8.7	nd	0.60	nd	nd	71.8	14.50
BX5 (C5 + Str + S)	nd	144.5	7.29	11.5	nd	1.61	nd	nd	134.6	7.14
OBX1 (P1 + Str + S)	nd	167.8	5.03	11.9	nd	0.38	nd	nd	63.9	31.32
OBX2 (P2 + Str + S)	nd	174.3	5.94	11.8	nd	0.39	nd	nd	151.0	30.25

[a] Dissolved organic carbon. [b] Total carbon microbial biomass. [c] Not determined.

Two bulk samples (1000 g of dw) from each biomixture were initially prepared and separated into 27 subsamples (30 g), which were individually treated with aliquots (0.2 mL g^{-1} of biomixture) of an aqueous solution containing a mixture of the above pesticides. The biomixture subsamples were thoroughly mixed to ensure uniform distribution of the pesticides, and moisture content was adjusted to 45% of the WHC with the addition of deionized water. This moisture level was selected as representative of the moisture content of the biomixture in on-farm biobed systems in the Mediterranean region during the cultivating season, which is characterized by low rainfall and high daily temperatures. The subsamples were subsequently transferred to aerated plastic bags and incubated in the dark at 25 °C. Immediately after pesticide application and at regular intervals thereafter (0, 3, 7, 14, 21, 28, 42, 56, and 70 days), triplicate samples from each treatment were removed from the incubator and stored at −20 °C until further analysis. The moisture content of the samples was maintained constant with regular additions of deionized water.

For analysis, triplicate subsamples (2 g of dw) for each sampling time and for each biomixture were weighed in 40 mL screw-capped vials and extracted with 10 mL of acetone. The vials were ultrasonicated for 10 min and shaken in an orbital shaker (200 rpm) for 1 h. After centrifugation (6000*g*, 10 min), 5 mL of the supernatant was collected and cleaned up through Supelclean Envi-Carb SPE cartridges (500 mg, Supelco) previously activated with 1 mL of hexane and 5 mL of acetone. Pesticides were eluted with 5 mL of acetone, and the eluent was subsequently evaporated to dryness in a rotary evaporator. The residue was redissolved in 1 mL (low dose) or 2 mL (high dose) of acetone and used for chromatographic analysis as described below.

The mean recovery values of pesticides, produced from recovery experiments realized in studied substrates, ranged from 93% for AZX to 120% for IND (four fortification levels with three replicates per level) with relative standard deviations of < 14%.

Biological Characteristics of the Biomixtures. Temporal changes in the size and activity of the microbial biomass in the different biomixtures during the degradation study were also determined by measuring microbial respiration, fluorescein diacetate hydrolytic activity, and ergosterol content. Microbial respiration was determined according to the substrate-induced respiration method (*28*). Ergosterol content was measured as proposed by West et al. (*29*). Total hydrolytic enzyme activity was estimated by using the fluorescein diacetate (FDA) method (*30*). All of the above assays were performed in the samples treated with the high pesticide dose rate, with which higher microbial responses were expected after exposure to the higher pesticide dose and which represent also a more realistic scenario regarding biobed exposure. Immediately after application and at fixed time intervals thereafter, subsamples of the different substrates were removed for microbial measurements. The total C microbial biomass was determined only at 0 days via quantification of ninhydrin reactive N as described by Mele and Carter (*31*).

Adsorption−Desorption Studies. Among the eight pesticides used in the degradation study the pesticides chosen for the adsorption studies were TRB, MTR, and MTX because they are classified as medium to highly mobile (GUS index) and they are frequently detected in natural aquifers (*32*−*36*). Indoxacarb, a highly adsorbed pesticide, was also included in the study for comparative purposes, and its adsorption was tested in OBX, topsoil, and selected compost biomixtures (BX1 and BX2). For adsorption−desorption experiments the standard batch equilibration method was used in compliance with OECD guideline 106 (*37*). Biomixtures were prepared as described above, air-dried, and stored at room temperature. Stock solutions (1000 μg mL^{-1}) for each pesticide in acetone were prepared, and aliquots were dissolved in 0.01 M $CaCl_2$ aqueous solution for the preparation of pesticide solutions at concentrations of 2, 4, 6, 8, and 10 μg mL^{-1}.

For the adsorption study, air-dried substrate (2 g) was placed in 40 mL screw-capped vials and mixed with 10 mL of $CaCl_2$ pesticide solutions. Three replicates per pesticide and concentration level were prepared. Samples were shaken overnight in an orbital shaker (200 rpm) at room temperature. Subsequently, samples were centrifuged at 6000*g* for 10 min, and the supernatant was collected, weighed, and passed through a C18 SPE cartridge (500 mg/3 mL, IST, Biotage), previously activated with 2 mL of methanol and 2 mL of deionized water. Pesticide residues were eluted with 2 mL of ethyl acetate and stored at 4 °C prior to chromatographic analysis. A preliminary adsorption kinetics study showed that apparent equilibrium between the amount of pesticide adsorbed and the amount of pesticide in solution was reached within 8 h. However, for practical reasons a 24 h equilibration period was used as no significant loss of any of the pesticides tested was expected.

Desorption studies were performed immediately after adsorption using the single-point desorption method at room temperature. Desorption was measured at five concentration levels, 2, 4, 6, 8, and 10 mg L^{-1}. A known volume of the 0.01 M $CaCl_2$ solution contained in the vials used for the adsorption experiment was replaced with the same volume of pesticide-free 0.01 M $CaCl_2$ solution. The suspensions were shaken for 24 h and thereafter centrifuged at 6000*g* for 10 min. Pesticides were extracted from the supernatant with SPE, as described above, and determined by chromatographic analysis.

Analytical Procedures. A Hewlett-Packard 6890 gas chromatograph (GC) system equipped with a nitrogen−phosphorus (NPD) or a micro electron capture (μECD) detector and an autosampler was used for pesticide residue analysis. Analyses on both GC systems (GC-NPD, GC-μECD) were performed on an SGE BPX35 capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness) attached to a 1 m precolumn. Column temperature was set to 80 °C initially and gradually increased

Table 2. Mathematic Expressions for a Single Constant Rate Model (Simple First Order) and Five Variable-Rate, Multicompartment Models and Estimation of Half-Life ($t_{1/2}$) Values

model	mathematic expression[a]	half-life estimation
simple first order (linear)	$C = C_0\, e^{-kt}$	$t_{1/2} = \ln 2/k$
hockey stick model	$C = C_0\, e^{-k_1 t}$ for $t \le t_b$	$t_{1/2} = \ln 2/k_1$
	$C = C_0\, e^{-k_1 t_b}\, e^{-k_2(t-t_b)}$ for $t > t_b$	$t_{1/2} = t_b + (\ln 2 - k_1 t_b)/k_2$
biexponential model	$C = C_1\, e^{-k_1 t} + C_2\, e^{-k_2 t}$	iterative method
Gustafson−Holden model	$C = C_0/(t/\beta + 1)^{\alpha}$	$t_{1/2} = \beta(2^{1/\alpha} - 1)$
Hamaker model	$C = [C_0^{(1-n)} + (n-1)kt]^{1/(1/n)}$	$t_{1/2} = C_0^{1-n}(0.5^{1-n} - 1)/(n-1)k$

[a] t_b refers to the time point when the k_1 rate changes to k_2.

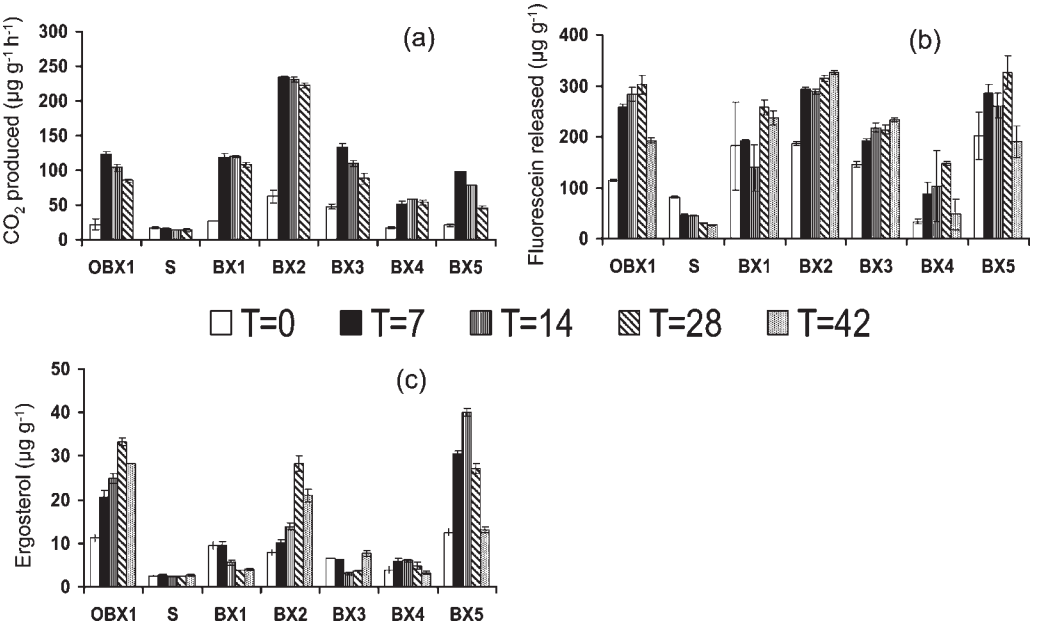

Figure 1. Temporal changes in the size and activity of the microbial biomass in the different substrates in response to pesticide application: (**a**) microbial respiration; (**b**) fluorescein diacetate hydrolytic activity; (**c**) ergostrerol content measured at different days (0, 7, 14, 28, and 42) during the degradation experiment. Error bars represent the standard deviation of the mean. The least significant difference (LSD = 0.05) of the interactions between time and substrate is also presented.

to a final temperature of 280 °C. The carrier gas (helium) flow rate was maintained at 1.5 mL min^{-1} for 12.5 min and programmed to 2.5 mL min^{-1} until the end of the run (25.99 min). Injector temperature was at 250 °C, and the splitless injection was carried out with the purge valve on at 1 min. Hydrogen 3 mL/min and air 60 mL/min were used as fuel gases for the NPD, whereas nitrogen 60 mL/min and helium 6 mL/min were used as auxiliary gases for the μECD. Both detector temperatures were at 310 °C.

Determination of pesticides was performed in the GC-NPD system with the exception of indoxacarb, which was determined in the GC-μECD system. Quantitation was performed by the external standard method using matrix-matched standard solutions of the studied pesticides.

Data Analysis. The first-order kinetics (FOK) model and four multicompartment kinetics models the including hockey stick, the Gustafson−Holden model (*38*), the biexponential model, and an exponential equation proposed by Hamaker (*39*) were used for fitting the degradation patterns of the eight pesticides in the different substrates (**Table 2**). For the selection of the kinetics model that best describes the degradation results, FOCUS workgroup guidance recommendations were followed (*40*). The χ^2 test was used to test the quality of the measured data and the agreement between calculated and observed for a given fit:

$$\chi^2 = \sum \frac{(C-O)^2}{(\mathrm{err}/100\bar{O})^2} \quad (1)$$

In eq 1, C = calculated value, O = observed value, $\bar{O}$ = mean of observed values, and err = measurement error.

The error value at which the χ^2 test is fulfilled at a given degree of freedom should be below 15% (at 5% significance level). Parameters of the kinetics models were estimated by least-squares regression using the SPSS 16.0 statistical program. The same program was used to calculate the model efficiency (r^2) value. Correlations between degradation−sorption parameters and physicochemical−biological characteristics of the biomixtures were determined by Pearson's correlation coefficient (r).

The temporal data of the biological properties measured in the different biomixtures were subjected to a two-way-ANOVA to identify if the effects of sampling time or biomixture and their interactions were significant. In cases when significant interactions between the two factors were identified, statistical differences between biomixtures at the same time were further identified using the least significant difference test (LSD = 0.05).

RESULTS AND DISCUSSION

Physicochemical and Biological Properties of the Biomixtures. The physicochemical characteristics of peat and composts were consistent with the average values presented in the literature (**Table 1**). The two peat types used showed higher organic C and lower N content than the composts tested (except C3), lower density, and higher WHC (**Table 1**). Generally, the BX showed higher total carbon microbial biomass compared to soil and OBX1. However, significantly higher values ($p < 0.05$) were evident only in BX2, BX5, and OBX2 compared to soil, OBX1, and the other BX substrates (**Table 1**).

Temporal changes in the size (ergosterol) and activity (microbial respiration and hydrolytic activity) of the microbial biomass in biomixtures and soil were determined during the

Table 3. Assessment of the First-Order (Linear) and Four Biphasic Kinetics Models for Describing the Degradation Patterns of the Eight Pesticides (Applied in High Dose) in Selected Substrates (BX1, Soil, and OBX1) by Calculation of Model Efficiency (r^2), χ^2 Error, and $t_{1/2}$ (Days)

		kinetics models														
		linear			Gustafson−Holden			hockey stick			biexponential			Hamaker		
substrate	pesticide	r^2	χ^2	$t_{1/2}$	r^2	χ^2	$t_{1/2}$	r^2	χ^2	$t_{1/2}$	r^2	χ^2	$t_{1/2}$	r^2	χ^2	$t_{1/2}$
BX1	TRB	0.882	7.6	57.8	0.934	21.4	41.0	0.941	3.6	43.0	0.947	2.7	41.0	0.934	3.8	40.8
	DIM	0.942	13.2	5.8	0.900	15.8	5.8	0.900	−[a]	2.7	0.900	−	6.0	0.735	0.8	5.0
	MTX	0.865	11.4	34.7	0.882	9.3	45.1	0.974	2.4	49.1	0.882	10	49.0	0.963	3.8	52.0
	MTR	0.979	6.6	21.0	0.966	6.4	22.7	0.968	6.5	23.9	0.966	6.9	24.0	0.956	9.7	27.1
	BUP	0.975	6.0	28.9	0.974	5.0	23.6	0.983	3.6	23.9	0.983	3.4	23.0	0.974	5.3	22.4
	IPR	0.760	27.2	31.5	0.895	5.9	9.4	0.904	2.2	9.8	0.902	3.4	9.5	0.895	5.9	9.4
	IND	0.441	35.2	53.3	0.833	18.4	8.6	0.916	11.6	7.1	0.896	14.1	7.5	0.833	18.4	8.5
	AZX	0.866	22.8	25.7	0.932	9.4	7.9	0.931	10.9	7.8	0.940	8.4	7.0	0.932	9.4	7.9
soil	TRB	0.800	5.2	99.0	0.922	2.6	206.5	0.906	3.4	105.1	0.924	2.6	173.0	0.922	2.6	205.5
	DIM	0.972	35.3	5.9	0.995	3.9	7.2	0.997	2.3	7.9	0.998	4.5	7.5	0.998	1.5	7.9
	MTX	0.650	5.6	173.3	0.929	2.0	1920.4	0.900	2.8	236.5	0.936	1.9	−	0.906	2.5	700
	MTR	0.841	17.1	34.7	0.980	5.5	13.8	0.964	8.2	11.7	0.979	5.7	14.0	0.980	5.5	13.8
	BUP	0.728	8.8	86.6	0.949	3.1	74.0	0.933	4.2	73.0	0.962	2.2	−	0.949	3.1	74.1
	IPR	0.745	6.9	86.6	0.891	3.1	110.3	0.880	4.0	75.0	0.893	3.6	69.0	0.890	3.1	108.6
	IND	0.015	54.9	231.0	0.343	48.2	14.5	0.621	38.7	7.7	0.586	40.3	11.0	0.343	48.2	14.5
	AZX	0.730	10.8	69.3	0.968	2.6	41.8	0.945	4.7	48.7	0.967	3.1	45.0	0.968	2.6	41.9
OBX1	TRB	0.970	5.1	38.5	0.976	1.6	30.5	0.977	1.0	31.4	0.976	1.6	30.5	0.976	1.6	30.5
	DIM	0.962	25.3	6.0	0.910	16.5	9.0	0.978	1.3	10.8	0.910	18.9	10.5	0.935	−	11.5
	MTX	0.027	4.1	−	0.062	4.2	−	0.140	4.5	−	0.113	4.1	−	0.027	4.4	5936
	MTR	0.978	4.9	27.7	0.967	4.4	25.1	0.969	4.2	27.2	0.968	4.5	27.0	0.967	4.4	25.4
	BUP	0.833	7.0	86.6	0.944	1.9	88.6	0.937	2.7	71.3	0.944	2	74.0	0.944	1.9	89.3
	IPR	0.198	2.9	−	0.191	2.8	−	0.257	3.1	−	0.238	2.9	−	0.197	2.8	−
	IND	0.708	6.1	115.5	0.736	5.9	222.0	0.764	5.8	134.8	0.745	6.1	145.0	0.736	5.9	221.6
	AZX	0.924	15.3	17.3	0.931	9	13.7	0.935	8.5	13.1	0.933	9	15.0	0.901	−	15.0

[a] −, no value was produced by the formula.

degradation study. Overall, both the sampling time and the substrates used as well as their interactions had a significant effect on the size and activity of microbial biomass ($p < 0.001$). Biomixtures (both BX and OBX) showed significantly higher ($p < 0.001$) microbial activity and ergosterol content compared to soil throughout the incubation study (**Figure 1**). Generally, there was a microbial response to components mixing and pesticide application in the biomixtures (BX and OBX) but not in the soil. This is mirrored in the initial significant increase ($p < 0.05$) in the microbial respiration observed in all biomixtures at 7 days after treatment (**Figure 1a**), whereas a significant increase ($p < 0.05$) in hydrolytic activity was evident at the same date only for OBX1, BX2, and BX5 (**Figure 1b**). With regard to ergosterol content, a significant increase ($p < 0.05$) was observed at 7 days after treatment only in OBX1 and BX5, whereas a later increase, at 28 days, was evident in BX2 (**Figure 1c**).

Generally, OBX1 showed microbial respiration (**Figure 1a**) and hydrolytic activity (**Figure 1b**) comparable with those of most BX throughout the study. The only exception was BX2, which showed the highest microbial respiration ($p < 0.05$) and hydrolytic activity ($p < 0.05$) compared to the other biomixtures tested. With regard to ergosterol, OBX1 showed similar concentrations with BX5 ($p > 0.05$), whereas significantly lower values ($p < 0.05$) were evident in the other BX and soil. Among BX substrates, BX2 (olive leaf compost) showed the highest microbial respiration (**Figure 1a**) and hydrolytic activity (**Figure 1b**), whereas BX5 (cottonseed compost) showed the highest ergosterol content (**Figure 1c**). Significant correlations between organic C content and total C microbial biomass (0.583, $p < 0.05$), hydrolytic activity (0.755, $p < 0.05$), and ergosterol content (0.559, $p < 0.05$) were observed.

Degradation Kinetics and Half-Life Estimation. Five different kinetics models (**Table 2**) were tested to identify which best describes the degradation of the pesticides in the different substrates. Model efficiency (r^2), χ^2 error, and $t_{1/2}$ values calculated for the different pesticides in three selected substrates are shown in **Table 3**.

The degradation of DIM, BUP, MTX, and TRB was best described by the first-order kinetics (FOK) model in most of the substrates tested (see Supporting Information Figure 2) with χ^2 error values being below the trigger value of 15% (**Table 3**). Degradation of MTR in most substrates was also best described by FOK at the high dose rate, whereas a biphasic degradation pattern was observed in half of the substrates at the low dose rate (**Table 5**). The degradation of IND, AZX, and IPR was biphasic in most of the substrates tested (see the Supporting Information) and most particularly at the low dose rate (**Table 3**). The biphasic character of IND degradation in soil has been previously reported (*41*). For those pesticides, an initial rapid degradation phase was followed by a much slower degradation phase until the end of the incubation. Application of the FOK model for those pesticides failed to meet the χ^2 error criterion and led to overestimation of $t_{1/2}$ values (**Table 3**). The application of biphasic kinetics models for these pesticides showed that the goodness of fit differentiated on a case-by-case basis; however, the hockey stick model showed an overall higher efficiency proven by the higher r^2 and the lower χ^2 error values observed in most cases, and it was used for curve fitting and $t_{1/2}$ estimation in those cases when the FOK model was not appropriate (**Table 3**).

Pesticide Degradation in Various Substrates. The two OBX showed overall similar degradation behavior for the pesticides studied, although the rates of degradation were lower in OBX2,

Table 4. Parameters Describing the Degradation of the Different Pesticides Applied at the High Dose Rate in Soil and Compost-Containing (BX) and Peat-Containing Biomixtures (OBX)

pesticide	substrate	C_0 (% of initial)	k_1 (day^{-1})	k_2 (day^{-1})	t_b (days)	r^2	$t_{1/2}$ (days)
TRB	soil	90.6	0.007			0.800	99.0
	BX1	84.9	0.012			0.882	57.8
	BX2	60.0	0.005			0.201	139
	BX3	95.7	0.009			0.912	77.0
	BX4	90.9	0.015			0.886	46.2
	BX5	100.0	0.236	0.036	3.4	0.970	2.9
	OBX1	92.0	0.018			0.970	38.5
	OBX2	95.0	0.022			0.958	31.5
DIM	soil	115.6	0.118			0.972	5.9
	BX1	108.5	0.140			0.833	5.0
	BX2	142.7	0.445			0.962	1.6
	BX3	175.8	0.267			0.958	2.6
	BX4	127.9	0.278			0.966	2.5
	BX5	94.6	0.067			0.942	10.3
	OBX1	149.7	0.123			0.981	5.6
	OBX2	100.0	−0.006	0.182	4.8	0.991	8.8
MTX	soil	88.9	0.004			0.697	173
	BX1	114.3	0.020			0.865	34.7
	BX2	92.9	0.054			0.884	12.8
	BX3	119.7	0.081			0.910	8.6
	BX4	90.9	0.009	0.061	27.3	0.927	34.7
	BX5	80.6	0.002			0.061	346
	OBX1	99.2	0.001			0.161	693
	OBX2	113.0	0.002			0.168	346
MTR	soil	96.9	0.059	0.016	11.8	0.964	11.7
	BX1	110.7	0.033			0.979	21.0
	BX2	100.0	0.126	0.031	7.5	0.989	5.5
	BX3	101.2	0.044			0.979	15.8
	BX4	99.9	0.039			0.935	17.8
	BX5	88.9	0.011			0.745	63.0
	OBX1	100.0	0.025			0.978	27.7
	OBX2	102.3	0.025			0.957	27.7
BUP	soil	84.5	0.008			0.728	86.6
	BX1	90.9	0.024			0.975	28.9
	BX2	79.4	0.013			0.708	53.3
	BX3	102.6	0.016			0.977	43.3
	BX4	89.3	0.017			0.906	40.8
	BX5	98.6	0.099	0.013	8.1	0.970	7.0
	OBX1	85.7	0.008			0.833	86.6
	OBX2	95.9	0.011			0.920	63.0
IPR	soil	85.9	0.008			0.745	86.6
	BX1	99.3	0.071	0.011	16.2	0.904	9.8
	BX2	100.0	0.202	0.094	4.6	0.996	3.4
	BX3	101.2	0.066			0.991	10.5
	BX4	101.1	0.081	0.047	7.0	0.891	9.7
	BX5	70.0	0.000			0.005	–
	OBX1	99.3	0.001			0.198	693
	OBX2	102.6	0.002			0.288	346
IND	soil	128.1	0.090	0.017	16.9	0.621	7.7
	BX1	104.0	0.098	0.008	12.9	0.914	7.1
	BX2	100.8	0.106	0.019	7.6	0.986	6.5
	BX3	108.9	0.047	0.007	18.2	0.924	14.7
	BX4	100.9	0.061	0.021	7.0	0.918	19.7
	BX5	75.5	0.000			0.001	–
	OBX1	98.7	0.006			0.708	116
	OBX2	89.5	0.015			0.901	46.2
AZX	soil	79.6	0.010			0.730	69.3
	BX1	96.7	0.089	0.017	10.1	0.922	7.8
	BX2	100.0	0.248	0.039	4.4	0.995	2.8
	BX3	101.2	0.072	0.002	9.8	0.876	9.6
	BX4	85.1	0.013			0.714	53.3
	BX5	100.0	0.255	0.017	3.7	0.918	2.7
	OBX1	106.9	0.053	0.029	29.9	0.935	13.1
	OBX2	98.6	0.021			0.876	33.0

especially at the low dose rate (**Table 5**). Compared to soil, degradation of most pesticides was significantly slower in the two OBX (**Tables 4** and **5**). This was more prominent for MTX, IPR, BUP, and IND and less prominent but still visible for MTR. For the first four pesticides the $t_{1/2}$ values calculated in the OBX were up to 70-fold higher compared to those for BX and soil. The reduced degradation of these pesticides in OBX could be partially ascribed to their acidic pH (pH 5.0−5.9), which is not considered conducive for pesticide-degrading bacteria (*42*, *43*). Previous degradation studies of IPR in soils with variable pH showed a negligible degradation at pH 5, whereas $t_{1/2}$ values at pH 6.5 were 2-fold lower than the corresponding values observed in a soil having pH 5.7 (*44*). Alternatively, the high adsorption capacity of OBX compared to soil might have also contributed to reduced bioavailability of the tested pesticides and thus slower pesticide degradation compared to soil. On the other hand, TRB (at the high dose rate, **Table 4**) and AZX (at the low dose rate, **Table 5**) degraded more rapidly in the OBX compared to soil and most BX. Our data regarding TRB are in line with previous findings by Castillo and Torstensson (*45*), who found a positive correlation between TRB degradation and peat levels in the biomixture. Similarly, Fournier (*46*) reported that the absence of peat in the biomixtures of Phytobac/biobac resulted in a slow degradation of TRB. These results were attributed to the known vulnerability of triazine herbicides such as TRB to chemical hydrolysis at acidic soil conditions (*47*). With regard to AZX, our data are in agreement with previous findings revealing a negative correlation between pH and DT_{25} for this substance (*48*).

Overall, the faster degradation for most of the pesticides tested was observed in the BX substrates. The only exceptions were the negligible degradation of the highest dose rate of TRB in BX2 and of MTX, IPR, IND, and MTR in BX5. The high hydrolytic activity (**Figure 1b**) and ergosterol content (**Figure 1c**) observed in BX5 contradict the slow pesticide degradation in this substrate. BX5 showed the highest N content and the lowest C/N ratio among the substrates tested (**Table 1**). These characteristics might favor the proliferation of heterotrophic microbial populations, which are capable of degrading simple N-containing organic substances and consequently dominate the pesticide-degrading populations. A similar discrepancy between pesticide degradation and microbial activity was also evident for BX4 and OBX1. The former showed significantly lower hydrolytic enzyme activity (**Figure 1b**) and ergosterol content (**Figure 1c**) compared to OBX1. However, a higher degradation for most pesticides was evident in BX4 compared to OBX1. Overall, no correlation was found between total C microbial biomass, microbial respiration, hydrolytic activity, ergosterol content, and pesticide degradation rates. This is in contrast with previous findings by Castillo and Torstensson (*45*), who observed a positive correlation between basal respiration and degradation of several herbicides in peat-based biomixtures, which rely mainly on co-metabolic degradation processes. In contrast, previous studies in compost-based biomixtures, which rely mainly on metabolic degradation processes, did not reveal any correlation between soil respiration and

Table 5. Parameters Describing the Degradation of the Different Pesticides Applied at the Low Dose Rate in Soil and Compost-Containing (BX) and Peat-Containing Biomixtures (OBX)

pesticide	substrate	C_0 (% of initial)	k_1 (day^{-1})	k_2 (day^{-1})	t_b (days)	r^2	$t_{1/2}$ (days)
TRB	soil	91.6	0.017			0.943	40.8
	BX1	87.5	0.030			0.879	23.1
	BX2	95.3	0.021			0.845	33.0
	BX3	96.8	0.046			0.920	15.1
	BX4	81.7	0.037			0.937	18.7
	BX5	92.1	0.049			0.900	14.1
	OBX1	87.1	0.027			0.977	25.7
	OBX2	92.6	0.015			0.873	46.2
DIM	soil	90.8	0.405			0.968	1.7
	BX1	98.0	0.671			0.976	1.0
	BX2	99.4	1.483			0.988	0.5
	BX3	99.9	0.286			0.957	2.4
	BX4	113.6	0.329			0.918	2.1
	BX5	90.6	0.246			0.942	2.8
	OBX1	101.1	0.229			0.973	3.0
	OBX2	100.0	0.016	0.230	2.8	0.993	5.7
MTX	soil	97.5	0.016	0.057	26.7	0.989	31.4
	BX1	96.4	0.040			0.927	17.3
	BX2	108.3	0.043			0.930	16.1
	BX3	111.2	0.121			0.960	5.7
	BX4	91.1	0.033			0.946	21.0
	BX5	101.5	0.011	0.026	24.3	0.868	40.7
	OBX1	94.9	0.004			0.555	173
	OBX2	99.4	−0.002			0.103	−
MTR	soil	82.0	0.040			0.967	17.3
	BX1	96.9	0.067	0.216	7.0	0.939	8.0
	BX2	100.0	0.031	0.100	3.8	0.963	9.6
	BX3	99.5	0.082	0.000	36.9	0.984	8.5
	BX4	99.5	0.109	0.003	25.9	0.975	6.4
	BX5	85.1	0.039			0.901	17.8
	OBX1	97.5	0.030			0.981	23.1
	OBX2	100.8	0.017			0.837	40.8
BUP	soil	98.2	0.015			0.878	46.2
	BX1	99.3	0.033			0.949	21.0
	BX2	93.5	0.023			0.873	30.1
	BX3	95.3	0.036			0.964	19.3
	BX4	95.9	0.036			0.944	19.3
	BX5	80.8	0.029			0.883	23.9
	OBX1	97.1	0.007			0.828	99.0
	OBX2	101.5	0.023	0.001	14.0	0.713	385
IPR	soil	89.8	0.014			0.833	49.5
	BX1	99.5	0.134	0.029	18.4	0.970	5.2
	BX2	99.7	0.102	0.038	7.0	0.901	6.8
	BX3	91.0	0.068	0.031	14.0	0.838	10.2
	BX4	92.1	0.057	0.029	7.7	0.874	16.5
	BX5	84.3	0.032			0.768	21.7
	OBX1	120.7	0.007			0.444	99.0
	OBX2	93.5	0.002			0.082	347
IND	soil	99.8	0.103	0.020	7.6	0.991	6.7
	BX1	99.1	0.078	0.010	16.4	0.974	8.9
	BX2	100.0	0.169	0.015	4.4	0.939	4.1
	BX3	97.9	0.084	0.013	10.1	0.982	8.3
	BX4	100.0	0.172	0.013	3.8	0.734	7.4
	BX5	94.4	0.148	0.003	7.2	0.832	4.7
	OBX1	98.9	0.027	0.003	42.0	0.904	25.7
	OBX2	101.0	0.028	−0.003	32.9	0.958	24.8
AZX	soil	89.8	0.018			0.943	38.5
	BX1	98.6	0.097	0.046	25.3	0.896	7.1
	BX2	97.5	0.098	0.012	21.0	0.975	7.1
	BX3	93.3	0.052	0.018	11.2	0.836	17.3
	BX4	92.2	0.059	0.017	12.4	0.845	11.7
	BX5	100.0	0.113	0.030	4.0	0.905	11.9
	OBX1	100.0	0.441	0.025	4.3	0.998	1.6
	OBX2	99.7	0.110	0.002	10.4	0.926	6.3

pesticide degradation (*16*). The discrepancy between pesticide degradation and microbial activity observed in our study could be attributed to either the involvement of abiotic factors such as pH on pesticide degradation or the fact that growth-linked biodegradation of pesticides is driven by the proliferation of a small fraction of the total microbial community, which is not mirrored in broad measurements of microbial activity (*49*).

None of the biomixtures tested exhibited high degradation efficiency for all pesticides tested and at both application rates. Certain biomixtures were more efficient than others on a case-by-case basis. For example, TRB was most efficiently degraded in BX5, DIM showed the most rapid degradation in BX2, and MTX was most efficiently degraded in BX3 at both application doses. The most consistent biomixture in stimulating microflora (high microbial respiration, hydrolytic enzyme activity, and ergosterol content) and enhancing pesticide degradation was BX2. This was particularly the case for DIM, MTX, IND, IPR, and AZX, whereas the same biomixture showed a reduced capability to degrade BUP but especially TRB. The degradation efficiency of this compared to the other biomixtures was more pronounced at the high dose rate (**Tables 4** and **5**). Previous studies in compost-based and peat-based biomixtures reported a decrease in pesticide degradation rates at increasing pesticide dose rates (*50*, *51*). This is in agreement with our findings for all of the biomixtures tested with the single exception of BX2. This property of BX2 is particularly desirable for biobed systems in which biomixtures are expected to be exposed to high doses of pesticide mixtures. This tendency of higher degradation rates at higher application rates in BX2 might be a result of a general toxic effect exerted by the pesticide mixture utilized on the members of the microbial community that are not involved in pesticide degradation. This favors the proliferation of the pesticide-degrading microorganisms that utilize pesticides as energy sources and can thrive in a low competition environment.

Adsorption−Desorption Studies. Generally, the adsorption of the four pesticides tested (TRB, MTR, MTX, IND) was best described by the Freundlich equation, which was used for calculation of the adsorption parameters (K_{fads}, $1/n_f$) (**Table 6**). The overall better fit of the Freundlich equation indicates modifications in the affinity between pesticide molecules and solid phases as pesticide concentrations increase.

Pesticide adsorption was influenced by both the pesticide physicochemical properties and the type of biomixture used. Pesticide adsorption in the different substrates followed the order IND > TRB > MTX = MTR, which is consistent with previously reported data and the physicochemical properties of the individual pesticides (*52*−*55*). The K_{foc} coefficients (K_{fads} normalized for organic C content) for the adsorption of the tested pesticides in the different substrates were calculated to identify the contribution of organic C on the adsorption of the pesticides. The K_{foc} values for IND and TRB did not vary between the different substrates, suggesting that organic C is the key adsorption site for those pesticides. This is further supported by the significant positive correlation between organic C content and

Table 6. Adsorption and Desorption Parameters for the Pesticides in Soil, Peat-Containing (OBX), and Compost-Containing Biomixtures (BX)

	adsorption			desorption				
							HI[a]	
substrate	K_{fads} (L kg^{-1})	$1/n_{ads}$	K_{foc} (L kg^{-1})	%[b]	K_{fdes} (L kg^{-1})	$1/n_{des}$	LC	HC
				TRB				
OBX1	51.05	0.80	419	2.73	108.93	0.88	0.74	1.06
soil	4.39	0.99	244	41.33	6.03	1.18	0.40	0.91
BX1	33.74	0.83	319	nd[c]	nd	nd	nd	nd
BX2	35.73	1.85	345	7.73	47.06	1.26	0.59	0.18
BX3	16.53	0.94	254	18.08	28.87	1.00	2.32	3.23
BX4	29.25	1.13	333	8.70	40.77	1.09	0.49	0.34
BX5	32.93	0.79	283	3.91	74.77	1.14	1.72	2.37
				MTX				
OBX1	14.96	0.87	127	9.57	35.77	1.11	1.04	1.98
soil	3.84	1.07	213	18.77	21.28	1.07	0.60	0.90
BX1	4.81	1.05	46	29.07	9.12	1.04	0.89	0.82
BX2	12.35	0.85	118	9.33	29.27	1.13	0.94	2.30
BX3	5.88	0.76	91	13.33	18.71	0.92	2.10	3.20
BX4	9.64	0.87	112	10.85	29.62	0.99	1.91	2.60
BX5	8.60	0.95	73	10.48	31.17	1.11	2.61	2.82
				IND				
OBX1	655.96	0.95	4995	0.23	1012.70	0.95	0.56	0.54
soil	89.12	1.04	4767	3.53	163.53	1.10	0.56	0.72
BX1	462.23	0.87	4300	0.36	835.99	1.01	0.03	0.30
BX2	557.73	0.91	5048	0.34	1386.60	1.04	0.34	0.50
				MTR				
OBX1	15.14	0.97	126	11.37	21.05	1.25	0.26	0.75
soil	4.42	0.99	250	24.45	14.01	1.48	2.37	5.96
BX1	7.45	1.02	71	17.72	15.01	1.26	0.90	1.88
BX2	6.18	1.02	59	26.62	9.67	0.92	0.46	0.46
BX3	3.91	1.04	62	27.44	8.02	1.20	1.10	1.74
BX4	10.28	0.99	123	15.78	20.50	0.98	0.92	0.97
BX5	12.85	0.94	111	13.37	18.68	1.11	0.33	0.79

[a] Hysteresis index calculated for the lowest (LC) and highest (HC) pesticide concentration tested, respectively. [b] Pesticide desorption as a percentage of previously adsorbed pesticide. [c] Not determined.

K_f values for IND (0.975, $p < 0.05$) and TRB (0.832, $p < 0.01$). On the other hand, for the more water-soluble pesticides MTX and MTR, their K_{foc} values in the different substrates varied significantly, indicating that organic C was not the only factor controlling their adsorption. This is in line with previous findings (*55*) reporting a significant variation in the K_{oc} values of MTR in soil supplemented with different amounts of fly ash. Similarly, high variations (6−23-fold) in the K_{oc} values of MTX in six different organic substrates were also reported (*56*). High variation in the K_{foc} values of a pesticide in the different substrates indicates the involvement of complex interactions between the biomixture and the pesticide. The outcome of these interactions depends on the particular characteristics (relative proportion of humic substances, aromatic character, degree of humification, DOC content, pH) of the individual components of the biomixtures (*57*).

Biomixtures (BX and OBX) showed a higher adsorption affinity for the pesticides studied as indicated by the higher K_{fads} values compared to soil. K_{fads} values decreased in the order OBX > BX > soil for all pesticides (**Table 6**). This ranking is in agreement with similar previous studies which also found that pesticides showed higher adsorption affinity for peat compared to composted materials (*56*, *57*). The higher adsorption observed in the OBX cannot be explained solely on the basis of their higher organic C content (11.9%) because BX5, which had a similar organic C content (11.5%), showed significantly lower adsorption capacity for the pesticides tested. This suggests that the organic C of the OBX substrates was more efficient in retaining the more soluble pesticides MTX and MTB compared to the organic C of the BX substrates. The high adsorption capacity of OBX compared to soil is in agreement with the slower degradation of MTX, MTR, and IND in the former substrate.

Compost biomixtures (BX) showed variable adsorption behavior. The highest adsorption was evident in BX2, whereas the four other BX did not show a consistent pattern and their adsorption efficiency varied with pesticides. BX3, characterized by the lowest organic C content among biomixtures, failed to substantially retain pesticides. Previous studies have reported a negative effect of adsorption on pesticide degradation, and this was attributed to a reduced availability of pollutants for degrading microorganisms (*58*−*60*). However, in our study a positive relationship between degradation rate and K_{fads} coefficients among certain BX substrates was evident. Thus, BX2 was the most efficient biomixture in pesticide degradation and at the same time showed the highest affinity, among the other BX, for adsorption of TRB, MTX, and IND. This could be attributed to the fact that exogenous organic C might have a positive influence on both degradation and adsorption processes. This is in line with previous results reported in ref *61*, which suggested that adsorption is not necessarily negatively linked with pesticide degradation.

The single-point desorption isotherms obtained showed a tendency for higher desorption constants ($1/n_f$) than the corresponding adsorption constants (mean $1/n_{fdes} = 1.08$ and $1/n_{fads} = 0.95$). The higher K_{fdes} coefficients were observed for OBX1 followed by BX5. A positive correlation between K_{fads} and K_{fdes} ($p < 0.01$) was evident for all pesticides tested, implying that substrates with high K_{fads} showed higher adsorption strength as lower amounts of the adsorbed pesticides were desorbed from the biomixture. Hysteresis was evaluated using the hysteresis index (HI) as proposed by Huang et al. (*62*). Hysteresis phenomena were evident in almost every pesticide−substrate combination with values ranging from 0.18 for TRB in BX2 to 5.96 for MTX in soil, indicating low reversibility of the adsorption process. Higher HI values were evident at the higher concentration level (10 mg L^{-1}), which suggests that there was a noticeable increase of hysteresis at higher pesticide concentrations.

Conclusions. Biomixture constitutes the most important component of biobed systems, and its correct composition is a prerequisite for successful decontamination of pesticide-containing wastewaters. Our study shows that composted materials could successfully replace peat in the traditional biomixture used in biobed systems in northern Europe. This is based on the significantly higher degrading capacity of BX compared to corresponding OBX and topsoil. Composts are low-cost alternatives to peat and could be easily produced using organic materials from the local agriculture. The origin of the compost has a significant effect on the overall efficiency of BX. According to our findings, certain physicochemical characteristics could be used as indicators of the eligibility of a compost to be used as a biomixture component. Composts characterized by high organic C content, neutral pH, sufficient N content, and high microbial activity could be suitable for use in biomixtures. Among the BX tested, olive leaf compost-containing biomixture (BX2) showed the higher degradation activity as well as high adsorption capacity for most of the pesticides tested. The increasing adsorption capacity of this biomixture offers another advantage for the efficient adsorption of very mobile pesticides that are resistant to microbial degradation. Therefore, this compost could be an effective alternative to peat in biobed biomixtures in southern Europe where this substrate is largely available at no cost.

Supporting Information Available: Supplementary figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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