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Effect of different organic amendments on the dissipation of linuron, diazinon and myclobutanil in an agricultural soil incubated for different time periods

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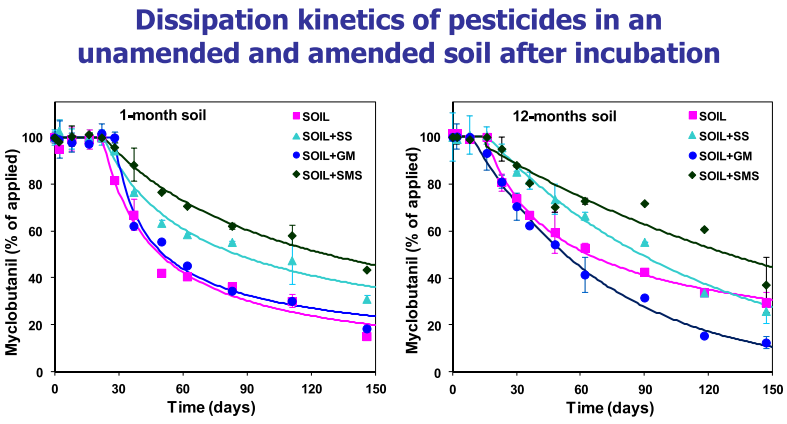
HIGHLIGHTS

- Soil amendment with organic residues affected differently the dissipation of pesticides in an agricultural soil.
- Dissipation increased (linuron) or decreased (diazinon and myclobutanil) in amended soil.
- The highest pesticide dissipation was recorded in amended soil with the highest soluble carbon.
- Effect of soil aging on dissipation was consistent with changes in pesticide sorption.
- Different dissipation mechanisms were revealed from mineralized and extractable amounts.

GRAPHICAL ABSTRACT



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ABSTRACT

Dissipation kinetics of pesticides belonging to three chemical groups (linuron, diazinon and myclobutanil) was studied in an unamended agricultural soil and in this soil amended with three organic residues: sewage sludge (SS), grape marc (GM) and spent mushroom substrate (SMS). The soils were incubated with the residues outdoors for one and 12 months. Mineralized, extracted and non-extractable fractions were also studied for ^{14}C-linuron and ^{14}C-diazinon. The dissipation kinetics was fitted to single first-order or first-order multicompartment models. The dissipation rate (k) decreased in the order diazinon > linuron > myclobutanil, and DT_{50} values decreased for linuron (1.6–4.8 times) or increased for myclobutanil (1.7–2.6 times) and diazinon (1.8–2.3 times) in the amended soils relative to the unamended soil. The lowest DT_{50} values for the three pesticides were recorded in GM-amended soil, and the highest values in SMS-amended soil. After 12 months of soil incubation, DT_{50} values decreased in both the unamended and amended soils for linuron, but increased for the unamended and SMS-amended soil for diazinon and myclobutanil. A certain relationship was observed between the sorption of pesticides by the soils and DT_{50} values, although it was significant only for myclobutanil ($p < 0.05$). Dissipation mechanism recorded the lowest mineralization of ^{14}C-pesticides in the GM-soil despite the highest dissipation rate in this soil. The extracted ^{14}C-residues decreased with incubation time, with increased formation of non-extractable residues, higher in amended soils relative to the unamended soil. Soil dehydrogenase activity was,

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in general, stimulated by the addition of the organic amendments and pesticides to the soil after one month and 12 months of incubation. The results obtained revealed that the simultaneous use of amendments and pesticides in soils requires a previous study in order to check the environmental specific persistence of these compounds and their effectiveness in amended soils.

1. Introduction

Soil protection is a priority objective in modern agriculture. Agricultural soil is a high value resource, and so its irreversible degradation needs to be avoided to guarantee its fertility and its present and future agronomic value. Accordingly, the application of organic amendments to agricultural land is considered a common soil management practice because it avoids the decline in the organic matter (OM) content of agricultural soils, especially soils with low OM content (<2%), such as European semi-arid Mediterranean soils. Moreover, these residues provide both macro- and micronutrients to crops, increase water-holding capacity and porosity, and decrease bulk density, thereby contributing to the improvement of the soil's physical and chemical conditions for plant production (Goss et al., 2013).

The management of different organic residues from urban, agricultural and industrial activities has therefore become a priority in many countries today, and different strategies for recycling such materials as organic amendments have been investigated (Moreno Casco and Moral Herrero, 2008) and controlled to avoid the possible threats and risks to human health that may result from their use, as laid down by current Spanish legislation (MARM, 2009; MPR, 2013).

However, the OM in these residues may interfere with the dynamics of the pesticides applied simultaneously with these residues to increase agricultural production and uphold food quality and protection. Pesticides reach the amended soil either by direct application or by the subsequent wash-off from treated plants, and their interaction with the OM of the residues may modify its behavior in the soil with respect to unamended soil (Briceño et al., 2008; Wang et al., 2010; Rojas et al., 2013). Considering that the nature and composition of the OM in residues are different to the OM in natural soil, it is of special interest to know how the sorption–desorption, mobility or dissipation of pesticides is affected by soil amendment with organic residues. Changes in these processes might explain the increasingly frequent presence of residues of these compounds in surface and ground waters in agricultural areas (Herrero-Hernández et al., 2013).

Dissipation of pesticides in amended soils can be decreased by the enhanced sorption of these compounds by the OM of the amendments (Grenni et al., 2009; Marín-Benito et al., 2012a,b; Rodríguez-Cruz et al., 2012b) although an apparent increased dissipation may be also observed if irreversible sorption occurs with formation of bound residues (Alexander, 2000). Furthermore dissipation can be affected if soil microbial activity is stimulated by the addition of organic amendments and pesticide biodegradation is enhanced (Moorman et al., 2001; Kadian et al., 2008). To date, a few studies have studied the influence of selected residues on the degradation and persistence of some pesticides in soils amended (Sánchez et al., 2004; Kadian et al., 2008; Fernández-Bayo et al., 2009; Marín-Benito et al., 2012b), but only in some of them the dissipation mechanism has been evaluated.

Our group has conducted a research project designed to clarify some of these unexplored aspects regarding the addition of organic residues to soil as amendments and their influence on the behavior of pesticides. The organic residues studied were sewage sludge (SS) from municipal wastewater treatment operations and the by-products of other agricultural activities generated by the wine industry (grape marc (GM)) and mushroom farming (spent mushroom substrate (SMS)). They are commonly applied to agricultural land in Spain with or without prior treatment. In previous works, we studied the adsorption (Rodríguez-Cruz et al., 2012a) and the mobility (Marín-Benito et al., 2013) of linuron, diazinon and myclobutanil, in one-month and 12-month incubated soil amended with SS, GM and SMS. The selected pesticides represent groups of compounds with different chemical structures and widely used in agriculture. They are applied in large amounts to a very wide range of crops to control annual grass and broad-leaved weeds, insects and mites or fungal diseases (Tomlin, 2000). However, no dissipation studies have been conducted in these amended soils, and further research is required to assess the risk of persistence of these compounds over time and their possible contribution to soil and/or water pollution.

Accordingly the aim of this research was to study the effect of the organic residues – SS, GM and SMS – on the dissipation of linuron, diazinon and myclobutanil in a soil amended with these residues after one month and 12 months of incubation in outdoor conditions. We investigated the following: 1) the dissipation kinetics, metabolite formation, and dissipation mechanism of the pesticides to analyze the effect of pesticide properties and the nature and aging of organic residues, and 2) the soil dehydrogenase activity as an indicator of the soil microbial activity to analyze the effect of amendments and pesticides had on the microbial community.

2. Materials and methods

2.1. Chemicals

Non-labeled linuron (N′-(3,4-dichlorophenyl)-N-methoxy-N-methylurea) was supplied by Riëdel de Haën (Hannover, Germany) (>99% purity). Non-labeled diazinon (O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate) and myclobutanil (α-butyl-α-(4-chlorophenyl)-1-H-1,2,4-triazole-1-propanenitrile) from Pestanal were supplied by Sigma-Aldrich Química SA (Madrid, Spain) (>98% purity). [Ring-U-^{14}C]-linuron (specific activity 9.62 MBq mg^{-1} and 99.07% purity) was supplied by Institute of Isotopes Co., Ltd. (Budapest, Hungary) and [4-methyl-^{14}C]-diazinon (specific activity 610 MBq g^{-1} and 97% purity) was supplied by International Isotopes (Munich, Germany). Myclobutanil was not available as ^{14}C-labeled compound and it was used in the experiment in non-labeled form. The physicochemical properties and environmental fate parameters of the three pesticides, linuron, diazinon and myclobutanil, are given in Table 1 (FOOTPRINT, 2011; Tomlin, 2000).

Linuron metabolites (N-(3,4-dichlorophenyl)-N′-methylurea, N-(3,4-dichlorophenyl)-N′-methoxyurea, N-(3,4-dichlorophenyl)urea and 3,4-dichloroaniline) were supplied by Hoëchst AG (Germany) and their purity was >99.5%. Diazinon metabolite (2-isopropyl-6-methyl-4-pyrimidinol) from Chem Service was supplied by Sigma-Aldrich Química SA (Madrid, Spain) and its purity was 99.5%. HPLC grade methanol and acetone were supplied by Merck (Germany). 2,3,5-Triphenyltetrazolium chloride (TTC) and 2,3,5-triphenylformazan (TPF) were supplied by Sigma-Aldrich Química SA (Madrid, Spain).

2.2. Organic residues

Sewage sludge (SS) from a domestic waste treatment plant and stabilized by anaerobic digestion was supplied by Aqualia SA (Salamanca, Spain). Grape marc (GM), which is comprised of grape stalks, seeds and skins left after the crushing, draining and pressing stages in wine production, was supplied by San Gabriel winery (Aranda de Duero, Spain). Spent mushroom substrate (SMS) from *Agaricus bisporus* (75%) and *Pleurotus* sp. (25%) cultivation is a pasteurized mixture of cereal straw and poultry litter, ammonium nitrate, urea, and minerals (gypsum and/or calcium carbonate), which was further composted for