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Influence of Organic Amendment on the Biodegradation and Movement of Pesticides

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An increase of organic waste coming from different humans and productive activities is a continuous concern, and their application in soil is proposed many times as a solution to disposal problem. In agricultural soil, this practice is actually more popular because of its contribution as a fertilizer and soil enhancement. Recently, increased interest has been focused on assessing the influence of organic waste added to the soil related to pesticides behavior. The studies carried out show that addition of organic matter and nutrient mainly can affect the adsorption, movement, and biodegradation of pesticides. This review shows the factors involved, trend, and result obtained with pesticide behavior in soil amendment. Contradictory trends are reported in the literature on the pesticides' fate. These are mainly because soil type differences, pesticide characteristics, and source amendment are difficult to organize in a tendency pattern, and can significantly complicate the understanding of pesticides fate.

KEY WORDS: adsorption, amendment soil, leaching, manures, organic matter, pesticides

1. INTRODUCTION

The humans and productive activities have led to the generation of an increase in the amount of organic waste originated from different sources

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(biosolids, manures, etc.). The management of the organic waste has been a theme of public, environmental, and social interest due to problems of disposal, emission, and leaching (Dickerson, 2000; Moral et al., 2005). In search of solutions as viable alternatives is the application of these residues to the soil. The application of organic waste, specifically to agricultural soils, is a practice that for some residues has been carried out for centuries, due to its fertilizer properties and contribution to the physicochemical and biological properties of the soil (Balesdenta et al., 2000; Cooperband, 2002); actually this is a common agricultural practice in diverse countries (Palma et al., 2002; Vorkamp et al., 2002; Said-Pullicino et al., 2004).

Recently, an increasing interest has been focused on assessing the consequences of exogenous sources of organic carbon (OC) on the behavior of pesticides in soils (Albarrán et al., 2004; Blacksaw et al., 2005), because the efficiency of some pesticides and their persistence and potential as environmental contaminants depend on their retention and degradation on soil constituents (Worrall et al., 2001). The environmental fate of pesticides may be greatly influenced by organic amendments, because this practice increases the soil organic matter (SOM) content. The organic matter (OM) is reported as a major controller component in the sorption, transformation, and transport of many organic pollutants in soil (Albarrán et al., 2004). Specifically, pesticide sorption has shown an increase through organic amendment addition to the soil. However, through organic amendment, dissolved organic matter (DOM), is incorporated, which affects the pesticide sorption and movement (Cox et al., 2001). On the other hand, the addition of organic amendment to soil normally results in an increase in the microbiological activity due to the availability of simple organic molecules such as sugar and amino acids (Cox et al., 2001). Pesticides in amendment soil have reported different responses, and diverse influences have been recognized.

Knowing the interest in understanding the fate and behavior of pesticides, the aim of this review is to analyze the influence of organic waste in the pesticides' fate, with special concern for the factors that affect their adsorption, movement, and biodegradation in amended soil.

2. ORGANIC WASTE AS SOIL AMENDMENT

2.1. Benefit and Limitation

The organic wastes originated by human and productive activity are classified according to physical state as solid, semisolid, and liquid waste, and according to the source as forestry or farming wastes, agro-industrial, urban, and industrial by-product. Varnero (2004) gives the following distribution: 10% residential waste, 85% forestry–farming, and 5% agro-industrial waste.

The problems associated with waste disposal have been of public social and environmental concern. At the present, the application of organic waste on soil is considered and proposed as a possible solution (Palma et al., 1993, 1995; U.S. EPA, 1998, 1999; Guerrero et al., 2000; Zheng et al., 2003; Sánchez et al., 2004). The application of some organic waste is a practice carried out by centuries as replacement or supplement of commercial fertilizer, while OM of waste materials has been considered to improve structure and soil fertility (Balesdenta et al., 2000; Chantigny et al., 2002; Blacksaw et al., 2005; Dittert et al., 2005). Currently, this practice shows an increase in Europe, the United States, and many other countries.

Addition of organic waste to soil contributes to enhancement of active humified components, such as humic acid (HA) and fulvic acid (FA) (Plaza et al., 2003), which exert an important role in geochemical processes as sources of nutrients for plants and microorganisms, in acid–base buffering capacity of soils, and promoting a good soil structure, thereby improving aeration and moisture retention (Graber et al., 2001; Marschner et al., 2003); in agronomic aspects, addition of organic waste enhances biological activity and fertility, because through the waste are added nutrients and diverse groups of microorganisms, such as bacteria, fungi, and actinomycetes (Namkoong et al., 2002; Zagal et al., 2002; Dungan et al., 2003b; Böhme et al., 2005; Wanner et al., 2005); and in environmental processes the addition plays an important role in the fate of xenobiotic compounds such as heavy metals, aromatic hydrocarbons, and pesticides (Fogarty and Tuovinen, 1991; Büyüksönmez et al., 1999, 2000; Alexander, 2003; Hartlieb et al., 2003).

The organic waste in some cases can generate adverse effects, such as contributing to phytotoxic components of crops and soil (e.g. phenolic compound of bark, ammonia from animal manures, soluble salts, fats, weed seeds, and pathogens microorganisms; Hernández-Apaolaza et al., 2000; Ohno et al., 2000; Alexander, 2003; Peigné and Girardin, 2004; Ceotto, 2005) and restricting the seed germination, destroying roots and suppressing plant growth (Mantovi et al., 2003; Zmora-Nahum et al., 2005); nutrient losses occur because of lixiviation to groundwater and superficial water (N and P) (Neeteson, 2000; Hansen et al., 2001) or emission to the atmosphere (Su et al., 2003; Mei et al, 2004). The application of fresh or immature organic waste may produce adverse effects on the soil properties, including partial mineralization of soil organic C through extended microbial oxidation and the modification of the status, quality, and functions of SOM (U.S. EPA, 1999), or a wide proportion of carbon–nitrogen (C:N) may result in rapid immobilization of inorganic N and thus minimal net N mineralization (Amlinger et al., 2003); aerobic zones may be developed in soils with low aeration status after a period of high heterotrophic activity, resulting in a decreased CO_2 production and decomposition of C, thus resulting in the accumulation of microbial metabolites such as volatile fatty acid (Perrin-Ganier et al., 2001; Chantigny et al., 2002). Finally, some organic waste are associated with inorganic and organic toxic compounds (heavy metals and pesticides) (Fogarty and Tuovinen 1991; Eberle, 1997; Büyüksönmez et al., 1999; Cooperband, 2002; Mantovi et al., 2003) that are incorporated into soil, in some cases constituting a pollution source in soils and therefore causing effects on microorganisms and crops (Eberle, 1997; U.S. EPA, 1999; Mantovi et al., 2003).

The problems associated with waste application can be mitigated by chemically and biologically stabilizing soluble nutrients to more stable organic form, which is the composting strategy, the most common practice proposed currently, previous to the application of organic amendment on agricultural soil (Hernández-Apaolaza et al., 2000; Cooperband, 2002; Tiquia and Tam, 2002; Peigné and Gerardin, 2004). Even though the composting practice is every day more often suggested, it has not been adopted totally, because of its associated to economical cost (Tiquia and Tam, 2002); a common practice in most countries is thus the application of organic waste in raw form.

2.2. Legislation of Organic Wastes Use

The main organic wastes used for soil amendment are compost, biosolid, and animal manure. In this sense, vast rules that control the disposal of organic waste have been generated around the world. In the United States biosolids regulation is controlled by Standards for the Use or Disposal of Sewage Sludge, which were published in the *Federal Register* in 1993. This rule establishes the regulations limiting the pollutants and pathogens in biosolids. Also discussed are the municipal solid waste landfill regulations, published in 1991. In practice, biosolids compost is more commonly used by nurseries, landscapers, and soil blenders than for agricultural purposes (U.S. EPA, 1999). In the European Union, sewage sludge has been used in agriculture over a long time. According to the report carried out recently by European Commission (2001), sewage sludge application in agriculture is only one source for organic contamination of soils, water, and plants. Consequently, environmentally sound decisions are based on an integrative evaluation of contaminant sources and transfer pathways. Considering what has been said, the different countries regulate the monthly variations in toxic organic content (European Commission, 2001). The application of animal manure to soil is a common practice carried out as a fertilizer, principally in grassland and arable land (Chambers et al., 2001a, 2001b). In the European commission its application is regulated by animal by-product regulation (European Commission) 1774/2002 (DEFRA, 2002), and the application rate is carried out according to the fertilizer requirement (Amlinger et al., 2003). According to Moral et al. (2005), horse, cow, pig, sheep, goat, rabbit, chicken, and ostrich manures can be used as amendment in agricultural soil, due to their high organic content; however, the stabilization process will start after the application to the soil.

In Chile, the biosolids application to soil has been proposed recently through regulation for management of nonhazardous biosolids generated in water processing plants (CONAMA, 2005), and its use is proposed for agricultural soil, nurseries, and soil erosion, depending on topography and physicochemical soil properties, and according to the biosolids characteristics (metal content, pathogens, moisture, etc.). The application rate for agricultural soil is proposed according to nitrogen, phosphorus, and potassium requirements, with a maximum application rate of 15 t year^{-1} (in modification). On the other hand, a specific rule for animal manure application to soil does not exist, but is proposed through Good Agricultural Practices and Clear Production by Agriculture Ministers as soil fertilizer and soil bioremediation (CONAMA, 1998). Because of the benefit for use of compost in soil, the composting strategy is an increasingly common practice. The Chilean Norm NCh 2880 considers an aim to establish the classification and quality of the organic compost produced from residues and from other organic materials generated by human activity, such as industrial, agricultural, animal, and fishing, and from markets and free fairs in which people market vegetable products themselves, for the maintenance of parks and gardens, and for residues from house lawns, those originating at water processing plants, and those from nonhazardous industrial residues (Sadzawka, 2004).

As a difference from Chile, Brazil has had since 2004 a normative (instructive number 15) with specifications and warranties, tolerances, registration, and how to pack and letter simple mixed fertilizer, compost, and biofertilizer destined for agriculture (Ministerio da Agricultura, Pecuária a Abastecimento, 2004).

2.3. Chemical Properties of Organic Amendment

Knowing the composition of organic waste is a requirement for its application on soil. However, the application is carried out without knowing the main compositions of macro and micro nutrients, which in some cases are found in excess amount and in this form are applied to soil.

As already mentioned, the main amendments used are compost, biosolid, and animal manure. All of these amendments contain nutrients for plans. However, compost is typically not characterized as a fertilizer (Alexander, 2003), because for the N-dynamics in compost amendment soil, generally it is assumed that the availability of N to plants is low. The majority (>90%) of total compost N is related to the organic N-pool (Amlinger et al., 2003). Animal manure has been used as a source of nutrients and OM on agricultural soils. Typically manures have been applied in a fresh form, but are currently available for agricultural and horticultural usage in aged, dehydrated, or stabilized form (Cooperband, 2002). When raw manures are applied, it is suggested that planting be delayed 2 to 4 weeks after application and incorporation, to allow for stabilization (Chambers et al., 2001b). When raw manure has not been stabilized, the nitrogen is often readily available and subject to leaching and loss (Neeteson, 2000; Moral et al., 2005). Composted manures will contain a more stable form of nitrogen and a lower content of OM (Alexander, 2003); during storage, 20–40% of N storage in heaps may be lost during the composting (Sommer, 2001), and 24–53% of organic carbon (OC) (Newton et al., 1996; Thomsen, 2000). Most of the nitrogen (N), phosphorus (P), and potassium (K) in livestock diets is excreted in dung and urine and feces. Manures contain useful amounts of these plant-available nutrients, as well as other nutrient and trace elements (Burton, 1999; Thomsen, 2000; Hansen et al., 2001).

Biosolids are by-products of municipal wastewater and sewage disposal. There are several technologies in use that separate and dewater solids following aerobic or anaerobic digestion of municipal sewage. Biosolids commonly contain 3–6% N, 1–4% P, 0.2–1% K, and 50–60% OM. Biosolids also contain Ca, Mg, and high concentrations of heavy metals, with this last constituting the restriction for no longer being applied to agricultural soil (Dendoncker et al., 2004). The main parameters considered to characterize each amendment are pH, nutrient content, OM, trace elements/heavy metals, and others. In Table 1 are shown some typical parameters and the ranges that are commonly found. Because treatments and sources of biosolids create very different composition, only one date is shown as reference. However, is possible to observe a bigger microelements amount in biosolid compared to compost and manure, and this is the reason that use of biosolids as soil amendment is questionable.

TABLE 1. Typical Chemical Characteristics of Compost, Animal Manure, and Biosolids

Parameters	Compost[a]	Animal manure[a]	Biosolid[a]
pH	7.2–8.3	7.2–8.7	7.0
EC (mmhos/cm)	2.2–47.3	9.2–43.2	10.7
Total N (%)	1.3–3.0	1.7–3.7	3.8
OM (%)	39.6–46.0	52–83	69[b]
C/N ratio	10–32	11–21	10.7
NO_3-N (ppm)	194–905	6.6–87.4	2.9
P (%)	1.0–1.8	0.45–2.71	1.7
K(%)	0.7–2.3	1.15–3.10	0.09
Ca(%)	3.6–4.8	1.55–15.1	3.99
Na(%)	0.04–0.46	0.18–0.49	0.2
Mg(%)	0.71–1.05	0.27–0.73	0.29
Fe(ppm)	4500–9600	225–8540	13,040
Zn(ppm)	152–309	101–443	694
Mn(ppm)	193–263	196–513	187
Cu(ppm)	31–215	19–47	775
B(ppm)	34–57	27–57	38
Al(ppm)	4750–5702	370–7944	12,848

[a] From Dickerson (2000).
[b] From Varnero (2004).

3. PESTICIDES

Pesticide use in protection of crops from weeds and diseases is steadily increasing, and is indispensable for the conventional labor-extensive farming system. On soil, the pesticides present diverse behavior, including volatilization, biodegradation, transfer to organisms, uptake by plants, chemical degradation, binding to soil, and leaching into groundwater (Semple et al., 2001; Ceballos et al., 2004). According to Barriuso et al. (1996), 2, 5, and 0.6% of pesticide is volatilizing, in runoff, and leaching, respectively; the difference is distributed in sorption, degradation, and available form. The fate of pesticides is complex and dependent on factors such as the properties of the pesticide, soil properties, environmental conditions, etc. (Miller and Westra, 2004; Fang et al., 2001; Hutchinson et al., 2001; Holland, 2004). The environmental fate of pesticides is a great concern today due to the problems resulting from use of mobile and persistent molecules, affecting soil quality and surface waters and groundwater quality (Miglioranza et al., 2003; Palma et al., 2004).

3.1. Sorption and Nonextractable Residues in Soil

Adsorption is the binding of chemical to the surface of solid particles through weak and reversible bonds (Büyüksönmez et al., 1999). The process of adsorption–desorption of the chemicals by the soil directly or indirectly controls the movement and degradation through microbial attack (Büyüksönmez et al., 1999; Thorstensen et al., 2001; Sorensen et al., 2003; China et al., 2004; Boivin et al., 2005; Khna and Anjaneyulu, 2005). The degree of adsorption depends on many factors, and the SOM type and content are often implicated as the soil characteristics exerting dominating influence on pesticide sorbent, due to the porous, large surface of the humic substances, where a variety of functional groups are present. However, where the OC is low, the association of pesticides with mineral surfaces may become significant (Clausen et al., 2001). Another factor involved is physicochemical properties like pH, texture, and cation exchange capacity (Thorstensen et al., 2001; Worrall et al., 2001; Khna and Anjaneyulu, 2005).

Weakly acid pesticides, those ionizing in soil solution to form anionic species (A^-), are repelled by the negative charges of soil colloids. When pH decreases, more molecular species are formed, and their sorption is increased in OM compared to anionic species. Weakly basic pesticides are adsorbed through ionic bonds and/or by physical adsorption, depending on the pH of the system, because basic pesticides in acidic medium form protonated species (HB^+) (Thorstensen et al., 2001). Ionic pesticides can interact with the surface sites through, electrostatic interactions, ion-exchange reactions, or surface complexation, and pesticides adsorption to mineral surfaces may be significant (Clausen et al., 2001).

Nonextractable residues are formed in soils during application of pesticides (Kästner et al., 1999). Strong interaction has been shown through studies with ^{14}C-radiolabeled pesticides, which have shown that a fraction of the added compound becomes nonextractable or "bound" in soil and that this fraction increases with aging in soil (Park et al., 2003; Semple et al., 2001; Gevao et al., 2005). Approximately 10 to 25% of a pesticides constitutes nonextractable pesticides residues in soils (Kästner et al., 1999; Mordaunt et al., 2005); a part of them and their conversion products can become bound to the OM soil, and cannot be extracted by normal analytical methods (Semple et al., 2001, 2003; Gevao et al., 2005). Nonextractable pesticide residues involve interactions such as covalent bonding and diffusion between the compound and the soil structure (Kästner et al., 1999). Functional groups, such as hydroxylic, carboxylic, nitro, amino, or phosphate, may contribute to cross-linking reactions with compounds in the SOM over time; many bound residues will become indistinguishable regarding SOM (Barraclough et al., 2005). Phenolic or aniline compounds have a great tendency to form bound residues (Kästner et al., 1999). Recently, Mordaunt et al. (2005) found that compounds such as triazine (atrazine), benzoic acid (dicamba), phenyl urea (isoproturon), organochlorine (lindane), bipyridylium (paraquat), and 2,6-dinitroaniline (trifluralin) form nonextractable residues at levels of 26.2, 67.4, 64.5, 8.0, 92.0, and 21.3%, respectively, after 91 days of incubation in soil.

Covalently bound residues may be processed further following microbial degradation of SOM (Barraclough et al., 2005). The role of microorganisms in the formation and release of nonextractable residues in soil was assessed by Gevao et al. (2005), who estimated the formation and release step for nonextractable residues of [^{14}C]-Dicamba and showed that the microbial effect was higher by a factor of three for formation relative to the release process. On the other hand, the forming of bound portion was explained by Kästner et al. (1999) as the microbial conversion of pesticide to one or more metabolites, which are capable of interacting with SOM through covalent bonding. However, it has been described that metabolism results in more polar metabolites, which would be less sorbed by soil (William et al., 2001), and thus release as the microorganisms consume the SOM as their primary substrate. The bound pesticide/metabolite molecules are released from their entrapment within the humic macromolecules, suggesting that binding of contaminant can be reversed through microbial activity (Wanner et al., 2005). To degrade soil-sorbed pesticides, bacteria must either use sorbed molecules directly or facilitate desorption in some manner, for example, by producing surfactants (Park et al., 2003). Through the microbially induced breakdown of starch is produced cyclodextrin (cyclic oligosaccharides), which presents high extracting power toward the pesticides adsorbed on the soil, due to the formation of water-soluble inclusion complexes between pesticide and cyclodextrin. This complexation may result in considerable improvement of the properties that favor solubility and bioavailability (Morillo et al., 2001).

3.2. Biodegradation in Soil

Biological decomposition of pesticides is the most important and effective way to remove these compounds from the environment (Dabrowska et al., 2004). The microorganisms have the ability to interact, both chemically and physically, with substances, leading to structural change or the complete degradation of the target molecule (Raymond et al., 2001; Wiren-Lehr et al., 2002). Among the microbial communities, bacteria, fungi, and actinomycetes are the main transformers and pesticides degraders (Häggblom, 1992; De Schrijver and De Mot, 1999).

In soil the microorganisms metabolize organic pesticides either aerobically or anaerobically. In most cases, the microorganisms degrade the molecules and utilize them as a source of energy and nutrients (Abdelhafid et al., 2000; Topp, 2001; Parales et al., 2002; Getenga, 2003; Boivin et al., 2005), or use them through cometabolism, which occurs when an organic compound is not used by the microorganism for growth, but is metabolized in conjunction with another substrate used for growth (Häggblom, 1992; Kumar et al., 1996; Sánchez et al., 2004). According to Van Eerd et al. (2003), the microbial metabolism of pesticides may involve a three-phase process. In phase I, the initial properties of a parent compound are transformed through oxidation, reduction, or hydrolysis to generally produce a more water-soluble and usually a less toxic product than the parent. In phase II, the conjugation of a pesticide or its metabolite is involved, to a sugar or amino acid. Conjugation of pesticides often involves utilization of existing enzymatic machinery and is therefore called a cometabolic process. Microbial pesticide conjugation reactions include xylosylation, alkylation, acylation, and nitrosation and can occur intra- or extracellularly. Phase III involves conversion of phase II metabolites into secondary conjugates, which are also nontoxic (Van Eerd et al., 2003).

Fungi generally biotransform pesticides and other xenobiotic by introducing minor structural changes to the pesticide, rendering it nontoxic; the biotransformed pesticide is released into the soil, where it is susceptible to further metabolism by bacteria (Gianfreda and Rao, 2004). Both fungi and bacteria use methylation as a conjugation reaction to detoxify xenobiotic (Van Eerd et al., 2003). Some compounds are transformed into intermediates, which are highly resistant to microbial attack or are more toxic than the parent compound (Golovlena et al., 1990). For example, diuron, an herbicide belonging to the phenylamide, family and the subclass of phenylurea, is used to control a wide variety of annual and perennial broadleaf and grassy weeds. In soil it tends to break down, leading to 3,4-dichloroaniline, and according to the laboratory studies carried out with microorganisms isolated from the soil, this degradation product accumulates in the medium for long time (Kumar et al., 1996; Giacomazzi and Cochet, 2004).

Enzymes cause microbial decomposition of substances, and this generally occurs after an initial latency period during which the microorganisms adapt to substratum (Dabrowska et al., 2004). The decomposition rate of chemical compounds is a function of availability to microorganisms or enzymatic systems able to degrade those (Van Eerd et al., 2003). Van Eerd et al. (2003) presented oxidative transformations where oxygenation is the most frequent first step in the biotrasformation of pesticides. Many oxidatives enzymes play an important role in pesticides degradation, for example, peroxidases, laccases, etc. (Durán and Esposito, 1997, 2000; Durán et al., 2002; Durán, 2003; Tortella et al., 2005). Oxidative enzymes such as cytochrome P-450s, peroxides, and polyphenol oxidases mediate many of these reactions. In microorganisms, numerous enzymes from many different pathways are capable of oxidizing nitroaromatic compounds through oxidative reactions where enzymes such as monooxygenases, flavin monooxygenases, and dioxygenases are generally involved; many take a role in biotransformation of halogenated compounds (Häggblom, 1992) and nitroaromatic pesticides (Van Eerd et al., 2003). An other type of transformation is hydrolytic, cleaving bonds of a substrate by adding H or OH from H_2O to each product. There are many hydrolytic enzymes among the esterases, lipases, and proteases. Kumar et al. (1996) carried out an extent review of the enzymes and microorganisms involved in the pesticide degradation, De Schrijver and De Mot (1999) focused on actinomycetes exclusively, and Van Eerd et al. (2003) carried out work on pesticide metabolism in microorganisms. Several investigative works were carried out to get to know new organisms involvement in pesticides degradation; for example, *Pseudomona* sp. and *Azospirillum* sp. degrade ethion (organophosphate) (Foster et al., 2004), *Flavobacterium* sp. and *Sphingomonas paucimobilis* degrade cadusafos and ethoprophos (organophosphates) (Karpouzas et al., 2005), *Klebsiella* sp., *Harbaspirillum* sp., and *Bacillus* sp. degrade trifluralin (nitroaromatic) (Bellinaso et al., 2003), and finally *Pseudaminobacter* sp., *Pseudomonas* sp., and *Nocardiodes* sp. degrade atrazine (Topp, 2001). In Table 2 are shown the main enzymes and microorganisms involved in biodegradation of pesticides.

The principal cause of pesticide persistence in soil is commonly the lack of favorable conditions for microbial degradation (Golovlena et al., 1990; Moorman et al., 2001). Besides these, the most important are availability, levels of nutrient, moisture conditions, aeration level, temperature, pH, etc. (Fogarty and Tuovinen, 1991; Büyüksönmez et al., 1999; Awasthi et al., 2000; Romantschuk et al., 2000; Peigné and Girardin, 2004; Khna and Anjaneyulu, 2005). All of them differ in importance, depending on the pesticide involved (Haney et al., 2002). The optimal temperature has been reported to 30°C (Dungan et al., 2003a), while even at 20°C the degradation can proceed

TABLE 2. Enzymes and Microorganisms Involved in Degradation of Pesticides

Chemical class	Enzymes	Microorganisms
Organophosphorus (diazinon, fenitrothion, parathion)	Esterase[a]	*Azospirillum* sp., *Pseudomonas* sp.,[c] *Flavobacterium* sp., *Sphingomonas paucimobilis*[d]
Organochlorines (endosulfan, DDT, chlordane)	Dehydrogenase, dioxygenase P-450, dehalogenase, ligninase, oxygenase, hydrolase[a]	*Enterobacters aerogenes, E. coli, Pseudomonas putida, Pseudomonas* sp., *Phanerochaete chysosporium*[a]
Carbamates (Carbofuran, aldicarb)	Hydrolase[a]	*Pseudomonas* sp., *Flavobacterium* sp., *Achromobacter* sp., *Arthrobacter* sp., *Rhodococcus* sp.[a]
Acetanilides (Alachlor, metolachlor, propanil)	Acylamidase, peroxidase[a] GlutathioneS-transferase[b]	*Aspergillus ustus, Fusarium oxysporium, Penicillum* sp.[a] *Streptomyces* sp.[b]
s-Triazines (Atrazine, simazine, ametryne)	Hydrolase[a]	*Pseudomonas* sp., *Nocardioides* sp.[e]; *Agrobacterium tumefaciens, Caulobacter crescentus, Pseudomonas putida, Sphingomonas yaniokuyae, Nocardia* sp., *Rhizobium* sp., *Flavobacterium oryzihabitans*, and *Variovorax paradoxus*[f]
Sulfonylurea (chlorsulfuron, ethametsulfuron–methyl, triasulfuron)	P-450 cytochrome, monooxygenase[b]	*Streptomyces griseolus*[b]
Phenoxyacetic (2,4-D, MCPA)	Oxygenase and hydrolase[a]	*Arthrobacter* sp., *Rhodococcus* sp., *Nocardioides* sp.,[b] *Aspergillus niger*[g]
Phosphonoglycine (Glyphosate)	Lyase[b]	*Arthrobacter* sp.[b]

[a] Kumar et al. (1996).
[b] De Schrijver and De Mot (1999).
[c] Foster et al. (2004).
[d] Karpouzas et al. (2005).
[e] Topp (2001).
[f] Smith et al. (2005).
[g] Häggblom (1992).
[h] Stamper and Tuovinen (1998).

slowly in soil (Barker and Bryson, 2002). The pesticides degradation has been found to increase with increasing soil moisture content (Dungan et al., 2003a). The optimal moisture content has been determined to range between 50 and 60% for bacteria (Miller et al., 2004). The microbiological decomposition of pesticides in topsoil occurs largely via aerobic metabolism; for aromatic pesticides, ring activation. and fission involving oxygenase activities (Fogarty and Tuovin, 1991), the optimal C/N ratio has been reported to be in the range of 20 to 40 (Büyüksönmez et al., 1999; Peigné and Girardin, 2004). If the C/N ratio is higher, the process becomes nitrogen limited. The soil pH plays an important role in the development of degradation (Singh et al., 2003a). Good and optimal enhancement in endosulfan degradation (above 40–50%) occurs at pH 7.5 and 8.5, respectively, in soil exposed to *Bacillus* sp. Bacterial degradation is favored by near-neutral pH (Singh et al., 2003a, 2003b), whereas fungi are favored at acid pH (Traquair, 1997). Several studies have shown that an increase in soil pH results in an increase in soil microbial biomass and enzymatic activities, favoring a rapid growth-linked degradation (Bending et al., 2003; Singh et al., 2003a).

3.3. Environmental Problems Associated With Pesticides

A complete understanding of the pesticides process in soil has been motivated principally for the intensive use in crops and its possible environmental pollution. The main effects are contamination in soil (Crecchio et al., 2001; Johnsen et al., 2001) and groundwater and superficial water bodies (Barra et al., 1999; Miglioranza et al., 2003; Palma et al., 2004).

The main problems arising from the use of pesticides in agriculture are their persistence in soil and their toxicity to nontarget organisms (Chen et al., 2001), even at low concentrations (Crecchio et al., 2001). As microorganisms are responsible for the biological transformations that make nutrients available for plants, it is particularly interesting to assess pesticide-induced soil microbial community changes and their influence in the soil fertility and maintenance of soil quality and structure (Ekelund et al., 2000; Chen et al., 2001; Burrows and Edwards, 2002; Ceballos et al., 2004). Some studies show that the microbial community is modified with dominance of new microbial species in soil exposed to fumigants (Ibekwe et al., 2001); microbial activity was influenced strongly by both benomyl and captan. Moreover, a negative effect was found in nitrogen transformation, which influenced plant growth and N uptake (Chen et al., 2001). Nitrification has been shown by Kinney et al. (2005) to be inhibited by mancozeb fungicide from 10 to 62% and 20 to 98% at lowest and highest doses, and nematodes and earthworms are reduced significantly by higher dose of carbendazim fungicide (Burrows and Edwards, 2002). At present, the variation in the structure of natural microbial communities is considered as a possible ecotoxicological indicator of pesticide effects, and molecular techniques have been shown that in the presence of the herbicide

2,4-dinitro-*ortho*-cresol, microbial diversity was drastically reduced and there was no visible restoration of the soil bacteria community after 45 days of exposure, evidencing an irreversible effect (Rousseaux et al., 2003).

On the other hand, in the soil the pesticides represent an agricultural nonpointsource; following application onto agricultural fields, a small percentage of the total amount applied (between 0 and to 5%) reaches the superficial water by erosion and surface runoff during heavy rainfall conditions (Wauchope, 1978; Barra et al., 1999; Stuijfzand et al., 2000; Schulz and Lies, 2001; Palma et al., 2004). However, pesticides cause considerable public concern, due to their toxic properties, regarding their possible impacts on both the ecosystem and human (Müller et al., 2002; Encina et al., 2003). An enormous amount of research into their environmental behavior and fate, principally in the United States and Europe, led to development of monitoring programs (Cooper and Muschal, 1998; Müller et al., 2002). In Chile, limited monitoring of pesticides and ecotoxicology assays in waters have been carried out; only a few studies deal with pesticides levels in aquatic systems (Barra et al., 2001; Palma et al., 2004). Through these works it has been possible to confirm that herbicides, insecticides, and fungicides are found in water bodies. Some representativ chemical groups are chlorinated (DDT and lindane), phenoxyacetic (2,4-D), triazine (Simazine), triazinone (hexazinone), pyridinecarboxylic acid (picloram), and benzimedazole (carbendazim); specifically for carbendazim, ecotoxicology assay found mortality of *Andesiops peruvianus,* a native benthic macroinvertebrate of the water bodies of Chile (Encina et al., 2003). Increasingly, herbicides are being investigated because herbicides of the new generation are more soluble in water than the ones used before, increasing the transport probability toward superficial water (Barra et al., 1999; Müller et al., 2002).

4. INFLUENCE OF ORGANIC AMENDMENT ON PESTICIDES

Recently, increased interest has been addressed to assessing the influence of added OM on pesticides behavior in soils (Albarrán et al., 2004; Blacksaw et al., 2005). The efficiency of some pesticides and their persistence and potential to act as environmental contaminants depend on their retention and degradation in soil constituents (Worrall et al., 2001). Through added organic waste is incorporated an important amount of OM, which may modify movement (sorption and leaching pesticide) in soil, in some cases reducing pollution of groundwater by pesticides (Abdelhafid et al., 2000; Cox et al., 2001; Graber et al., 2001; Singh, 2003; Si et al., 2005). Moreover, this can accelerate or increase biodegradation by the stimulation of microorganisms due to nutrient incorporation (Abdelhafid et al., 2000; Cox et al., 2001; Namkoong et al., 2002; Dungan et al., 2003b; Sánchez et al., 2004). As shown in the next section, contrasting trends have been reported in the literature about the pesticides fate, due to differences in soil types, pesticide characteristics, and source of amendment. These factors have hindered obtaining a tendency pattern, and can significantly complicate the understanding of the fate of pesticides (Graber et al., 2001).

4.1. Influence on Pesticide Movement: Adsorption and Leaching

The addition of OM through the application of organic waste in soil may decrease mineralization of pesticides residues by increasing pesticide sorption, as the humic substances are the major factor controlling this process (Senesi et al., 2001; Barker and Bryson, 2002; Wanner et al., 2005). A benefit from sorption of pesticides to OM is that this generally restrict their leaching; however, decreased leaching may not be only due to the presence of additional OM in amendment soil, but also due to structural changes in the porosity induced by the higher OC content (Worrall et al., 2001). Cox et al. (2001) showed a reduction of large conducting pores (>1 μm) upon amendment with solid sewage sludge compared to liquid amendment of sewage sludge, suggest that nonsoluble OM cements and aggregates together soil particles, blocking large conducting pores. This decrease could result in an increase in contact time of the pesticides with soil surfaces, enhancing sorption and degradation process and, consequently, rendering differences in leaching behavior (Cox et al., 2001). However, a contrary result has been reported, where in soil amendment with sewage sludge, the pore size distributions showed an increase in soil porosity (10 μm) upon amendment addition, without increasing the simazine leaching (Albarrán et al., 2004). On the other hand, it has been established that dissolved organic matter (DOM) addition through the amendment plays an important function in benefit in terms of pesticides movement, diminishing the sorption and increasing leaching (Huang and Lee, 2001). Total OM include both the soluble and insoluble fraction of OM, although the proportion of soluble OM in soil is usually very small, as the amendment has a great content present of organic waste (Chantigny, 2003). This review takes into special consideration two principal factors involved in the movement of pesticides: the influence of humification grade and influence of DOM in substrates soil-amendment.

4.1.1. HUMIC COMPONENTS AND DISSOLVED ORGANIC MATTER

The SOM and especially its more active humified components, that is, humic acids (HAs) and fulvic acid (FAs), exert an important role in interaction with pesticides (Plaza et al., 2003), and through of the application of organic amendment to soil can be modified according to their characteristics and source (Alexander, 2003).

The application of animal manure (pig slurry) to soil increases the contents of C, N, S, total acidity, COOH, phenolic OH, and aliphaticity, and decreases O content, O/C ratio, and concentration of FAs (Plaza et al., 2003).

However, during the storage period the OM of this waste is not completely humified (Moral et al., 2005). In the raw sludge, HAs are predominately aliphatic, characterized by a low oxygenated functional group, high S- and N-containing groups, polysaccharide components, high molecular heterogeneity, low ring polycondenstation and polymerization, and low humification degree. However, the application of the dewatered sludge induced only limited modifications in the structural and chemical properties (Rovira et al., 2002). Compost commonly is found to have a minor total OM content, to present a reduction in the water-soluble organic matter fraction, and to have major aromaticity compared with the precursor material (Sluszny et al., 1999). Then through compost application, the humus level increases 0.4–0.5% in soil (Amlinger et al., 2003; Douglas and Magdoff, 1991).

Dissolved and water-extractable organic matter accounts for only a small proportion of the total organic matter in the soil. Nevertheless, it is now recognized that those molecules have influence on the biological activity of the soil, which decreases with increasing cumulative amount of amendment applied, probably as a result of extent microbial respiration (Kalbitz et al., 2003).

Amending the soil always induces an increase in DOM (Chantigny, 2003), and the pesticides can interact with the soluble form of SOM; the extent and nature of these interactions depends on factors such as molecular weight and polarity of the pesticide (Spark and Swift, 2002). However, Li et al. (2005) assessed two chemicals with different characteristics (solubility and polarity), and found that chlorpyrifos (hydrophobic compound) and 2,4-D (very high solubility and polarity) showed similar results from two different organic-fertilizer-derived DOMs. Both pesticides showed a decrease in the sorption; however, different sorption between two kinds of DOM was presented for this chemical, possibly due to different chemical properties of DOM (Li et al., 2005). Thus the quality and quantity have influence and can modify the sorption of pesticides.

In the presence of soils, an increase in the concentration of DOM results in an increase in pesticide mobility, influencing transport and ultimate distribution in the soil profile (Li et al., 2005). The DOM has characteristics similar to surfactants and has the ability to lower the surface tension and increase the solubility of the compounds decreasing the sorption capacity (Li et al., 2005). The reduced sorption may be attributed to the complex formation of DOM with organic chemicals, competition for sorption sites, or through the incomplete interaction of pesticides strongly hydrophobic with the solid-state organic or inorganic matter in the soil facility transport maybe colloids form (Huang and Lee, 2001; Spark and Swift, 2002; Singh, 2003; Li et al., 2005), and may thus lead to groundwater contamination (Ertunç et al., 2002; Bolan et al., 2004). The relative effects of DOM on solubility and sorption will be greater for more hydrophobic chemicals and will be attenuated by the concentration, source, size, polarity, and molecular configuration of the organic colloids (Huang and Lee, 2001). The interaction with pesticides is through internal hydrophobic interaction with pseudo-micellar structures of DOM (Barker and Bryson, 2002; Burauel and Bamann, 2005), as has been shown for atrazine and ametryne (Ilani et al., 2005). Chemically reactive OM of soil could be influenced by the ionic composition of the soil solution, and it is proposed that various SOM components are capable of configurationally changes between linear and sphero-colloidal shapes and that these transformations are dependent on the ionic nature of solution (Gao et al., 2003; Wanner et al., 2005; Burauel and Bamann, 2005). On the other hand, the DOM can potentially affect degradation and mineralization kinetic (Park et al., 2003) as a consequence of the formation of stable complexes that also protect pesticide molecules from soil microbial degradation (Cox et al., 2001; Li et al., 2005; Si et al., 2005; Spark and Swift, 2002).

4.1.2. PESTICIDES MOVEMENT ON AMENDED SOIL

A series of works have been carried out to evaluate the behavior of pesticides movement through assessment in amended soil or testing the individual effects of DOM extracted of organic waste. The main results obtained from recent literature are given next.

The application of raw or composted amendment to soils generally increased OC content and increased the retention of pesticides (Celis et al., 1998; Barriuso et al., 1996). Albarrán et al. (2004) assessed the behavior of a triazine (simazine) in soil (OC 0.56%; pH 5.3) amendment with two rates of sewage sludge (5% and 10% w/w), corresponding to about 60 and 120 t ha^{-1}. The final amended soil presented an increase in OC of 2.20 and 3.62%, respectively, and there was no pH variation. For simazine, the result showed a great increase in sorption after amendment addition with following Freundlich adsorption coefficient (K_f)values 0.94, 1.69, and 2.34 for 0%, 5%, and 10% amended soil. An increase of sorption irreversibility was also observed. On the other hand, the breakthrough curves in soil columns with amended soil showed retarded vertical movement of the herbicide and greatly reduced amounts available for leaching, 55% and 29% when the soil was amended with 5% and 10%, respectively, while a leaching of 87% of pesticide was observed in no-amendment soil. An increase in the sorption has been showed by Senesi et al. (2001), where pesticides molecules of the chemical classes chloroacetanilide (alachlor), imidazolinone (imazethapyr), and sulfonylurea (rimsulfuron), which are moderately water-soluble and rich in polar functional groups, can be adsorbed by HAs by multiple-binding mechanisms including hydrogen bonds, ionic bonds and charge-transfer bonds, in soil amended with sewage sludge. Pesticides of the chemical class of thiocarbamate (triallate) and organoclorine (chlordane), which are characterized by low water solubility, low polarity, and high lipophilicity, are expected to form hydrophobic bonding with aliphatic and aromatic hydrophobic moieties of HAs, macromolecules that are rich in soil amended with pig slurry, in raw form. According to this author, the sorption capacity of HAs for hydrophobic pesticides is two to three orders of magnitude higher than that for polar ones. In both amendments used, the sorption of pesticides assess was increased in amendment soil. However, indicating the nature of the binding mechanisms, the type of adsorption and adsorption capacity of humic acid from various soil and organic amendment for different pesticides appear to depend more on the molecular structure and chemical reactivity of the pesticide than on the structural and functional properties of the HAs (Senesi et al., 2001; Spark and Swift, 2002).

Sluszny et al. (1999) assess the influence of composted sewage sludge differently treated, applied to soil at 10 t ha^{-1} (according to the rate used in Israeli agriculture), in two soils (OC 0.40%, pH 7.9; OC 1.55%, pH 7.5). It was shown for *s*-triazine herbicides such as atrazine, ametryne, and terbuthylazine the sorption increase (23–74%) was a function of soil type. In all the cases, sorption to amended soil was bigger for than nonamended soil, and this was associated with the amendment with organic matter. The major increase in adsorption was for the soil with low initial organic carbon content. As examples are showed the response for atrazina with a K_d of 1.10 in control soils, while those in amended soil were 1.19 to 1.24, in soil with more organic carbon content. Associated with this response, an increase of OC (12–42%) was observed after amended. However, despite significant compositional differences between the organic amendments in regard to HAs (21.9, 15.8, 20.4%) and FAs (21.4, 32.8, 11.7%) content, humin content (56.7, 51.4, 67.9%), soluble organic matter content (10.0, 1.82, 1.13%), and total organic matter content (64, 62, 51%) in activated sludge, anaerobic digestion, and aerobic composting, respectively, there were not discernible effects other than sorption. Si et al. (2005) assess the influence of organic amendment on the adsorption and leaching of the sulfonylurea herbicid, ethametsulfuron-methyl, in acidic soils (OC 1.02%, pH 4.95). The amendment used was HAs, and they found higher adsorption of ethametsulfuron-methyl compared with nonamended soil. This response indicated that C=O and C=N groups of ethametsulfuron-methyl directly are involved in the interaction with humic substances, possibly by H-bond formation with suitable functional groups, such as carboxylic and/or phenolic hydroxyls, of the humic substances molecules. On the other hand, the study of leaching showed that the amount of ethametsulfuron-methyl was retained in the range of 68.4% for the column filled with the original soil to 92.4% for that filled with HA amendment soil. Finally, Said-Pullicino et al. (2004) assessed the influence of municipal waste composted in the fate of sulfonylurea (triasulfuron) herbicide on two soils (pH 8.0, OC 1.41%, and pH 8.3, OC 0.86%) The results show that the adsorbent (amended or no amended soil) has a moderately lower affinity for the pesticide at higher final concentration; however, the affinity increased with the higher compost amendment and with treatment HA and hydrophobic dissolved organic matter (HoDOM). The addition of compost to soil increased the adsorption of triasulfuron significantly only when applied at a dose of 99 t ha^{-1} (compared to 33 t ha $^{-1}$), related to the addition of OM, which increased the sorption sites available for adsorption. On the other hand, an increase in triasulfuron adsorption in soil–HoDOM combination was found, maybe due to coupled effect of triasulfuron adsorption to HoDOM and HoDOM sorption to soil. The percentage sorption of HoDOM in both soils was about 80%, supporting the hypothesis that DOM applied to the soil will undergo sorption reactions with the soil and in the sorbed state, and it will serve to increase the adsorption capacity of the soil for hydrophobic chemicals (Said-Pullicino et al., 2004). This author reports the important influence of DOM in pesticide behavior discussed in the next section. In Table 3 is shown a summary of the pesticides associated with an increase in sorption and the conditions that benefit this behavior.

As discussed previously, an increase sorption has been founded in amendment soil. However, the opposite response has been reported too. Through the work carried out by Worrall et al. (2001) assessing the limit of amendment in soil, it wasestablished that a finite risk remains over an organic layer that will store pesticide, enhancing future leaching. In this sense, it is considered that soluble organic matter dominated by FAs is probably the main cause of the adverse effects of amendment (Plaza et al., 2003). However, for phenoxyacetic herbicide (2,4-D) there was minor sorption when the DOM increased of 23 to 117 ppm. These effects were explained as possible competition effects for adsorption sites between the pesticide and the soluble organic matter, rather than due to a positive interaction between the pesticide and the soluble fraction of SOM (Spark and Swift, 2002).

It has been corroborated its effect related to pesticide movement is very different. For example, Cox et al. (2001) assessed the effect of exogenous carbon on movement of a triazine (simazine) and phenoxyacetic (2,4-D) herbicides in soils (OC 0.66%, pH 7.1), using three amendments, consistent in liquid amendment and solid humic amendment. The amendments were added to soil at a rate of 5% (w/w) and the results showed that simazine and 2,4-D sorption increases, showing the following $K_{\rm oc}$ values: for simazine 89 in unamended soil, 66 in liquid amendment soil, and 172 in solid amendment soil; and for 2,4-D no sorption was observed in unamended soil, 102 in liquid amendment soil, and 184 in solid amendment soil. The lower sorption of both herbicides in amendment soil with liquid waste was attributed to higher DOM content, material that plays a minor role in the interaction of simazine residues and organic amendment (Hartlieb et al., 2003). For the case of 2,4-D the persistence was much higher ($t_{1/2}$ 43 days in soil with liquid amendment compared to $t_{1/2}$ 0 days in unamendment soil); the high stability was attributed to 2,4-D–dissolved organic C interactions. Huang and Lee (2001) assess the effect of DOM isolated of animal manure in the sorption of organophosphorus insecticide (chlorpyrifos) in two soils (soil 1. OC 13.0%,

TABLE 3. Influence of Organic Amendments on Pesticide Movement in Soil

Chemical class/pesticide	Soil	Amendment[a]	Response and observations	References
Triazine				
Simazine	OC 0.56%; pH 5.3	(1)	(↑) Adsorption. K_f 0.94; 1.69, and 2.34 (unamended, amended with 60 t ha^{-1} and 120 t ha^{-1}, respectively. (↓) Leaching. Residues leaching 87%, 55%, and 29% for each treatment, respectively. This is associated to increase in organic carbon content.	Albarrán et al. (2004)
Atrazine				
Ametryne	OC 0.40%; pH 7.9	(3)	(↑) Adsorption 23–74%, because increases OC amount 42%. The amendment applied at a rate of 10 t ha^{-1}.	Sluszny et al. (1999)
Terbuthylazine	OC 1.55%; pH 7.5			
Chloroacetanilide				
Alachlor		(1)	(↑) Adsorption. Depends more on the molecular structure and chemical reactivity of the pesticide than on the structural and functional properties of the Has.	Senessi et al. (2001)
Imidazolinone				
Imazethapyr	—			
Sulfonylurea				
Rrimsulfuron				
Thiocarbamate				
Triallate		(2)	(↑) Adsorption. The sorption capacity of HAs for hydrophobic pesticides results from two to three orders of magnitude higher than for polar pesticides.	Senessi et al. (2001)
Organochlorine	—			
Chlordane				
Sulfonylurea				
Ethametsulfuron-methyl	OC 1.02%; pH 4.95	(4)	(↓) Leaching. Residues leaching 92.4% (unamended) and 68.4% (amended soil).	Si et al. (2005)
Triasulfuron	OC 1.41%; pH 8.0 OC 0.86%; pH 8.3	(5)	(↑) Adsorption associated to HoDOM incorporated with amendment rate of 33 t ha^{-1}.	Said-Pullicino et al. (2004)

[a] Amendments: (1) sewage sludge; (2) animal manure (pig slurry); (3) composted sewage sludge; (4) has; (5) municipal waste composted.

Note. (↑) increase; (↓) decrease.

pH 4.4; soil 2, OC 13.5%, pH 6.7), the DOM agreed was 70 mg L^{-1} in each soil, and the chlorpyrifos sorption by soil decreased in the presence of DOM as 19% to 43% in soil 1 and 13% to 52% in soil 2, apparently by an increase in chlorpyrifos solution concentration. On the other hand, the affinity of DOM for soil and associate with chlorpyrifos presented with the less polar DOM a higher affinity. The HAs of DOM had the highest C/(O + N), used by this work as an indicator denoting decreasing DOM polarity.

The field work carried out by Graber et al. (2001) assessed the spatial distribution of the herbicides chemical classes, uracil (bromacil), and triazine (atrazine), and terbuthylazine. The soil (sand 77%, silt 6.3%, and clay 16%) was treated with sewage sludge at rate of 35 t ha^{-1}. The distribution with depth of pesticides in profiles from soil was compared after application of 50 mm of irrigation water. The relative depth distributions of individual pesticides in the profiles were also compared between control and sludge-treated fields. The results showed that distribution in the control field and the sludge-treated field shows a readily apparent difference. In the control field the distribution of pesticides was in the upper 0–40 cm, while the middle distribution of individual pesticides was of 15.6, 14.9, and 17 cm for bromacil, atrazine, and terbuthylazine, respectively. Contrarily, in the sludge-amended field the pesticides were distributed to great depths (70 cm), with means at 28.8, 31.2, and 34.1 cm for bromacil, atrazine, and terbuthylazine, respectively. This indicate that the application of sludge had a pronounced and persistent effect on the transport of all three pesticides throughout the irrigation season, resulting from complex interplay of different controlling mechanisms of transport, maybe increasing the transport of compound. This can happen due to complexation with mobile dissolved, colloidal, and suspended OM (Graber et al., 2001).

Wanner et al. (2005) evaluated the influence of the amendment of corn straw on the behavior of the fungicide dithianon in soil (sand 6.4%, silt 78.2%, clay 15.4%, OC 1.2%). Aged residues were produced by incubating for 64 days, after which it was incubated for 18 months. The pesticide was desorbed using different concentration of dissolved organic carbon (DOC) (1.5, 28, 190, and 483 mg L^{-1} DOC). The result showed augmentation of the DOC concentration in the desorption solution causing an increase of desorbed radiocarbon dithianon, and a desorption solution with 483 mg L^{-1} DOC resulted in an enhancement of approximated 60% in relation to the lowest concentration (1.5, 28, and 190), assuming that quantity of the DOM is a main factor influencing the potential enhancement of the solubility of a pesticide, besides its physicochemical properties (Graber et al., 2001; Plaza et al., 2003; Ling et al., 2006).

Li et al. (2005) assessed the influence of the DOM extracted for two organic fertilizers above the sorption and leaching of phenoxyacetic herbicide (2,4-D) and organophosphorus insecticide (chlorpyrifos) in soil mixture taken from different sources (OC 0.48% and OC 7.8%). The results showed that chlorpyrifos sorption for soil 1 decreased with increasing DOM concentration; K_{oc} values were 5299 for 0.01 M $CaCl_2$ (control), 2,464 for 0.01 M $CaCl_2$ with 60 mg L^{-1} DOC, and 1796 for 0.01 M $CaCl_2$ with 120 mg L^{-1} DOC. They explained this decrease in K_{oc} value by a possible effect in the reduction of the surface tension with DOM addition (70 mN m^{-1} surface tension with 30 ml L^{-1} DOC and 45 mN m^{-1} surface tension with 650 ml L^{-1} DOC) where an inflection point appeared in 650 ml L^{-1} DOC, increasing the solubility of the compound. A similar sorption trend was found between 2,4-D and chlorpyrifos. The K_{oc} values (136 and 235) were significantly reduced with 120 mg L^{-1} DOC as compared to control. On the other hand, the total percentage of leached out chlorpyrifos was 82.6% for 0.01 M $CaCl_2$ alone and 93.3% for 0.01 M $CaCl_2$ with 120 mg L^{-1} DOC. The maximum concentration of chlorpyrifos in leachates increased approximately 45% from 0.11 mg L^{-1} to 0.16 mg L^{-1}, indicating that DOM increased transport in studied soil. On the other hand, Singh (2003) showed that addition of OM though animal manure addition increased sorption of the herbicide chemical class chloroacetanilide (metolachlor) in soil, and this increase was positively correlated with the increasing OC content of the cow manure amendment. The application of the amendment decreases soil pH and increases DOC content of the soil, and even after a significant increase in DOC content of the soil solution in cow manure-soils, metolachlor sorption significantly increased. An influence on the leaching of this pesticide appeared when adding manure and its mobility was reduced, even after increasing DOM, proving that the pesticide was bound to bulk-phase OM and not to DOM. In Table 4 is, a summary of some pesticides that reduce their sorption and in some cases increae their lixiviation.

4.2. Biodegradation in Amended Soil

The amendments in soil incorporate a source of microorganisms such as bacteria, actinomycetes, and fungi (Sánchez et al., 2004), primary agents for degradation of pesticides to complete mineralization (Boivin et al., 2005; Khna and Anjaneyulu, 2005). Moreover, an important source of OM and nutrients, is added, affecting strongly the structure and activity of bacterial and fungal populations as a result of increased metabolism of the readily available nutrients (U.S. EPA, 1998; Namkoong et al., 2002; Alexander, 2003; Dungan et al., 2003b; Suhadolca et al., 2004). Next we show the influence of different amendments on the soil microbiology.

4.2.1. AMENDMENT AND INFLUENCE ON SOIL MICROORGANISMS

The activity and biomass of the soil microflora are influenced by environmental conditions, and this biological parameter may be larger in soils with greater OC content and nutrients (Guerrero et al., 2000; Zagal et al., 2002; Böhme et al., 2005).

TABLE 4. Influence of DOM on the Pesticide Movement in Soil Amendments

Chemical class/pesticide	Soil	Amendment[a]	Response and observations	Reference
Triazine				
Simazine	OC 0.66%; pH 7.1	1	(↓) Sorption (liquid amendment). It is attributed to 1300 mg L^{-1} DOC in soil amendment, while (↑) sorption (solid amendment) because to 400 mg L^{-1} DOC in soil amendment. No influence in leaching.	(Cox et al., 2001)
Atrazine	Sand 77%, silt 6.3%, and clay 16%	2	(↑) Distribution in soil profile, attributed to complexation with mobile dissolved matter.	(Graber et al., 2001)
Terbuthylazine	Sand 77%, silt 6.3%, and clay 16%	3	(↑) Distribution in soil profile, attributed to complexation with mobile dissolved matter.	(Graber et al., 2001
Phenoxyacetic				
2,4-D	OC 0.66%; pH 7.1	1	(↑) Sorption in soil amendment with solid waste. The soil, while that (↑) leaching with liquid waste.	(Cox et al., 2001)
		2	(↓) Sorption with increase DOM of 0 to 120 mg L^{-1} DOC (↑) Leaching in 45%.	(Li et al., 2005)
Organophosphorus				
Chlorpyrifos	OC 13.0%, pH 4.4; OC 13.5%, pH 6.7	3	(↓) Sorption (soil amendment with 70 mg L^{-1} DOC).	(Huang and Lee, 2001)
			(↓) Sorption with increase DOM of 0 to 120 mg L^{-1} DOC and (↑) leaching.	(Li et al., 2005)
Uracil				
Bromacil	Sand 77%, silt 6.3%, and clay 16%	1	(↑) Distribution in soil profile, attributed to complexation with mobile dissolved matter.	(Graber et al., 2001)
Quinone				
Dithianon	Sand 6.4%, silt 78.2%, clay 15.4%, OC 1.2%	4	(↑) Desorption 60% with 483 mgL^{-1} DOC compared to low concentration of DOC.	(Wanner et al., 2005)
Chloroacetanilide				
Metolachlor		5	(↑) Sorption and (↓) leaching. Both responses front to increase DOC.	(Singh, 2003)

[a] Amendments: (1) sewage sludge; (2) DOC extracted from commercial organic fertilizer; (3) DOM extracted from animal manure; (4) corn straw + DOC; (5) animal manure.

Note: (↑) Increase; (↓) Decrease.

Accordingly, an increasing in the microbial activity was reported in soil (OC 1.4% pH 6.2) amended with sewage sludge (OC 26.6%, total N 10.1%), where release of CO_2 was twofold greater than in the soil not amended, attributed to a large amount of OM, because when N-P fertilization was tested it did not have these effects. On the other hand, no effects were observed in soil with or without heavy metals having similar mineralization (Perrin-Ganier et al., 2001). In this context it has been demonstrated that effects on microorganisms or the restoration of the microbial community and/or activities would occur more rapidly in amended soil than in unamended soil (Dungan et al., 2003b). The same authors hypothesized that restoration of the microbial community and/or activity could occur more rapidly in soil amended with composted steer manure after fumigation than in unamneded soil (two fumigants 1,3-dicloropropeno (1,3-D) and propargyl bromide (PBr) in a soil (OC 0.51%, pH 7.2), they amended with composted steer manure of moisture content 39% (pH 8.8, OC 14%). The result showed beneficial effects in soil amendment where the substrate inducing respiration was 2.2 times higher on average than in unamended soil. PBr was more toxic to the microorganisms biomass than 1.3-D, as indicated by the reduced dehydrogenase (DHA) activity; however, by week 4 in amended soil, the DHA activity had returned to levels observed in the untreated control. On the other hand, through molecular techniques, it was observed that during the course of the experiment, the impact of both fumigants on the microbial community was less dramatic in the composted amended soil. The responses presented in amended soil are attributed apparently to the added microbial community from the composted steer manure, either by enhanced degradation of the fumigants (mentioned in biodegradation of pesticides item), which likely would reduce the amount of pesticides that come in contact with the microorganisms, or by stimulation of microbial growth as a result of the added nutrient, or both (Dungan et al., 2003b).

Compost increases the microbial population in an amended soil (U.S. EPA, 1998). It has been reported that in amended soil with municipal solid waste compost with a high level of fungi (6800×10^3 CFU g^{-1}), the fungi population into soil increased from 84×10^3 to 143×10^3 CFU g^{-1} with 2 kg compost m^2 soil after 90 days, while bacteria populations increased from 64×10^5 to 109×10^5 CFU g^{-1} soil after 30 days (Guerrero et al., 2000). Finally, Moorman et al. (2001) show that compost and aged cattle manure in amended soil increased bacterial populations compared to unamnedment soil, and stimulated the microbial activity. This response was greater when higher amendment doses were applied (Cox et al., 2001; Moral et al., 2005).

4.2.2. EVALUATIONS OF BIODEGRADATION IN AMENDMENT SOIL

Sewage sludge, animal manure, compost, and crop straw in soil have an effect beyond the microorganisms and mineralization of pesticides. For example, the work carried out by Sánchez et al. (2004) showed that the tendency in evolution of microorganisms in soil (OC 0.4%, pH 5.26) amended with sewage sludge (OM 74.1%, total N 6.4%) was an increase in aerobes and higher numbers of colony-forming unit, where at day 90 these were almost 3 times higher than for control samples. This increase in microorganisms number was directly associated with degradation of three insecticides chemical class organophosphorus (fenitrothion, diazinon, and dimethoate), where the pesticides residues for fenitrothion and dimethoate are always below the curve of the evolution of the same pesticide in untreated soil, indicating a lower percentage of residues in the treated soils. In the light of these results it may be said that the pesticide persists less in matrices, including sludge. The same tendency was not showed for diazinon, where level of the residues was 22% in soil at 90 days after amendment, explicated by the complexity of this molecule. In a soil (sand 78%, silt 18%, and clay 4% with OC 2.4%, N 0.05%, and pH 6.5) amended with animal manure with C/N ratio among 10 to 50 (not specified) was evaluated the degradation of three herbicides chemical class triazine (atrazine), cloroacetanilide (metolachlor), and dinitroaniline (trifluralin). Previously to amendment, these pesticides were aged for 63-day incubation, presumably became less available to microorganisms. At the end of the experiment 30% of the atrazine, 33% of the metolachlor, and 44% of the trifluralin was degraded in nonamended soil, whereas in amended soil, atrazine degradation was enhanced by 0.5% manure present, with a concentration of 25 mg kg^{-1} soil for atrazine residues compared to 125 mg kg^{-1} soil in control. Metolachlor degradation was enhanced by a 5% level of manure present, with a pesticide residue concentration of 90 mg kg^{-1} soil compared to 120 mg kg^{-1} soil in the treatment control. For trifluralin the amendment did not enhance degradation. Microbial populations and activity were measured during the experiment, and the results show that amendment did not affect fungal or actinomycetes populations, but the 5% rate of manure increased DHA activity by 200% because of the influence of the higher C/N ratio (Moorman et al., 2001).

Getenga (2003) evaluated the influence of compost (N 1.14%, P 0.72%, Cu 140 ppm, Mn 2217 ppm, Fe 1272 ppm) in soil (pH 6.08, clay 60%, sand 28%, silt 12%) above the fate of atrazine degradation, and after 112 days of the experiment, only 30.7% of the pesticide was mineralized to $^{14}CO_2$ in unamended soil, while in the soil with the highest compost concentration (5000 ppm), 55.1% of the pesticide was mineralized, explained by the contribution of microorganisms in consortium in the amendment and because the atrazine remained in the desorbed state, which was accessed easily by microorganisms to degrade it as a carbon source (Getenga, 2003). This same author evaluated the mineralization of phosphonoglycine herbicide (glyphosate) using the same compost and soil, and found that the mineralization of glyphosate in soil with compost presented a mineralization curve with only two phases: the initial rapid phase, followed by a slow final phase.

The rapid phase lasted for 20 days. The initial rapid phase of degradation was attributed to microbial action on free glyphosate, while the slower phase was due to the subsequent attack on the adsorbed pesticide; however, the compost applied to soil does not appear to stimulate the microbial degradation of glyphosate, because only 10.9% of the initial total ^{14}C applied to soil was recovered as $^{14}CO_2$ gas from the soil with compost, while 10.7% was recovered as $^{14}CO_2$ in soil without compost, with an explanation that the microbes had adapted to conditions in the soil used in this study, or that compost had a high concentration of iron (1272 ppm), which increased the adsorption of glyphosate by soil, as a result reducing pesticides mineralization. On the other hand, the formation of the nonextractable residue (51.0%) portion was a biotic degradation process because the lowest amount was formed in the autoclaved soil (47.5%). The amount of $^{14}CO_2$ evolved during mineralization of glyphosate from soil was not proportional to the amount of extractable residues in soil. This supports the hypothesis of both nonextractable and extractable residues of glyphosate having been mineralized to $^{14}CO_2$ (Getenga and Kengara, 2004).

The assessment of fungicide methyl isothiocyanate degradation in soil (pH 7.2, OM 0.92%) amended with chicken manure shows that in treatment at 20°C with an amendment of 1.0, 2.5, and 5.0% there is a persistence of 3.5, 2.5, and 2.2 days, while that in unamended soil was of 5.8 days, the degradation of methyl isothiocyanate was two times faster in nonsterilized than in sterilized unamended soil, meaning about 50% of the degradation can be attributed to biological mechanisms (Dungan et al., 2003a). Dungan et al. (2003b) assessed the effect of two fumigants, propargyl bromide (PBr) and 1,3-dichloropropeno (1,3-D), in soil (pH 7.2, OM 0.92%) amended with composted steer manure (pH 8.8, OC 14%); the result showed that compared to the unamended soil control, the degradation of PBr and 1,3-D was enhancement by addition of 3% of steer manure. In PBr-treated soil at concentrations of 10, 100, and 500 mg kg^{-1}, the degradation rate was 3.9, 6.0, and 3.5 times higher in amendment soil, respectively, than in unamended soil. In amended soil treated with 1,3-D at the same concentration, the degradation rate was 2.3, 1.4, and 1.4 times higher, respectively, than in unamended soil. The slower rate of 1,3-D degradation at the higher concentration (i.e., 100 and 500 mg kg^{-1}), and the fact that first-order coefficients are nearly the same in both unamended soil and amended soil may be attributed to 1,3-D posing inhibitory effects on degrading organisms. This author, to determine the long-term impact of PBr and 1,3-D on the soil activity, used the DHA measurement. The incorporation of aged steer manure into nonfumigated soil significantly increased the DHA over the 12-week incubation period compared to the unamended soil control. In unamended and amended soil treated with PBr at 10 mg kg^{-1} or 1, 3-D at 10 and 100 mg kg^{-1}, the DHA was similar to that of the nonfumigated control. Coincidentally, the higher rate of fumigant degradation in the amended soils at these concentrations corresponds well with the increased DHA in the amended soil treatments. PBr was more toxic in highest concentration for microorganisms (reduced DHA); however, after week 4 in the amended soil, the DHA returned to levels observed in the untreated soil control. The benefits of amended soil above the microbial community exposed to pesticides have been reported for other amendments, but a brief mention is described in the next section.

Finally, the degradation of fungicide dithianon was evaluated in a soil (sand 6.4%, silt 78.2%, clay 15.1%, OC 1.2%) amended with maize straw. The result showed that large amounts of $^{14}CO_2$ deriving from biodegradation of the compound were trapped at a rate representing more than 33% of the applied compound after 64 days of incubation; at the same time, nonextractable residues were formed containing more than 63% of the applied compound after 64 days of incubation in unamended and amended soil. However, differences were presented during previous days, where the amendment with straw decreased the formation of $^{14}CO_2$ compared to the unamended soil after 2 days of incubation, assuming that the strawly amendment had a lasting effect on the amount of slowly mineralizable radiocarbon, maybe due to incorporation of radiocarbon into the biomass of the soil. By contrast, straw addition had a major effect on biotic parameters such as the microbial activity measurement; after 64 days the straw amendment led to a threefold value of the microbial activity compared to the control samples, due to the stimulating effect of the readily bioavailable carbon source (Wanner et al., 2005). The table 5 shows the biodegradation of pesticides in soil amendment and the amendment applied.

5. OTHER ASPECTS RELATED TO AMENDED SOIL

As was described already, the different amendments in soil tend to modify the sorption capacity of pesticides, in some cases increasing the sorption, while in others accelerating the degradation. Both responses are associated with the decrease in extreme result in significant reduction in the biological efficacy of several soil-applied pesticides, resulting in emergence, for example, of weeds in crops (Golovlena et al., 1990), and this response has been explained through the assumption that only pesticides in soil solution are available to plants and microorganisms to control soil-borne pests (China et al., 2004; Tao et al., 2004). An accelerated degradation of pesticides can result from extensive and repeated use of pesticides, due to the pesticides beingdegraded so quickly that they are unable to carried out its control (Singh et al., 2005). This can be due to enrichment in the populations of microbial degraders in the soil, from increased enzymatic activity, or from combination of these factors (Di Primo et al., 2003; Singh et al., 2005). Nowadays, studies carried have been focused on the microorganisms able to degrade pesticudes quickly. Recently, Karpouzas et al. (2005) isolated two bacteria in soil from

TABLE 5. Pesticide Biodegradation in Soil Amendments

Chemical class/pesticide	Soil	Amendment[a]	Response and observations	Reference
Triazine				
Atrazine	OC 2.4%; pH 6.5	1	(↑) Degradation. 25 mg kg^{-1} soil residues compared to 125 mg kg^{-1} soil in control. No effects on fungal or actinomycetes populations, but increased DHA activity by 200%.	(Moorman et al., 2001)
	pH 6.08, clay 60%, sand 28%, silt 12%	2	(↑) Degradation associated with (↑) desorption; 30.7% of the pesticide was mineralized to $^{14}CO_2$ in unamended soil, while that in the amended soil was 55.1%.	(Getenga, 2003)
Dinitroaniline				
Trifluralin	OC 2.4%; pH 6.5	1	(—) No influence on degradation	(Moorman et al., 2001)
Organophosphorus				
Fenitrothion			(↑) Degradation.	
Diazinon	OC 0.4%; pH 5.26	3	(—) No influence on degradation because of molecule complexity.	(Sánchez et al., 2004)
Dimethoate			(↑) Degradation. Response associated to increase in microorganism number.	
Phosphoglysine,				
Glyphosate	pH 6.08, clay 60%, sand 28%, silt 12%	2	(—) No influence in degradation, but (↑) nonextractable residue	(Getenga and kengara, 2004)
Chloroacetanilide				
Metolachlor	OC 2.4%; pH 6.5	1	(↑) Degradation, 90 mg kg^{-1} soil pesticide residue compared to 120 mg kg^{-1} soil in treatment control. No effects on fungal or actinomycetes populations, but increased DHA activity by 200%.	(Moorman et al., 2001)
Methyl isotiocianate	OM 0.92%; pH 7.2	4	(↓) Persistence of 1 day in amended soil to 5 days in no amendment soil	(Dungan et al., 2003a)
Propargyl bromide, 1,3-dicloropropeno	OM 0.92%; pH 7.2	5	(↑) Degradation associated to an increased DHA in the amended soil treatments	(Dungan et al., 2003b)
Quinone				
Diathinon	OC 1.2%	6	(—) No influence in degradation to short time	(Wanner et al., 2005)

[a] Amendments: (1) cattle manure; (2) compost; (3) sewage sludge; (4) chicken manure; (5) steer manure; (6) crop straw.

Note. (↑) increase; (↓) decrease; (—) no effect in response.

a potato monoculture, which were able to rapidly degrade cadusafos (48 h) with concurrent population growth; the two bacteria are *Flavobacterium* sp. and *Pseudomona paucimobilis* strain.

Contrary effects in weed and disease control have been reported for organic amendments such as compost, organic fertilizer (manures), and sludge (Craft and Nelson, 1996; Boulter et al., 2002). The fresh animal manures and sludge contain pathogenic organisms, so they are applied as aged or compost materials. Compost is known to suppress plant disease through a combination of physiochemical and biological characteristics. Physicochemical characteristics include any physical or chemical aspects of compost that reduce disease severity by directly or indirectly affecting the pathogens or host capacity for growth. Examples of these aspects include nutrient level, OM, moisture, pH, and other factors. Biological characteristics include compost-inhabiting microbial populations in competition for nutrients with pathogens, antibiotic productions, lytic and other extracellular enzyme productions, parasitism and predation, induction of host-mediated resistance in plants, and other interactions that increase microbial activity or decrease disease development. However, high levels of microbial activity in compost have been postulated as the primary mechanism of disease control (Miyasaka et al., 2001; Boulter et al., 2002). Boulter et al. (2002) found that compost (chicken manure, bark mix, and other sources mixture; C:N ratio 40) application was effective in suppressing to *Fusarium* pattch and *Typhula* blight. The non-treated plot had a significantly higher diseaserate (16 to 18%) compared to compost treatment (6% to 7%). High compost application (9.74 t ha^{-1}) displayed a more rapid rate of disease suppression compared to the lower rate (4.87 t ha^{-1}); the fact that higher rates of compost were better at disease suppression is a result of a combination of increased nutrient availability and increased antagonistic or competitive interactions among microorganism populations or their metabolites, although smaller amounts of OM were sufficient to stimulate the microbiota (Boulter et al., 2002). Brown and Tworkoski (2004) assessed the effects of compost mulch on abundance of weeds, apple scab, growth of the brown rot fungus, and two arthropod pests in apple orchards. The results showed that following application of glyphosate, compost application improved weed control; the mulched plots had 2% or less ground area covered with weeds, compared with 25% in control plots. With compost application no difference in apple scab was present, while a significant reduction in brown rot growth was found active compost compared with sterilized compost. In insect control, the addition of compost presents a major abundance, with spiders predominant. In this study it was possible to observe that compost was preferable to herbicide application, since beneficial predators were more abundant, herbivorous ones were reduced, and weed suppression was greater in mulched plots compared to herbicide treatment for at least the first year after compost application. Inhibition of brown rot fungus was most likely through competition for resources from the higher microbial biodiversity in the active compost (Brown and Tworkoski, 2004).

6. REMARKS

- Assessing the pesticide fate in amended soils has been motivated assuming that the amendment is applying an additional source of OM and microorganisms with properties for modifying the conduct of adsorption, movement, and biodegradation of pesticides.
- Contrary trends are reported in literature on pesticides fates, and these are largely because of the differences in soil types, pesticide characteristics, and sources of amendments, considered as complications for obtain a tendency pattern and making difficult the understanding of pesticide fates.
- The OM and mainly the humic component act as the principal factor controlling the adsorption process, in most cases increasing the adsorption of pesticides in the soil.
- The organic amendment caused an increase in the concentration of DOM, resulting in an increase in the mobility, influencing transport and ultimate distribution of pesticides in the soil profile, because of reduced adsorption, attributed to the complex formation of DOM with organic chemicals, competition for sorption sites, or through the incomplete interaction of pesticides with soil constituents.
- Through addition of amendments to soil are incorporated sources of microorganisms such as bacteria, actinomyces, and fungi, primary agents for degradation of pesticides, and an important source of OM and nutrients, influencing strongly the structure and microbial activity as a result of increased metabolism.
- The increase sorption and accelerated degradation of pesticides can be of benefit environmentally; however, these responses are associated in some cases with limits on the efficacy of pesticides, resulting in diminished weed control. However, in amended soil a weed and pest control has been reported such that the effects of competition by nutrients and the highest activity in soil amendment are the main factors for those controls.

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