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Performance of Digestate as a Contaminant Biosorbent and Plant Growth Promoter Before and After Composting and Vermicomposting

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Abstract

Aerobic bioprocessing can alter the compositional and structural properties of anaerobic digestate (DG), potentially affecting its performance as a soil amendment. This study assessed how the composting and vermicomposting of a mixed digestate (DG) affected contaminant retention and lettuce growth. The adsorption–desorption behavior of DG and its derived compost (CP) and vermicompost (VC) was evaluated for the fungicide penconazole (PEN), the herbicide S-metolachlor (S-MET), and the industrial contaminants bisphenol A (BPA) and 4-nonylphenol (NP). Adsorption was generally faster on DG than on CP or VC; the kinetic data were better described by a pseudo second-order model, suggesting a possible contribution of chemisorption. Among the three materials, DG exhibited the highest Freundlich adsorption constants (K_F) for PEN and S-MET (3.95 and 1.36 L g^{-1}, respectively), whereas CP and VC showed the highest K_F values for BPA (2.54 L g^{-1}) and NP (174 L g^{-1}), respectively. All materials, particularly DG, exhibited pronounced desorption hysteresis for all four contaminants over three desorption cycles. Growth chamber microcosm experiments were conducted using a silt loam soil amended with each material at application rates of 10 and 30 Mg ha^{-1}. Lettuce responses varied among amendments in terms of shoot and root biomass and root system expansion, with DG exerting the strongest phytostimulatory effects. DG increased root dry biomass by approximately 70% and 90% at 10 and 30 Mg ha^{-1}, respectively, compared with the unamended control, resulting in significantly higher values than those recorded for CP and VC at the same application rates. At the higher application rate, shoot biomass in the DG treatment was approximately 30% greater than in CP and 20% greater than in VC. Overall, CP and VC showed only modest differences from DG in contaminant retention but supported less lettuce growth under the conditions tested. These findings underscore the need to consider both contaminant retention and agronomic performance when selecting digestate-based soil amendments.

Keywords: agrochemical; xenoestrogen; pollution control; aerobic treatment; adsorption model; desorption; plant response; microcosm

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1. Introduction

Despite growing awareness of soil multifunctionality and ecosystem services, intensive industrial and agricultural activities, combined with inadequate environmental monitoring and protection measures, continue to threaten soil health worldwide. Declining organic

fertility and the accumulation of inorganic and organic contaminants are major concerns in agricultural soils across Europe and other regions, with implications for ecosystem functioning and food safety. Efforts to mitigate climate change by reducing fossil fuel consumption and increasing carbon sequestration have boosted the renewable energy sector. Over the last decade, bioenergy has maintained a steady 9% share of the global energy supply, with solid biomass accounting for nearly 83% of total bioenergy production [1].

In addition to biogas, anaerobic digestion (AD) produces digestate (DG), a by-product rich in organic carbon and plant nutrients [2,3]. Because of its high moisture content (approximately 90–95%), raw DG is generally mechanically separated into solid DG and clarified liquid fractions [4]. Depending on ingestate composition and AD operating conditions, including temperature, pH, and retention time, DG may have different physicochemical characteristics. Carbon contents typically range from 25% to 50% of dry matter [5–7].

As a soil amendment, DG supplies essential macronutrients, secondary nutrients, and micronutrients [8]. However, direct application may cause nitrogen losses and nutrient leaching [9,10]. Depending on ingestate nature, DG may also contain heavy metals and organic contaminants, including pharmaceutical and personal care products [11]. Further treatment through composting and vermicomposting produces compost (CP) and vermicompost (VC), respectively, and can enhance organic matter stabilization and humic-like substances formation [12], thereby modifying the functional properties of DG. During aerobic processing, microbial activity depletes readily biodegradable compounds and favors the relative enrichment of more stable aromatic macromolecules of high molecular weight. Changes in structure, stability, and humification are commonly assessed using fluorescence, infrared and Raman spectroscopy, and thermal analysis [13,14]. CP and VC can improve soil fertility, microbial activity, and plant growth [15,16]. Despite compositional differences, all three materials can potentially contribute to soil carbon storage [17].

DG, CP, and VC have also attracted increasing interest as low-cost bioadsorbents for environmental remediation [18]. Their porous structure, relatively large specific surface area, and abundance of reactive functional groups support the adsorption of inorganic and organic contaminants [19]. Adsorption and desorption can regulate contaminant mobility, bioavailability, and transfer within soil–plant–water systems [20], contributing to the environmental performance of these materials.

Pesticides and endocrine-disrupting chemicals (EDCs) are of particular concern because of their widespread occurrence, potential recalcitrance, and impacts on ecosystems and human health [21]. Intensive pesticide use and reuse of wastewater and waste biomass can introduce them into soils, potentially affecting microbial communities, crop quality, and food safety [22,23].

This study examined the fungicide penconazole (PEN; 1-[2-(2,4-dichlorophenyl)pentyl]-1,2,4-triazole), the herbicide S-metolachlor (S-MET; 2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(2S)-1-methoxy-2-propanyl]acetamide), and the xenoestrogens bisphenol A (BPA; 4,4′-(2,2-propandiyl)diphenol) and 4-nonylphenol (NP). PEN controls fungal diseases in horticultural and ornamental plants [24] and has shown potential endocrine-disrupting effects on aquatic organisms [25]. S-MET controls broadleaf weeds in a variety of crops [26], is classified by the European Chemicals Agency (ECHA) as a suspected human carcinogen [27], and has also been identified as a potential EDC [28]. BPA, used in the manufacture of epoxy resins and polycarbonate plastics, exhibits estrogenic and anti-androgenic activity and occurs in numerous everyday consumer products [29]. NP is a precursor to nonylphenol polyethoxylates and is a product of their anaerobic degradation; these nonionic surfactants are used in detergents, emulsifiers, lubricants, and pesticide formulations.

These contaminants occur in intensively cultivated soils and those receiving wastewater and/or biosolids. Their persistence depends on soil properties, particularly organic matter

content, and environmental conditions. Reported half-lives in soil include 55–207 days for PEN [30], 28–39 days for S-MET [31], and shorter, condition-dependent values for BPA [32] and NP [33]. Their fate in soil is governed by concurrent sorption, degradation, leaching, and plant uptake. Rapid adsorption modifies partitioning between the soil solution and solid phase, influencing mobility and bioavailability. Amendment sorptive properties, therefore, affect contaminant retention and release following single or repeated applications [34,35]. Retention by DG, CP, and VC may involve pore entrapment, hydrophobic partitioning, hydrogen bonding, van der Waals forces, and π–π interactions [19]. Composting and vermicomposting modify DG composition and structure [36]; however, their effects on contaminant retention and plant-growth-promoting properties remain poorly understood.

Lettuce (*Lactuca sativa* L.), a short-cycle crop with global production of approximately 28.2 Mt per year [37], was selected as the test plant. Its high sensitivity to inorganic and organic contaminants makes it suitable for bioassays assessing pollutant toxicity [38] and amendment effects [39]. Previous microcosm studies have shown that CP, DG, and manure can selectively regulate lettuce yield and physiological responses under inorganic contamination [40,41].

The environmental and agronomic functions of organic amendments are often investigated separately, with comparisons involving materials of different origins. A distinctive feature of this study is the evaluation of both functions using the parent DG and its two aerobic derivatives, CP and VC. Their common origin limits the influence of feedstock differences, enabling a comparison of how composting and vermicomposting affect contaminant retention and plant growth.

Specifically, adsorption kinetics and adsorption–desorption isotherms were used to characterize PEN, S-MET, BPA, and NP retention and the release of it by DG, CP, and VC under controlled aqueous conditions. Lettuce growth in soil microcosms provided a complementary assessment of the phytoregulatory effects of the same amendments. Together, these experiments provide a basis for further studies on contaminant uptake and accumulation in edible tissues. The findings may inform farmers' selection of amendments according to their intended use and guide biowaste management towards products with suitable environmental and agronomic properties.

2. Materials and Methods

2.1. Chemicals, Amendments, Soil and Plant

The fungicide PEN (CAS n. 66246-88-6), the herbicide S-MET (CAS n. 87392-12-9), and the EDC NP (CAS n. 104-40-5), each with a purity ≥ 98%, together with the EDC BPA (CAS n. 80-05-7), with a purity > 99%, were purchased from Merck KGaA (Darmstadt, Germany). The molecular masses of PEN, S-MET, BPA, and NP were 284.18, 283.80, 228.29, and 220.36 g mol^{-1}, respectively. Their corresponding log *Kow* values were 4.67, 3.24, 3.32, and 5.99; their water solubilities at 25 °C were 1.55, 50.9, 300 and 1.57 mg L^{-1}, respectively [42]. All other chemicals used in the experiments were of extra-pure grade. Individual stock solutions of the compounds were prepared in HPLC-grade methanol at a concentration of 2000 mg L^{-1}. These solutions were subsequently diluted with double-distilled water to obtain the working solutions used in all experiments, with the methanol content not exceeding 0.4%.

The amendments DG, CP, and VC were collected from an AD plant operated by C&F Energy Società Agricola S.r.l. located near Capaccio (Salerno, Italy). The ingestate consisted of 80% buffalo manure, 15% oil mill vegetation water, 3% agro-industrial waste, and 2% chicken manure. The AD process was carried out at 55–60 °C with a hydraulic retention time of 60 days. The rated power of the plant was 500 kW. The raw digestate leaving the digester was mechanically separated into a solid fraction (DG) and a clarified

liquid fraction. The solid DG was first thermally treated at 65 °C for 5 days and then subjected to aerobic bioprocessing to produce CP and VC. Composting was conducted under controlled conditions for approximately two months. Vermicomposting involved an initial four-day period of open-air stabilization of DG, followed by the addition of earthworms (*Eisenia foetida* L.) and a two-month period under aerated conditions with daily watering to maintain at least 80% moisture (*w*/*w*). Further details on the production conditions and a full characterization of the three amendments are provided in Loffredo et al. [36], while selected physicochemical properties are summarized in Table 1.

Table 1. Selected properties of digestate (DG) and its aerobically processed derivatives, compost (CP), and vermicompost (VC).

Parameter	DG	CP	VC
Moisture (%) [a]	12.2 ± 1.1	17.2 ± 0.4	14.12 ± 0.6
pH [b]	7.94 ± 0.01	7.89 ± 0.1	7.85 ± 0.1
EC [b] at 25 °C (dS m^{-1})	2.12 ± 0.03	1.17 ± 0.01	0.99 ± 0.01
Ash (%) [c]	12.1 ± 0.3	10.3 ± 0.01	16.6 ± 0.9
TOC (g kg^{-1}) [c]	447 ± 2.5	452 ± 4.4	425 ± 7.4
TN (g kg^{-1}) [c]	24.5 ± 0.4	19.7 ± 0.4	24.8 ± 0.4
C/N	18.3 ± 0.4	23.0 ± 0.4	17.1 ± 0.4

CP and VC were obtained from DG after 2-month composting or vermicomposting, respectively. Data are the average of 3 replicates ± standard deviation. [a]: air-dry basis; [b]: amendment: distilled water 1:10 (*w*/*v*), [c]: dry basis; EC: electrical conductivity; TOC: total organic carbon; TN: total nitrogen. Adapted from Loffredo et al. [36].

The silt loam soil used to fill the microcosm units was freshly collected from the Ap horizon (0–20 cm) of an organically managed citrus orchard located in the Sibari Plain (Calabrian region, Cosenza, Italy). The soil, classified as Calcari-Fluvic Cambisol showed a low carbonate content, a balanced Mg/K ratio, and an unbalanced Ca/Mg ratio, resulting in low calcium availability. The soil also exhibited good drainage and aeration, making it suitable for use in enclosed model systems. Soil physicochemical properties were determined using standard procedures [43] and are reported in Table S1.

Lettuce seeds (*Lactuca sativa* L. cv. 'Romana') were purchased from Fratelli Ingegnoli (Milan, Italy).

2.2. Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis (SEM–EDX)

A few milligrams of each sample were mounted on adhesive carbon tape, coated with gold (Au), and examined using a high-resolution field-emission scanning electron microscope (VP FESEM SIGMA 300, ZEISS, Oberkochen, Germany) equipped with an EDX elemental analyzer (Oxford Instruments NanoAnalysis, High Wycombe, UK). SEM micrographs were acquired at various magnifications using backscattered electron detection at an acceleration voltage of 5 kV.

2.3. Adsorption and Desorption Experiments

Batch experiments were conducted separately with DG, CP, and VC, using aqueous mixtures containing PEN, S-MET, BPA, and NP. The experimental conditions adopted are summarized in Table 2; the experimental workflow is shown in Figure S1.

Table 2. Experimental conditions for batch adsorption and sequential desorption of penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and nonylphenol (NP) on digestate (DG), compost (CP), and vermicompost (VC).

Parameter	Ratio Screening	Adsorption Kinetics	Adsorption Isotherms	Desorption Isotherms
Dry amendment mass (mg)	2, 5 10, 20	2	2	2; retained after adsorption
Solution volume (mL)	20	20	20	20 after each replacement
Solution-to-amendment ratio (mL g^{-1})	10,000; 4000; 2000; 1000	10,000	10,000	10,000
Initial concentration per contaminant (mg L^{-1})	2	2	0.4; 0.5; 1; 2	Preceding adsorption: 2. At each desorption cycle: see note
Stirring (rpm)	350; in the dark	350; in the dark	350; in the dark	350; in the dark
Contact time (h)	16	0.083; 0.167; 0.25; 0.5; 1; 2; 4; 8; 16	16	16 per cycle
Temperature (°C)	20 ± 1	20 ± 1	20 ± 1	20 ± 1
Solution replacement	—	—	—	15 mL removed and replaced with 15 mL double-distilled water
Replicates per condition	3	3	3	3
Centrifugation	10,000× *g*; 10 min	10,000× *g*; 10 min	10,000× *g*; 10 min	10,000× *g*; 10 min
Analysis	UHPLC, Section 2.4	UHPLC, Section 2.4	UHPLC, Section 2.4	UHPLC, Section 2.4

Note: Each adsorption solution contained all four compounds at the stated concentration per compound. DG, CP, and VC were tested separately. Desorption began with the amendments initially loaded at 2 mg L^{-1}. Fresh replacement water contained no added contaminants. With 5 mL retained and the volume restored to 20 mL, the nominal aqueous concentration immediately after replacement was 0.25 times the preceding equilibrium concentration, before further desorption.

The effect of the solution-to-amendment ratio was assessed using four amendment masses at a constant solution volume and contaminant concentration (Table 2). Adsorption kinetics and isotherms were subsequently evaluated in glass centrifuge tubes at the highest solution-to-amendment ratio. A 16 h equilibration period was selected from preliminary tests. Equilibrium was considered reached when the adsorbed amount did not differ significantly between consecutive sampling times (Student's *t*-test, $p \leq 0.05$, $n = 3$). Desorption was investigated immediately after adsorption using the samples initially added with each contaminant at 2 mg L^{-1}. Three sequential desorption cycles were performed.

Before analysis, supernatants from all adsorption and desorption experiments were filtered through 0.45 µm cellulose acetate filters (Millipore™, Burlington, MA, USA). Aqueous concentrations were determined by UHPLC, as described in Section 2.4. The kinetic experiments included amendment blanks containing 2 mg of amendment in 20 mL of double-distilled water. An amendment-free control containing the contaminant mixture was processed after 16 h; no significant changes in aqueous concentrations were observed.

The amount of each compound adsorbed at time *t*, *qt* (mg g^{-1}), was calculated as:

$$q_t = \frac{(C_0 - C_t)\ V}{m}$$

where C_0 and C_t (mg L^{-1}) are the initial concentration of the compound in solution and its concentration at time *t*, respectively, V (L) is the solution volume, and m (g) is the amendment mass. At equilibrium, C_t and *qt* are denoted as C_e and q_e, respectively.

Experimental sorption kinetics data were fitted to the pseudo first-order (PFO) and pseudo second-order (PSO) kinetic models to estimate the rate constants and investigate the possible sorption mechanisms involved [44,45]. The nonlinear forms of the PFO and PSO equations, together with the definitions of the variables and constants, are reported in Table S2.

Experimental sorption isotherm data were described using the two-parameter nonlinear Freundlich [46], Langmuir [47], and Temkin [48] models, as well as the linear Henry model [49]; the corresponding equations are reported in Table S2. Experimental desorption data were also fitted to the Freundlich and Henry isotherm equations (Table S2). The hysteresis coefficient, H, was calculated as the ratio of the Freundlich desorption exponent ($1/n_{des}$) to the adsorption exponent ($1/n$), according to Barriuso et al. [50]. An H value below 1 denotes hysteresis, i.e., slow and incomplete desorption of the compound from the adsorbent surface.

2.4. Chromatographic Analysis

The residual concentrations of the compounds in the supernatants were measured using a UHPLC apparatus (Dionex Ultimate 3000 RSLC, Waltham, MA, USA) equipped with a WPS-3000 autosampler, an HPG-3200 RS pump, a DAD-3000 RS diode-array detector (Dionex Ultimate 3000 RSLC, Waltham, MA, USA), and an FLD-3400 RS fluorescence detector (Dionex Ultimate 3000 RSLC, Waltham, MA, USA). The chromatographic conditions used for the four contaminants are listed in Table 3. The compounds were quantified using the external standard method.

Table 3. Chromatographic conditions for the analysis of penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and nonylphenol (NP).

Parameter	PEN	S-MET	BPA	NP
Mobil phase	H_2O (A): Acetonitrile (B)			
Column	Supelco^{TM} LC-18 column (Bellefonte, PA, USA) (250 mm × 4.6 mm; 3 µm particle size)			
Column temperature (°C)	25 °C			
Mobil phase flow rate (mL min^{-1})	0.8			
Gradient elution program	0–2 min, 60% B; 2–7 min, from 60% to 70% B; 7–15 min, from 70% to 80% B; 15–22 min, from 80% to 90% B; 22–27 min, 90% B; 27–30 min, from 90% to 60% B			
Retention time (min)	15.0	13.6	7.9	26.8
Detector	UV–Vis		Fluorescence	
Wavelength excitation/emission (nm)	211		200/290	230/310

2.5. Plant Assays

2.5.1. Experimental Setup

The lettuce assay was conducted using soil microcosms under controlled growth chamber conditions. Before sowing, soil was amended separately with DG, CP, or VC at different application rates, alongside an unamended control. Descriptions of the experimental set-up, treatment conditions, and growth duration are summarized in Table 4.

Table 4. Experimental setup and growth conditions used in the lettuce microcosm assays.

	Experimental Conditions
Microcosms units	Polyethylene black-colored square pots (9 cm × 9 cm × 20 cm, ~1620 cm^3 in volume), closed at the bottom with a nylon mesh membrane
Soil	1 kg dry soil equivalent per microcosm
Sowing density	One lettuce seed per microcosm
Biomass application rates	0 (control), 10 and 30 Mg ha^{-1} batch
Treatments	3 amendments × 3 dosages × 3 replicated experimental blocks (total microcosms = 27)
Growth chamber conditions	25 ± 1 °C temperature, 65% relative humidity, 12/12 h day/night photoperiod, 400 W m^{-2} at plant height photosynthetically active radiation (PAR)
Soil microcosms watering	Soil was kept at approximately 70% of water-holding capacity by watering every 2–3 days
Plant growth and sampling	60-day growing cycle followed by plant harvest and microcosm opening

2.5.2. Plant Analysis: Total Biomass and Root Morphology

At the end of the 60-day growing period, the microcosms were opened and lettuce plants were carefully removed from the soil. Plants were separated into shoots and roots, rinsed with deionized water, and weighed separately to determine their fresh weights. Shoot dry weight (g) was determined after oven-drying at 70 °C for 72 h. Root systems were stained with 0.1% (*w*/*v*) toluidine blue O solution for 5 min, thoroughly rinsed with water, and scanned at a resolution of 600 dpi using a WinRhizo STD 1600 system (Régent Instruments Inc., Québec, QC, Canada). The images were processed using WinRhizo® root analysis software to determine total root length, root surface area, and root volume. Root dry weight was subsequently determined after oven-drying at 70 °C for 72 h. The shoot-to-root dry weight ratio was also calculated by dividing shoot dry weight by root dry weight.

2.5.3. Statistical Analysis

Soil and plant data were assessed for normality using the Kolmogorov–Smirnov test and for homogeneity of variances using Levene's test. The block effect was not statistically significant ($p > 0.05$). Plant response data presented in Figures 5 and 6 were analyzed using two-way analysis of variance (ANOVA) with amendment type and application rate as factors. The least significant difference (LSD) test at $p < 0.05$ was used for pairwise comparisons of means. Statistical analyses were performed using Systat 13.0; graphs were generated using SigmaPlot 10.0 (both from SYSTAT Software Inc., Erkrath, Germany).

3. Results and Discussion

3.1. Micromorphological Characteristics of the Organic Amendments Studied

Scanning electron microscopy (SEM) images of all materials clearly revealed heterogeneous structure, highly porous texture with fibrous lignocellulosic residues, and numerous cavities, channels, and irregular surfaces (Figure 1). Distinct spiral-shaped structures in DG were consistent with preserved plant xylem tissues, while fine particulate deposits suggested mineral or organo–mineral aggregates. These features may facilitate solute diffusion and contaminant retention. Energy-dispersive X-ray (EDX) analysis revealed the presence of C, O, P, and alkali and alkaline earth metals, consistent with the composition of the biomass from which the materials originated (Figure 1). The relatively high electrical conductivity (EC) of DG may reflect its soluble salt content, whereas its alkaline pH may be associated with the degradation of organic acids and ammonia production during AD [51].

3.2. Adsorption and Desorption Study

3.2.1. Effects of the Solution-to-Amendment Ratio

Increasing the solution-to-amendment ratio from 1000 to 10,000 mL g^{-1} raised the equilibrium amounts adsorbed per unit mass by 2.2–11.6-fold across the compounds and amendments; NP adsorption increased by approximately tenfold on all materials (Figure 2). This trend was previously observed and attributed to increased exposure of the internal surfaces of the materials [18]. At the highest ratio, PEN, S-MET, and BPA adsorption was significantly higher on DG than on CP and VC. This ratio was, therefore, selected for subsequent experiments with all three amendments.

3.2.2. Adsorption Kinetics

NP reached adsorption equilibrium within a few minutes on all amendments, whereas PEN, S-MET, and BPA required approximately 4 h on DG and 4–8 h on CP and VC (Figure 3). For these latter compounds, rapid retention during the first 30 min was followed by a slower stage. It is plausible that, in the initial phase, the most exposed and energetically favorable sites were rapidly occupied, whereas subsequently, diffusion towards internal sites became the rate-limiting step of the process.

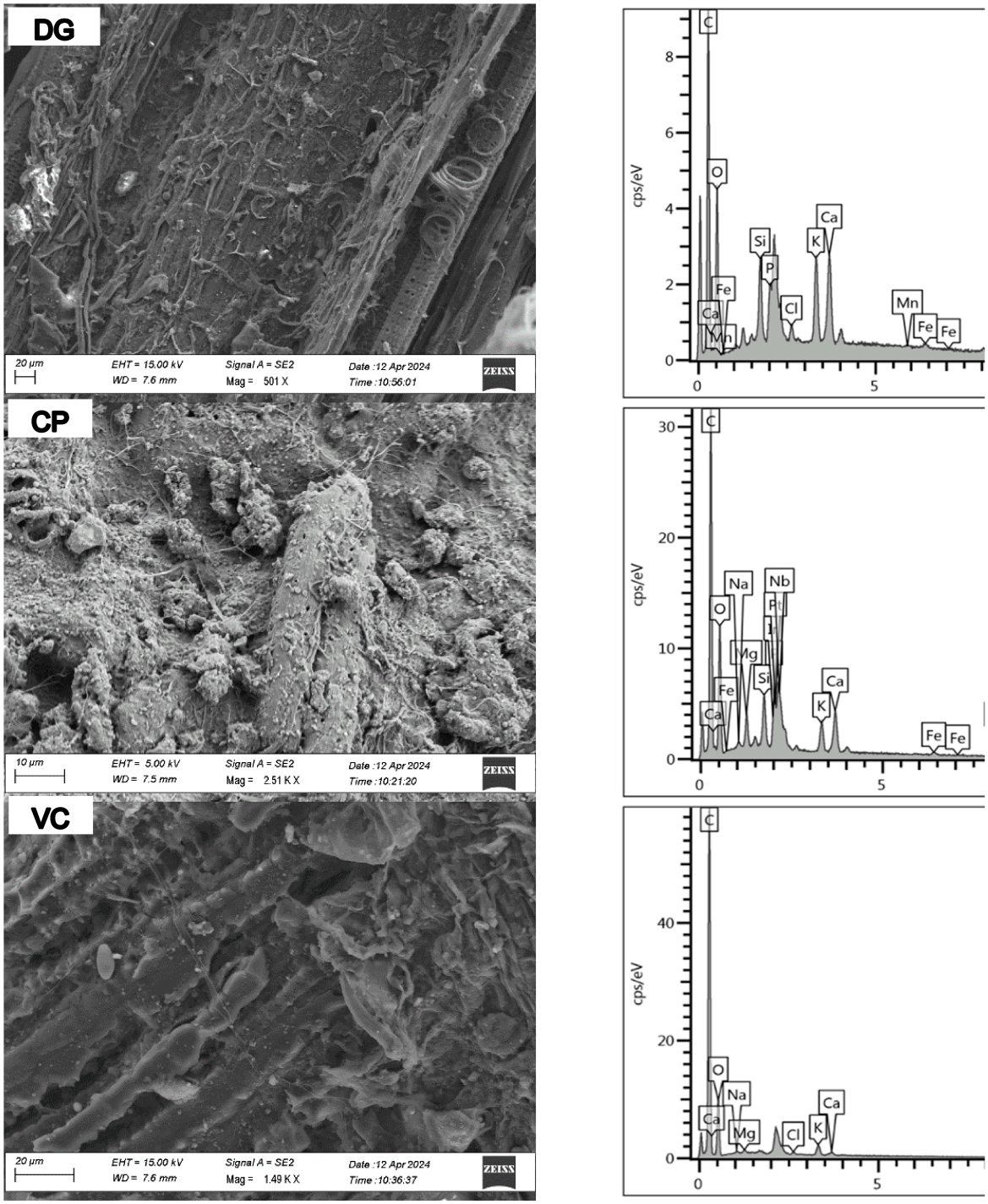

Figure 1. Scanning electron microscopy (SEM) images and corresponding energy-dispersive X-ray (EDX) spectra of digestate (DG), compost (CP), and vermicompost (VC).

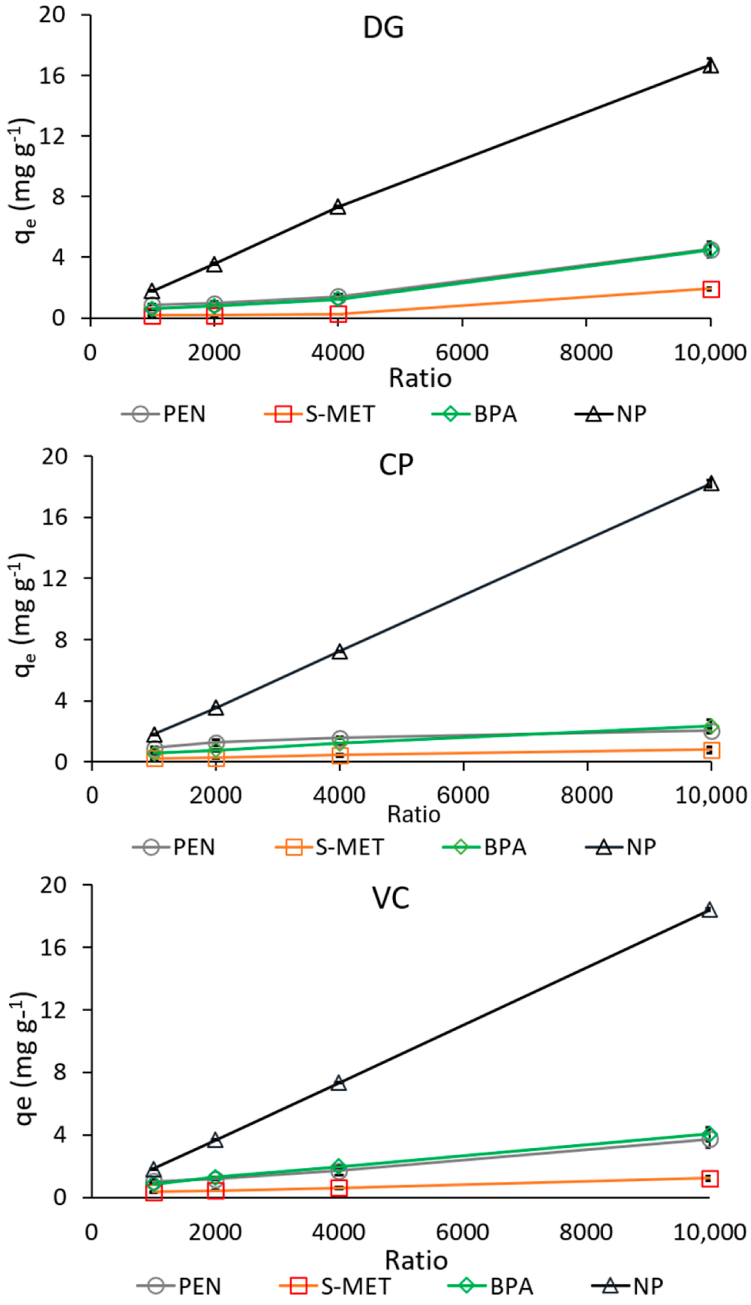

Figure 2. Effect of the solution-to-amendment ratio on the equilibrium adsorbed concentrations of penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and 4-nonylphenol (NP) on digestate (DG), compost (CP), and vermicompost (VC). Vertical error bars indicate standard errors ($n = 3$).

The experimental kinetic data were fitted into the nonlinear PFO and PSO equations (Table S2). The PFO model is generally associated with physisorption, whereas the PSO model assumes stronger interaction and high-energy bonds between the sorbate and the adsorbent (chemisorption). The PSO model generally described the kinetic data better than the PFO model, yielding higher r and lower SSR values (Table 5). The PSO rate constants (k_2) for PEN, S-MET, and BPA were generally higher on DG than on its derivatives. On DG, the modelled equilibrium amounts adsorbed per unit mass ($q_{e,2}$) followed the order of: S-MET (1.8 mg g^{-1}) < BPA (4.3 mg g^{-1}) ≈ PEN (4.3 mg g^{-1}) < NP (18.6 mg g^{-1}) (Table 5). A similar adsorption trend was observed on CP and VC, with the strong retention of NP consistent with its high hydrophobicity and low water solubility.

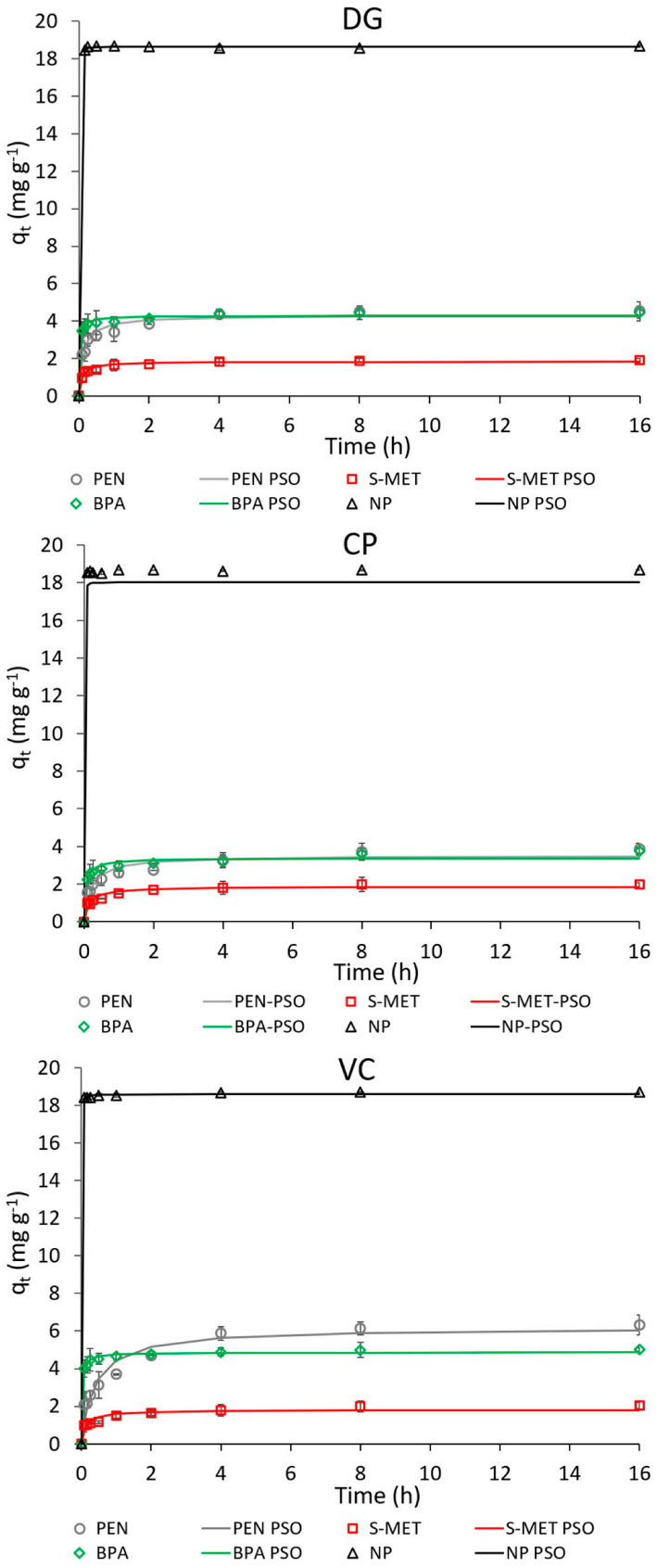

Figure 3. Adsorption kinetics of penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and 4-nonylphenol (NP) onto digestate (DG), compost (CP), and vermicompost (VC). Points represent experimental data, and lines show fits of the pseudo second-order (PSO) kinetic model. Vertical error bars indicate standard errors ($n = 3$).

Table 5. Kinetic parameters for the adsorption of penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and 4-nonylphenol (NP) onto digestate (DG), compost (CP), and vermicompost (VC) estimated by fitting kinetic models to the experimental data using nonlinear regression.

Compound	$q_{e,\text{experimental}}$ (mg g^{-1})	PFO Kinetics				PSO Kinetics			
		r	SSR	$q_{e,1}$ (mg g^{-1})	k_1 (h^{-1})	r	SSR	$q_{e,2}$ (mg g^{-1})	k_2 (g mg^{-1} h^{-1})
DG									
PEN	4.52	0.881	1.83	4.02	5.92	0.947	0.72	4.29	1.98
S-MET	1.91	0.896	0.20	1.73	7.72	0.969	0.05	1.83	6.53
BPA	4.48	0.733	0.54	4.14	19.1	0.902	0.20	4.28	9.53
NP	18.7	0.860	0.01	18.6	26.7	0.857	0.03	18.6	53.1
CP									
PEN	3.87	0.879	1.89	3.22	3.81	0.936	0.89	3.50	1.42
S-MET	1.97	0.871	0.49	1.74	4.72	0.932	0.21	1.86	3.70
BPA	3.76	0.778	0.94	3.20	11.2	0.887	0.45	3.65	5.48
NP	18.7	0.393	0.03	18.6	65.6	0.563	0.02	18.6	105
VC									
PEN	6.32	0.934	4.82	5.70	1.75	0.964	2.17	6.18	0.41
S-MET	2.03	0.853	0.57	1.74	4.76	0.920	0.26	1.87	3.65
BPA	5.01	0.775	0.44	4.72	20.4	0.938	0.12	4.86	9.80
NP	18.7	0.426	0.10	18.6	59.5	0.768	0.05	18.6	41.8

3.2.3. Adsorption and Desorption Isotherms

Adsorption isotherms showed broadly similar retention patterns among the amendments, with NP exhibiting the strongest affinity and S-MET the weakest (Figure 4; Table 6). The experimental data for the three amendments were fitted to the nonlinear Freundlich, Langmuir, and Temkin models, as well as the linear Henry equation. Freundlich and Langmuir models generally described the adsorption data satisfactorily; Henry fits were comparable for several compound–amendment combinations, while Temkin usually was the least appropriate. DG had the highest Freundlich K_F values for PEN and S-MET, whereas CP and VC had the highest values for BPA and NP, respectively. NP adsorption on CP was poorly described by all models, limiting interpretation of its fitted parameters (Table 6).

The Freundlich exponents were consistent with L-type adsorption of PEN and S-MET on DG ($1/n < 1$), whereas BPA and NP exhibited S-type isotherms ($1/n > 1$) in the Giles classification [52,53]. The latter behavior generally denotes cooperative adsorption and strong binding. For all three amendments, the distribution coefficient (Kd), Freundlich constant (K_F), and the organic carbon-normalized partition coefficient (K_{OC}) increased in the following order: S-MET < BPA < PEN « NP (Table 6). However, except for NP, all three parameters were generally higher for DG than for CP and VC.

This trend suggests that hydrophobicity played an important role in contaminant adsorption of contaminants onto the amendments. The Temkin parameter B followed the same trend as the adsorption constants. These results indicate progressively stronger adsorbate–adsorbent interactions along the same sequence. Positive B values of the Temkin equation are interpreted as evidence of heat release during adsorption; accordingly, the results obtained are consistent with an exothermic adsorption process.

Contaminants can interact with organic adsorbents through various concurrent mechanisms that influence the strength and reversibility of contaminant retention [54]. The coexistence of hydrophobic domains and polar functional groups in DG may, therefore, contribute to adsorption through partitioning, hydrogen bonding, and van der Waals forces [18]. Hydrophobic partitioning is likely to contribute to retention of all four compounds, while the phenolic hydroxyl groups of BPA and NP may additionally participate in hydrogen bonding, electron donor–acceptor or charge–transfer interactions. These interactions provide a possible explanation for the differences among contaminants without requiring a single dominant mechanism.

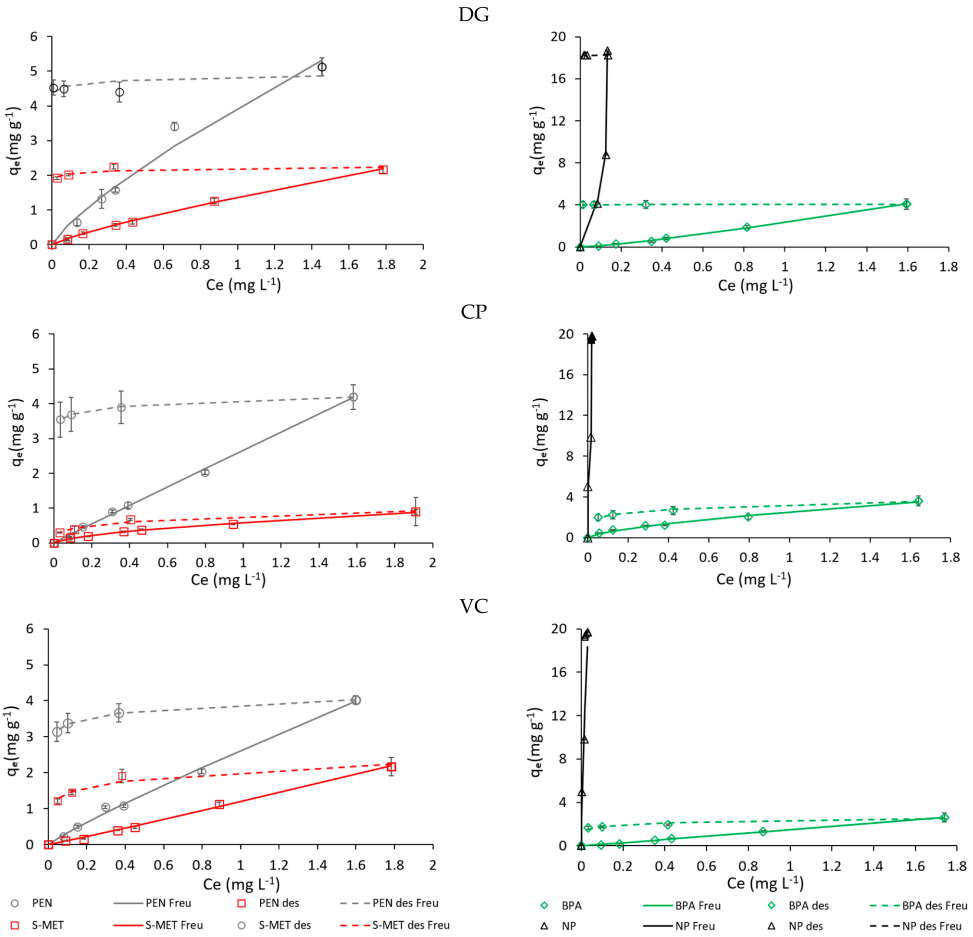

Figure 4. Adsorption and desorption isotherms of penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and 4-nonylphenol (NP) on digestate (DG), compost (CP), and vermicompost (VC). Points represent experimental data, and lines show fits of the Freundlich model. Vertical error bars indicate standard errors ($n = 3$).

The modest changes in adsorption following aerobic processing are consistent with the shared structural and chemical features of the materials. During AD, labile organic compounds of initial biomass, including polysaccharides, proteins, amino acids, and fatty acids, are preferentially decomposed, resulting in the relative enrichment of more stable components and aromatic features in DG. The progressive formation of humic-like and fulvic-like substances leads to an increase in the degree of humification (DH%) [55]. These compositional changes are consistent with organic matter stabilization. Subsequent composting can increase the humic-like fraction. Provenzano et al. [55] reported that a composted DG exhibited a lower tryptophan-like to fulvic-like fluorescence ratio than the parent DG, consistent with increased humification. However, Tambone et al. [56] reported only modest compositional changes, with substantial retention of O-alkyl carbon associated with cellulose and hemicelluloses. Previous characterization of the amendments examined here showed broadly similar FTIR–ATR and Raman features, including hydrophilic functional groups and hydrophobic moieties, alongside differences in band intensities [36]. These spectroscopic findings also indicated that composting promoted the formation of aromatic functional groups characteristic of humic-like substances [36]. BET surface areas were approximately 0.97, 1.0 and 1.6 m^2 g^{-1} for DG, CP, and VC, respectively [36]. The larger surface area of VC did not produce a consistent adsorption advantage, indicating that surface area alone does not explain the observed differences.

Table 6. Adsorption isotherm parameters for penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and 4-nonylphenol (NP) on digestate (DG), compost (CP), and vermicompost (VC), estimated by fitting isotherm models to the experimental data using nonlinear regression.

Compound	Henry				Freundlich				Langmuir				Temkin				
	r	SSR	Kd (L g^{-1})	K_{OC} (L g^{-1})	r	SSR	K_F (L g^{-1})	$1/n$	r	SSR	b (mg g^{-1})	K_L (L mg^{-1})	r	SSR	A_T (L g^{-1})	B	b_T (J mmol^{-1})
DG																	
PEN	0.986	1.17	3.87	8.66	0.983	0.54	3.95	0.79	0.990	0.30	13.3	0.44	0.972	0.96	10.2	1.75	1402
S-MET	0.995	0.08	1.29	2.89	0.999	0.003	1.36	0.81	0.999	0.003	6.91	0.26	0.942	0.32	9.92	0.64	3835
BPA	0.994	0.25	2.41	5.39	0.999	0.02	2.29	1.24	0.985	0.28	160	0.01	0.894	2.28	6.95	1.3	1883
NP	0.899	0.03	22.5	50.3	0.999	0.02	22.4	1.73	0.998	0.03	83.0	0.03	0.926	1.26	8.00	2.17	2103
CP																	
PEN	0.999	0.02	2.65	5.86	0.999	0.02	2.66	0.98	0.999	0.02	79.4	0.03	0.921	1.66	9.12	1.26	1940
S-MET	0.976	0.07	0.52	1.15	0.994	0.01	0.63	0.71	0.990	0.01	1.53	0.69	0.949	0.04	14.0	0.23	10,443
BPA	0.982	0.75	2.37	5.24	0.995	0.06	2.54	0.67	0.986	0.21	7.18	0.58	0.923	0.98	18.8	0.86	2838
NP	0.843	33.0	631	1396	0.781	45.6	29.0	0.16	0.793	79.5	281	2.46	0.765	47.3	26,577	1.39	1768
VC																	
PEN	0.998	0.104	2.57	6.05	0.998	0.044	2.62	0.90	0.997	0.06	26.6	0.111	0.927	1.36	10.2	1.18	2083
S-MET	0.999	0.011	1.21	2.85	0.999	0.008	1.19	1.05	0.998	0.012	222	0.005	0.909	0.54	7.51	0.67	3665
BPA	0.999	0.022	1.49	3.51	0.998	0.017	1.47	1.04	0.997	0.026	67.1	0.023	0.931	0.6	7.11	0.85	2891
NP	0.983	17.4	651	1532	0.948	14.4	174	0.64	0.953	17.4	441	1.53	0.863	28.7	2111	3.95	3767

The modest changes in adsorption following aerobic processing are consistent with the shared structural and chemical features of the materials. During AD, labile organic compounds of initial biomass, including polysaccharides, proteins, amino acids, and fatty acids, are preferentially decomposed, resulting in the relative enrichment of more stable components and aromatic features in DG. The progressive formation of humic-like and fulvic-like substances leads to an increase in the degree of humification (DH%) [55]. These compositional changes are consistent with organic matter stabilization. Subsequent composting can increase the humic-like fraction. Provenzano et al. [55] reported that a composted DG exhibited a lower tryptophan-like to fulvic-like fluorescence ratio than the parent DG, consistent with increased humification. However, Tambone et al. [56] reported only modest compositional changes, with substantial retention of O-alkyl carbon associated with cellulose and hemicelluloses. Previous characterization of the amendments examined here showed broadly similar FTIR–ATR and Raman features, including hydrophilic functional groups and hydrophobic moieties, alongside differences in band intensities [36]. These spectroscopic findings also indicated that composting promoted the formation of aromatic functional groups characteristic of humic-like substances [36]. BET surface areas were approximately 0.97, 1.0 and 1.6 $m^2\ g^{-1}$ for DG, CP, and VC, respectively [36]. The larger surface area of VC did not produce a consistent adsorption advantage, indicating that surface area alone does not explain the observed differences.

The desorption data were fitted to the Henry and Freundlich models (Figure 4; Table 7). For DG, PEN desorption was better described by the linear model, S-MET desorption was better described by the Freundlich model, and BPA desorption was described equally well by both. For CP and VC, the Freundlich model generally provided better fits for these three compounds. NP desorption was extremely limited from all amendments; neither model satisfactorily described its release from DG (Table 7). All the Freundlich desorption exponents ($1/n_{des}$) were below unity and substantially lower than the corresponding adsorption exponents, yielding hysteresis values (H) below 1 [50]. Hysteresis was positive and generally pronounced, indicating slow and limited release of the compounds. After three desorption cycles, DG released approximately 12%, 12%, 2%, and 2% of the adsorbed PEN, S-MET, BPA, and NP, respectively. Corresponding releases were 67%, 15%, 45%, and 2% from CP and 44%, 22%, 38%, and 2% from VC. Thus, DG retained PEN and BPA more strongly during desorption, whereas NP release remained minimal from all materials.

Table 7. Desorption isotherm parameters for penconazole (PEN), S-metolachlor (S-MET), bisphenol A (BPA), and 4-nonylphenol (NP) on digestate (DG), compost (CP), and vermicompost (VC), estimated by fitting isotherm models to the experimental data using nonlinear regression.

Compound	Henry				Freundlich				
	r	SSR	Kd_{des} ($L\ g^{-1}$)	K_{OCdes} ($L\ g^{-1}$)	r	SSR	K_{Fdes} ($L\ g^{-1}$)	$1/n_{des}$	H
DG									
PEN	0.920	0.05	0.45	1.01	0.621	0.21	4.83	0.02	0.02
S-MET	0.516	0.05	0.09	0.20	0.813	0.02	2.20	0.03	0.04
BPA	0.919	0.0003	0.03	0.07	0.919	0.0003	4.05	0.003	0.002
NP	0.523	0.03	0.19	0.42	0.422	310	23.4	0.002	0.002
CP									
PEN	0.680	31.7	3.22	7.12	0.998	0.001	4.10	0.04	0.04
S-MET	0.850	0.42	0.53	1.18	0.985	0.006	0.77	0.26	0.41
BPA	0.809	10.1	2.57	5.68	0.990	0.03	3.24	0.17	0.25
NP	0.950	0.01	153	339	0.951	0.01	34.1	0.14	0.87
VC									
PEN	0.767	4.91	1.45	3.41	0.971	0.03	2.04	0.16	0.15
S-MET	0.704	25.6	3.06	7.20	0.998	0.002	3.91	0.07	0.07
BPA	0.771	6.62	1.74	4.09	0.961	0.04	2.35	0.12	0.12
NP	0.978	66.4	842	1981	0.952	0.01	122	0.04	0.06

Direct comparisons in the literature remain limited. To the best of our knowledge, no previous studies have quantified and modelled the adsorption of PEN, S-MET, and NP on DG, and of all four contaminants on VC. Regarding BPA, the K_F value obtained in the present study (2.29 L g^{-1}) was considerably higher than that previously reported for the same compound adsorbed on a mixed DG (0.13 L g^{-1}) [18]. Studies in amended soils have shown increased PEN adsorption following compost addition [57] and increased S-MET adsorption in two compost-amended agricultural soils [35]. Recently, Carnimeo et al. [58] reported that soil amendment with CP and VC reduced the uptake and accumulation of organic contaminants, including BPA and NP, in cucumber plants. These findings support the relevance of these amendments to limit contaminant transfer from soil to plants, while the present batch results require verification in amended soils.

3.3. Lettuce Responses to Organic Amendment

3.3.1. Aboveground and Belowground Biomass Allocation

Lettuce growth was assessed under controlled microcosm conditions to complement the evaluation of amendment adsorption–desorption properties. Shoot dry biomass, root dry biomass, and their ratio responded markedly to the experimental treatments; in particular, DG promoted the greatest shoot and root biomass production (Figure 5A–C). Shoot dry biomass was strongly influenced by amendment type ($p < 0.001$) and its interaction with application rate ($p < 0.05$). At 30 Mt ha^{-1}, shoot dry biomass was approximately 12.3 g with DG, compared with 9.6 g with CP and 10.2 g with VC (Figure 5A). A particularly marked stimulatory effect of DG was observed for root dry biomass, which increased by approximately 70% at 10 Mg ha^{-1} and nearly 90% at 30 Mg ha^{-1} relative to the control, significantly exceeding CP and VC at the same application rates (Figure 5B). DG also reduced the shoot-to-root dry biomass ratio, particularly at the lower application rate, whereas CP and VC caused a dose-dependent increase in this ratio (Figure 5C).

The positive plant growth response to DG addition may reflect readily available nutrients, particularly mineral nitrogen, which promotes rapid vegetative growth, especially in short-cycle crops, such as lettuce [59,60], and root biomass allocation [61,62]. Hormone-like molecules released from solid DG may also contribute [63]. Slower nutrient release from stabilized organic matter may help to explain the weaker lettuce responses to CP and VC [64,65] and their greater allocation of biomass to aboveground tissues [66]. Collectively, these findings suggest that each amendment activates distinct mechanisms governing carbon and nutrient availability, biomass allocation between roots and shoots, and plant adaptation to amended soil conditions [67,68].

3.3.2. Root Morphology

Total root length was significantly influenced by amendment type ($p < 0.05$) and application rate ($p < 0.001$), with no significant interaction (Figure 6A). DG addition promoted a marked linear increase in total root length from approximately 280 m in unamended soil to 526 m at 10 Mg ha^{-1} (+ 88%) and 665 m at 30 Mg ha^{-1} (+ 137%). Differently, CP and VC produced smaller increases, reaching 515 m and 473 m, respectively (Figure 6A). Root surface area was significantly affected by amendment type and application rate (both $p < 0.001$) and their interaction ($p < 0.01$; Figure 6B). Compared with plants grown in unamended soil, DG application at 30 Mg ha^{-1} increased root surface area by approximately 40% to 4.3 m^2, whereas CP and VC reduced it at 10 Mg ha^{-1} and restored it to approximately 3.3 m^2 at 30 Mg ha^{-1}.

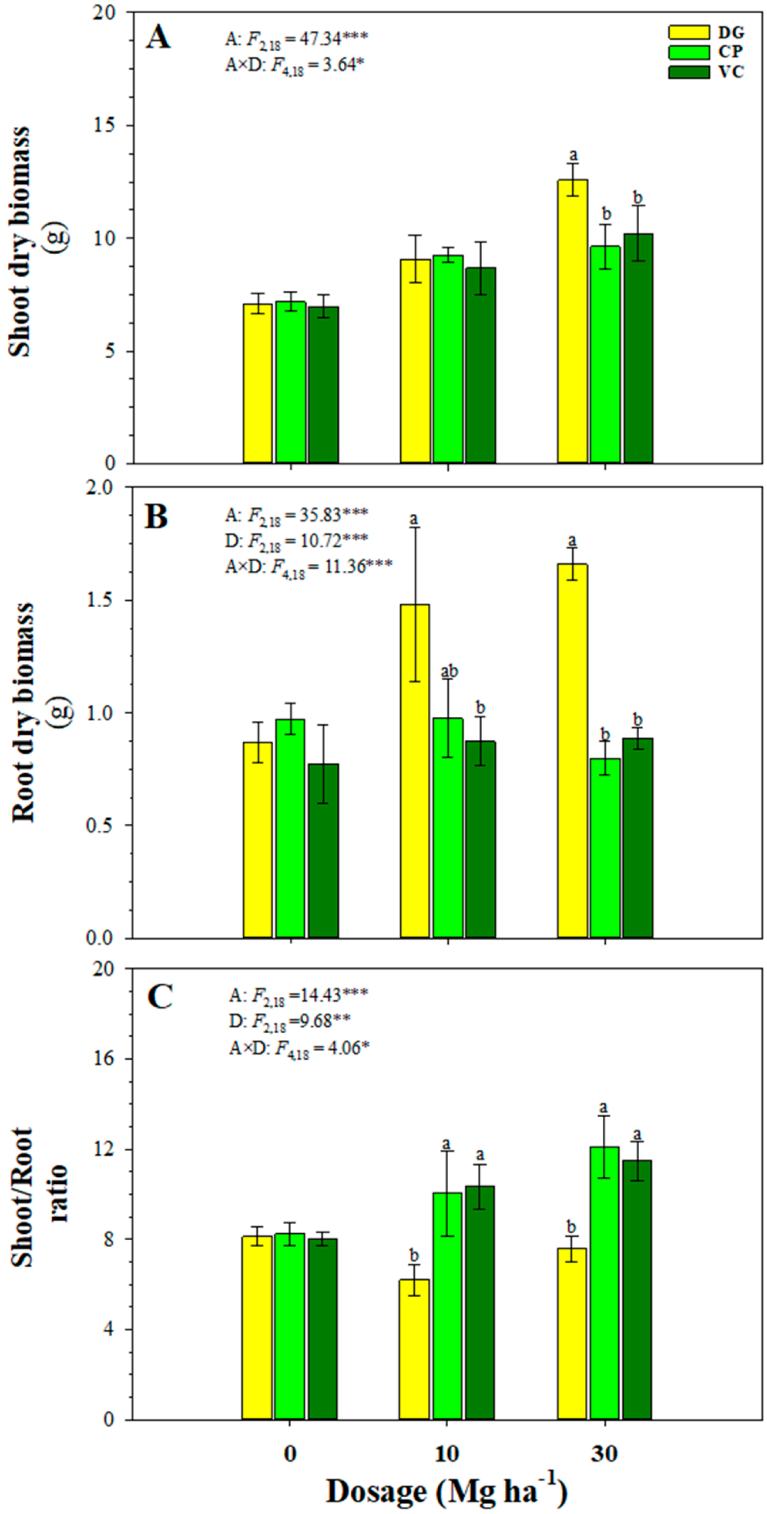

Figure 5. Shoot dry biomass, root dry biomass, and shoot-to-root dry biomass ratio of lettuce plants grown in unamended soil (0 Mg ha^{-1}) or soil amended with digestate (DG), compost (CP), or vermicompost (VC) at 10 or 30 Mg ha^{-1}. Values are means ± standard deviations (n = 3). Within each application rate, different letters, where shown, indicate significant differences among amendment types (LSD test, $p < 0.05$). F-values and significance levels from two-way ANOVA are reported for amendment type (A), application rate (D), and their interaction (A × D): * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

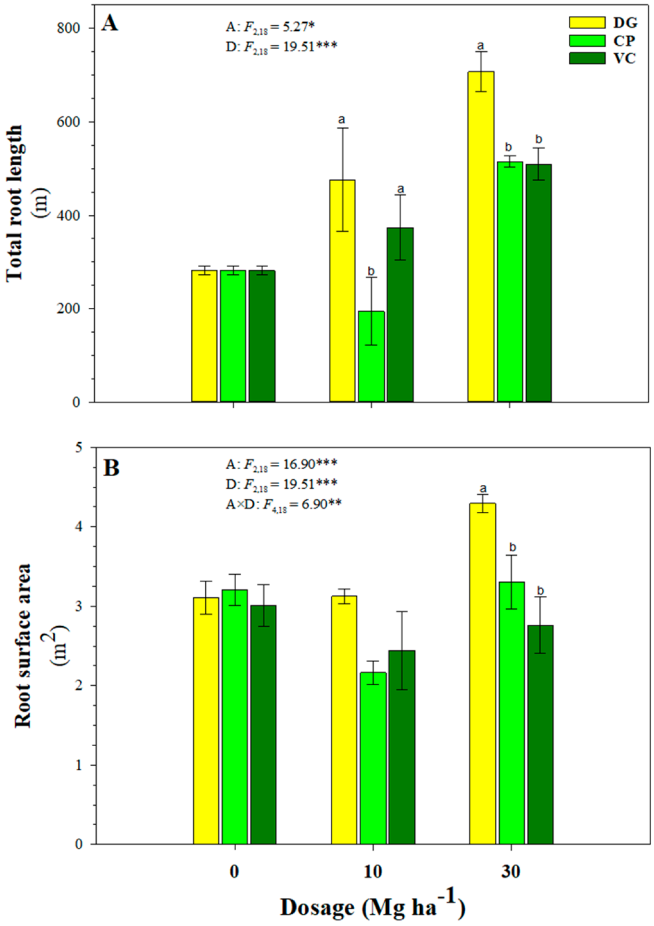

Figure 6. Total root length and root surface area of lettuce plants grown in unamended soil (0 Mg ha^{-1}) or soil amended with digestate (DG), compost (CP), or vermicompost (VC) at 10 or 30 Mg ha^{-1}. Values are means ± standard deviations ($n = 3$). Within each application rate, different letters indicate significant differences among amendment types (LSD test, $p < 0.05$). F-values and significance levels from two-way ANOVA are reported for amendment type (A), application rate (D), and their interaction (A × D): * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

These results support the view that root morphological traits respond more sensitively than total dry biomass to amendment type, reinforcing their value as early indicators of soil–plant interactions. The greater root system expansion in this short-cycle crop under DG, particularly at the higher application rate, may reflect the enrichment of readily available nutrients associated with labile organic carbon inputs [69,70]. Together with the biomass results, these responses indicate that DG supported more rapid root development than its aerobic derivatives during the 60-day experiment. Potential longer-term benefits of CP and VC for soil fertility and nutrient management require further investigation.

3.4. Future Research Directions

Although adsorption–desorption experiments and lettuce microcosm assays provided important complementary information on the performance of DG, CP, and VC as soil amendments, their combined effects on the overall dynamics of contaminants in soil–plant systems remain to be established. Batch adsorption cannot be directly extrapolated to amended soils; plant growth responses do not predict contaminant uptake and accumulation in edible tissues. Future studies will, therefore, examine retention, degradation and uptake of PEN, S-MET, BPA, and NP in integrated soil–plant experiments, including the possible effects of amendment-induced changes in root morphology on rhizosphere processes. Linking soil

improvement with reduced contaminant transfer is also consistent with the objectives of the of Directive (EU) 2025/2360, Soil Monitoring Law, which include improving soil health and reducing soil contamination to levels that are no longer harmful to human health and the environment [71].

Plant uptake represents a potential exposure pathway that should be considered alongside the agronomic benefits of amendment application. PEN and S-MET residues have been reported in lettuce following soil treatment [72,73]; BPA and NP uptake and distribution have been documented in hydroponic studies [74,75]. NP residues have also been detected in lettuce irrigated with reclaimed water [76]. These findings support the need to quantify contaminant accumulation under the specific soil and amendment conditions investigated here. Finally, longer-term experiments across different soils should establish whether contaminant retention persists as the amendments decompose, thus providing a stronger basis for selecting materials that support crop development while limiting contaminant transfer to edible plant parts.

4. Conclusions

This study provides new insights into how aerobic composting and vermicomposting modify the functional properties of anaerobic DG. Adsorption experiments with DG, CP, and VC revealed only modest differences in their capacities to retain PEN, S-MET, BPA, and NP. DG generally adsorbed contaminants more rapidly and retained PEN, S-MET, and BPA to a greater extent than CP and VC, whereas NP was adsorbed almost completely and instantaneously by all three amendments. Desorption exhibited pronounced hysteresis for all amendments and contaminants, particularly for BPA and NP onto DG, indicating slow and incomplete release over the three desorption cycles. More pronounced differences emerged in the 60-day microcosm experiments, in which DG promoted greater shoot and root biomass and more extensive root systems CP and VC. These findings indicate that aerobic processing did not consistently improve adsorption and reduced the short-term plant growth-promoting effects observed with the parent DG. Amendment selection should, therefore, consider agronomic effectiveness alongside practical aspects such as local availability, management requirements, and cost. These complementary laboratory and microcosm findings provide a basis for the further assessment of contaminant dynamics in amended soil–plant systems.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/environments13120645/s1, Table S1: Major physicochemical properties of the Calcari-Fluvic Cambisol soil selected for filling the microcosms. Figure S1: Experimental workflow. Table S2: Sorption models considered in this study.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

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