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PESTICIDE VOLATILIZATION IN BIOBED SYSTEMS' POTENTIAL SUBSTRATES. A VIABLE SIMPLE LABORATORY EXPERIMENT TO DETERMINE PESTICIDE LOSSES TO THE ENVIRONMENT

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Abstract: Pesticides in the environment represent a concern worldwide. Agriculture is the primary activity related to pesticide use and the main source of these compounds in the environment. To control and minimize pesticide use is a goal. The biobed systems are simple and proven systems retaining pesticides in agricultural plots, avoiding soil and water pollution. The biomixture is considered one of the most important aspects in these systems. The correct substrate selection guarantees the efficiency of the biobeds. Volatilization, runoff, and microbial activity are mechanisms that govern pesticide dissipation in biobeds. This research was developed to know the losses of pesticides in biobed systems due to volatilization. Five potential organic substrates (agricultural soil, sisal, corn stover, compost, and seaweed) were used in the biomixture. 2,4-D, atrazine, carbofuran, diazinon, and glyphosate, frequently used in Yucatan, México´s crops were selected and studied for 72 hours to different sampling times at microcosms level. A simple system was designed to catch the volatile pesticide. After 72 h, the highest values reported for volatile fraction were observed. Diazinon was the most volatile (~43% in soil), and glyphosate was the least (~43% in soil). Atrazine, considered as no volatile, was volatilized over 20% of the initial concentration in soil. The exposure time and pesticide type on the volatile fraction of pesticide were statistically significant ($P<0.05$). Substrate type was significant on pesticide volatilization ($P<0.05$). Pesticide type was the most significant factor in pesticide volatilization; the pH, lignin content, and the final moisture in the substrate (% SM) were physicochemical characteristics of substrates that affected the pesticide volatilization. The results show that selecting the appropriate substrates that allow less pesticide volatilization guarantees that greater dissipation is carried out by

degradation processes, taking into account that one of the main functions of biobeds is the confinement of agricultural effluents.

Keywords: biobeds; organic substrates; pesticide volatilization; physicochemical parameters

INTRODUCTION

Worldwide, pesticide use is extensive in agriculture to eradicate various pests to increase crop yields and ensure food quality, but also after harvesting to protect agricultural products from parasites and harmful organisms.

Biotic and abiotic processes are involved in the pesticide behavior in the environment. The volatilization, leaching, and diffusion are the three main abiotic processes responsible for the transfer of pesticide residues from soil to air and water compartments, respectively (Alletto et al., 2010). Volatilization of pesticide residues from the surface of the soil, plant cover, and also water conducts their dispersion to the air contributing to the exposure of human populations with possible health issues such as asthma and allergies and long-distance dispersal residues *via* rainfall (Wang et al., 1997). Among processes involved in pesticide fate in the environment, volatilization is the least studied even if it is responsible for up to 25% loss of the pesticide (Prueger et al., 2005).

Understanding all these processes is not only of interest to monitor pesticide fate in the environment but also to propose engineering approaches to clean the environment from pesticide residues by implementing bioremediation strategies or to treat pesticide effluents in rustic devices, such as Biobed to avoid point contamination sources which are known to account for a big part of the overall contamination (Karanasios et al., 2010).

The effect of substrate addition in biobed systems has shown that degradation is faster in biomixture materials compared to the soil alone (Vischetti et al., 2020); additionally, abiotic and biotic mechanisms such as adsorption and degradation of pesticides were found to be more effective in organic wastes than in soils (Coppola et al., 2010; Breure et al., 2018).

The effect of physicochemical characteristics of substrates of biomixtures and factors such as temperature and moisture in pesticide treatment in biobeds have been reported before (Góngora-Echeverría et al., 2017, Cordova-Mendez et al., 2021). However, studies related to biobeds never focus on the losses of pesticides by volatilization and the correct selection of substrates considering the abiotic process involved in pesticide behavior in the biobed systems.

This research aims to determine the volatile fraction of five pesticides (2,4-D, atrazine, carbofuran, diazinon, and glyphosate) applied to four substrates used in biobeds as biomixture components for the treatment of agricultural effluents and an arable soil in southeastern Mexico, plus the effect of the substrates' physicochemical properties on pesticide volatilization using a viable and simple procedure at laboratory level.

METHODOLOGY

PESTICIDES AND SUBSTRATES

The five studied pesticides were selected according to their use in crops in the Yucatan state, Mexico. The formulated products used were Agramina 6 (2,4-D, 81% of purity), Sanazina 500 (atrazine,45% of purity), Velfosato (VELSIMEX®, glyphosate, at 41% of purity), Furadan 350L (FMC®, carbofuran, at 33.21% purity) and Dragon 25E (DRAGON®, diazinon, at 25% of purity). A solution containing the five pesticides was prepared. Each pesticide was prepared at 10 mg/L in a 0.01M $CaCl_2$ solution in distilled water.

The use of local organic substrates and local soil is an aspect that makes biobeds economically viable to farmers around the world. For this research, the substrates were chosen due to their availability in the region. Biosorbents such as sisal bagasse, corn stover, compost, and seaweeds (from the Yucatán coast), and agricultural soil with a history of pesticide use were selected. All substrates were physicochemically characterized (Table 1).

VOLATILIZATION TRAP DEVICE

To catch the losses due to volatilization in each tested substrate, a practical and easy device was designed. The system to catch the volatile fraction consisted of a 100 mL sterilized glass container, a trap formed by sterile cotton mesh, and silica pellets (weight 2 g) with a final average weight of 2.55 ± 0.15 g in the top of the container. To avoid losses from the system, a parafilm seal on the top of the container was used.

MICROCOSM'S SYSTEMS IMPLEMENTATION

Ninety microcosms (15 systems for each substrate) were implemented using the volatilization trap device and incubated in the dark at room temperature (29.6 ± 2°C) and humidity (58.5 ± 5.8%). Each tested substrate (soil 1.65 g equivalent dry weight, compost 1.26 g, sisal bagasse 0.66 g, seaweed 0.62 g, and corn stover 0.47 g) was placed in the device; 1 mL pesticide mixture containing 10 µg of each pesticide was added, the silica trap was put on the top of the system and tightly closed. The moisture of the substrates was: soil 92%, compost 76%, sisal 71%, corn stover 30%, and seaweed 103% (saturation). Three microcosms per treatment were sacrificed after 2, 6, 12, 24, 48, and 72 hours of incubation.

VOLATILE FRACTION

To determine the volatile fraction, the volatilization trap device was disarmed, and the silica trap was removed after every sampling time and subjected to microwave extraction (800W, 110°C for 15 min) according to USEPA method 3546 (USEPA, 2007).

CHROMATOGRAPHIC ANALYSES

Pesticide residues were analyzed with a gas chromatograph-mass brand Thermo Scientific Trace GC Ultra 1300, coupled to an electron capture detector (ECD) in tandem with a nitrogen-phosphorus detector (NPD). Limit of detection (LOD) and limit of quantification (LOQ) for each of the pesticides tested were 2,4-D (LOD: 0.071 ± 0.045 mg/L and LOQ: 0.103 ± 0.059 mg/L), atrazine (LOD: 0.163 ± 0.071 mg/L and LOQ: 0.174 ± 0.069 mg/L), diazinon (LOD: 0.044 ± 0.025 mg/L and LOQ: 0.076 ± 0.048 mg/L) and glyphosate (LOD: 0.163 ± 0.016 mg/L and LOQ: 0.187 ± 0.023 mg/L).

DATA ANALYSIS

Data were analyzed using multifactorial analysis of variance (ANOVA) to determine the significance of factors (time, substrate, and pesticide) on the volatile fraction. Principal component analysis was performed to identify the importance of physicochemical parameters of substrates to explain the pesticide volatilization on the different substrates. The statistical analyses were done using Statgraphics Centurion XVI (StatPoint Technologies) and, Primer 6 version 6.1.16 & Permanova + version 1.0.6 (Primer – Ltd).

Substrate	Texture	BD[a] (g/cm^3)	RD[b] (g/cm^3)	OM[c] %	OC[d] %	N[e] %	(C/N)[f]	Lignin[g] %	H[h] %	pH[i]	WHC[j] %	FC[k] %
Soil	Sandy loam	0.55	1.22	35.51	20.60	1.71	12.06	ND	45	7.25	154	150.89
Compost	ND	0.50	1.11	44.00	25.52	0.83	30.60	20.84	58	7.85	285	114.22
Corn stover	ND	0.04	0.30	87.89	50.98	0.75	73.49	6.46	53	7.85	1270	ND
Sisal bagasse	ND	0.12	0.53	72.48	42.04	0.83	53.86	11.75	78	8.34	715	ND
Seaweed	ND	0.08	1.16	61.78	35.83	2.17	18.15	7.13	79	7.48	530	ND

Table 1 Physicochemical properties of the organic substrates and the arable soil used in this study.

[a]: bulk density; [b]: real density; [c]: organic matter; [d]: organic carbon; [e]: total nitrogen; [f]: carbon-nitrogen ratio; [g]: lignin content; [h]: moisture; [i]: hydrogen potential; [j]: water holding capacity; [k]: field capacity. ND: not determined.

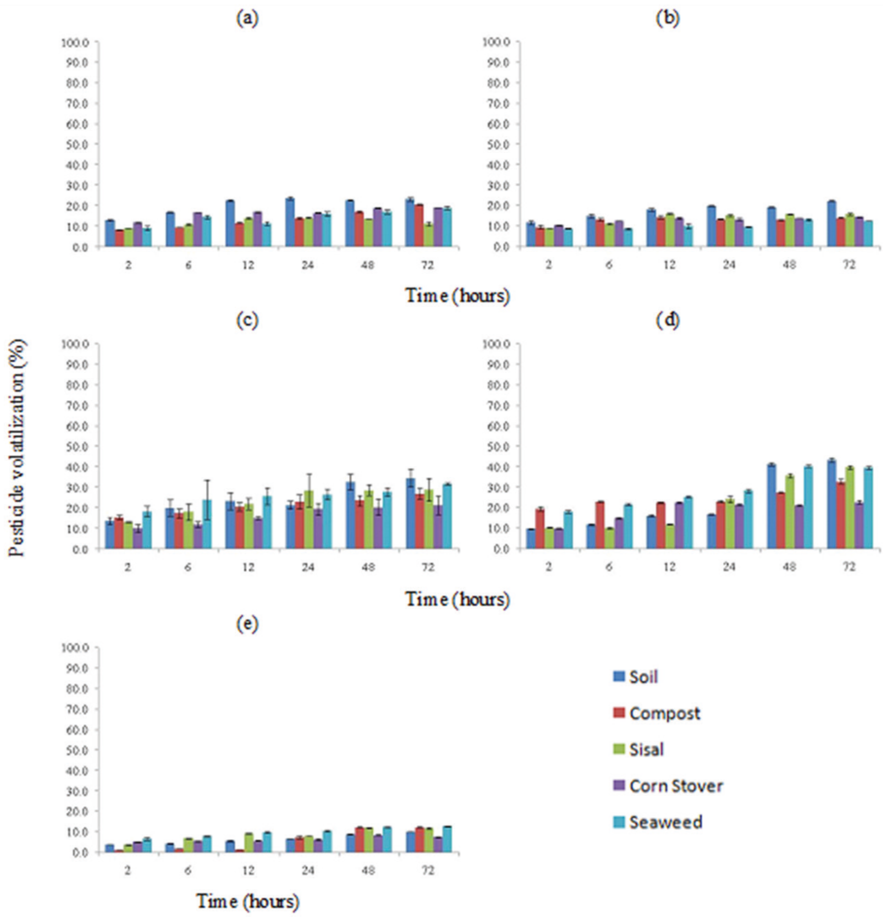

Figure 1 Pesticide volatilization (average %) in the five substrates used. **(a)** 2,4-D; **(b)** Atrazine; **(c)** Carbofuran; **(d)** Diazinon; **(e)** Glyphosate.

RESULTS AND DISCUSSION

PESTICIDE VOLATILIZATION

From the results, the volatilization increases from the beginning to the maximum time (2-72 h) for all pesticides in all substrates (Figure 1). Results showed that diazinon was the most volatilized pesticide in all the substrates, and glyphosate was the least, except in the sisal, where the 2,4-D was the least volatile. It coincides with that established in the Pesticide Properties DateBase (PPDB, 2016); this database establishes that diazinon is the most volatile of the pesticides used. The soil was the substrate where diazinon was more volatilized in this investigation, this can be attributed to the type of soil and the temperature under which the experiment was developed (29.6 ± 2°C). It important is to note that volatilization is the least likely mechanism for atrazine losses according to Hansen et al. (2013); however, in this research, it was verified that atrazine was volatilized in more than 10% of the initial amount applied at 12 hours in all the substrates.

As can be observed in Figure 1, corn stover showed the lowest volatilization for Carbofuran, Diazinon, and Glyphosate. The sisal showed the lowest volatilization for 2,4-D, and the lowest volatilization of Carbofuran was observed in the seaweed.

The fact volatilization is lower in some substrates supports that the addition of amendments to soil has been shown to improve pesticide adsorption (Cox et al., 2000), and the organic content is related to adsorption and biodegradation mechanisms (Karanasios et al., 2010; Góngora-Echevería et al., 2019), which reduce the pesticide losses by volatilization.

STATISTICAL ANALYSES

The ANOVA analyses at 95% confidence show that pesticide type, substrate type, and exposure time were statistically significant (P <0.05) on volatile fraction. The significance of the factors for volatile fraction is given by the relation TYPE OF PESTICIDE (F = 203.06)> TIME (F = 83.33)> TYPE OF SUBSTRATE (F = 13.20), which represents that the physicochemical characteristics of pesticides, such as solubility (del Puerto et al., 2014), the exposure time and the type of substrate play an important role on pesticide volatilization. The principal component analyses showed that the volatile fraction is more affected by the lignin content, the final moisture in the substrate (% SM), and the pH, the latter in an opposite sense. It is important to distinguish lignin since a decrease in lignin increases the volatilization of pesticides and vice versa, which could result in the presence of microbial activity and degradation of the pesticide in substrates with higher lignin contents and, therefore, a lower amount of pesticide available for volatilization. The importance of lignin in pesticide dissipation in biobed systems has been reported (Castillo & Torstensson, 2007; Ruiz-Hidalgo et al., 2014; Pinto et al., 2016); however, lignin effect on pesticide volatilization was not discussed.

CONCLUSIONS

Diazinon showed the highest volatilization at 72 hours (>43% in soil). The volatilization of the pesticides was directly related to the substrate where they were deposited; however, the contact time and type of pesticide seem to have a significant relationship with volatilization. From the effect of the physicochemical parameters, it can be seen that pH and lignin content were the ones that most affected the volatilization according to principal component analysis. With these results, it can be established that for biobeds, selecting the appropriate substrates, the losses by volatilization of the pesticides to the environment can be reduced, and can be guaranteed that the greater dissipation is carried out by degradation processes, taking into account that one of the main functions of biobeds is the confinement of agricultural effluents. Additionally, it cab be conclude that the device used to capture the pesticide dragged by the evaporation of the water in the substrates proved to be efficient and represents an easy way to test compounds volatilization at laboratory scale.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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