Persistence and Bioaccumulation of Persistent Organic Pollutants (POPs)

Tomaz Langenbach

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/56418

1. Introduction

Some organic pesticides are the most widespread POPs (Persistent Organic Pollutants) used in agriculture worldwide. Other POPs such as volatilized industrial pollutants as well as pollutants from fuel combustion can also contaminate large areas due to dispersion by wind and rainfall. Non biodegradable molecules persist in the environment and the soil serves as a large sink for them. These pollutants are able to move in the environment and in low concentrations over a long period of time, but through bioaccumulation they can have hazardous effects on the biota of the region. This article focuses mainly on pesticides and some other POPs that contaminate large areas. The chemical characteristics of persistent molecules that are resistant to biodegradation will be discussed in the context of the environmental conditions that enhance persistence.

Adsorption or not of a molecule in the soil is a key step to define bioavailability. The concept of "preferential partition" helps us understand the competitive mechanisms between the soil and biosphere. Bioaccumulation occur when concentrations in the biosphere are much higher than those found in the surrounding environment. The uptake of persistent molecules to levels of high concentrations can have hazardous effects on flora and, through the food chain, on fauna and human health.

Xenobiotics not adsorbed by the soil can become mobile and when the molecule is persistent it may be dispersed by water or air through the biosphere, polluting large geographical areas and affecting the biodiversity of the flora and fauna. A brief overview of this dispersion will be necessary to show how recalcitrant molecules in the environment make remediation inefficient. The application of pesticides over large areas can only be sustainable if their molecules biodegrade naturally. Remediation can be applied usefully to accidents in restricted areas but it is not feasible over large areas due to the high costs. The only efficient policy for recalcitrant molecules that can not be controlled by remediation is the restriction of their use or banning them altogether.

2. How molecules can escape degradation in the environment

The adsorption of molecules, due to their affinity to other chemical components of the soil matrix or soil biosphere, protects them from chemical degradation as well biodegradation. Non adsorbed molecules are bioavailable and therefore are exposed to degradation. Experiments with soils weathered for long time with ethylene bromide contamination in which was added ^{14}C-ethylene bromide, shows strong biodegradation of the new applied radioactive substance after sixty days at the same time that weathered contamination substance remains in the same concentration [1]. Microorganisms involved in biodegradation are active against a freshly applied radioactive molecule but are not efficient for the same substance entrapped in the soil. Weathered molecules by soil friction process in which the larger soil particles are broken into smaller ones results in the gradually desorption of the molecules with enhanced bioavalability [1]. Therefore it is a pitfall to conclude that the hazardous effects are only caused by pesticide concentrations in the soil [2].

The fate of pollutants in the soil depends on the soil properties and the physical chemical characteristics of these molecules. Essentially the uptake of pollutants in the soil can be understood to be the result of chemical attraction and bond strength. These processes in the soil are governed by a number of well described phenomena including: Van der Waals forces, hydrogen bonding, ion exchange, charge transfer mechanisms, lipophilic affinity, entrapment and covalent reactions to humic acids [3, 4]. In essence, pollutant molecules will move to the most attractive sites in the soil environment. Competition between plant roots, soil mesofauna, microbes and soil organic and inorganic components makes residue to bind in the most attractive site where residues will accumulate preferentially. Pollutants, such as pesticides, which are not held or bound to the living and non-living parts of the soil, will be leached through the soil, resulting in pollution of ground water, rivers and reservoirs or they will be volatilized.

2.1. Where molecules adsorb

In this section the factors that regulate the distribution of pollutants between the soil matrix and the biosphere including microorganisms, mesofauna and bioaccumulation in plants will be discussed. In aquatic environments, where polar water molecules predominate, lipophilic pollutants have affinity for organic matter and therefore always move toward the biosphere [5] (Figure 1). In this case the bioaccumulation factor depends on molecular size and correlates positively with a lipophilic character measured by the K_{ow} value [6]. However, polarity on its own cannot explain to which compartment POP's move to in the soil.

Soils are a highly variable mixture of mineral and organic materials with living, dead and decaying biologic components. There is a lipophilic fraction as well that can adsorb lipophilic pollutants. The binding process is complex considering the diversity of compartments such as microorganisms, mesofauna and plants that compete for the uptake of lipophilic pollutants. Despite difficulties to standardize a methodology for lipid determination [7], this parameter is used to calculate the bioaccumulation factor [8, 9]. Soils can function as a filter when they adsorb the remaining residues, which then become unavailable for the biosphere. On the other hand low adsorption capacity pollutants remain bioavailable and can contaminate water, air, fodder plants, livestock and moving along the food chain up to humans. The soils may function as a filter or as a source of pollutants and this depends mainly on the kind of soil.

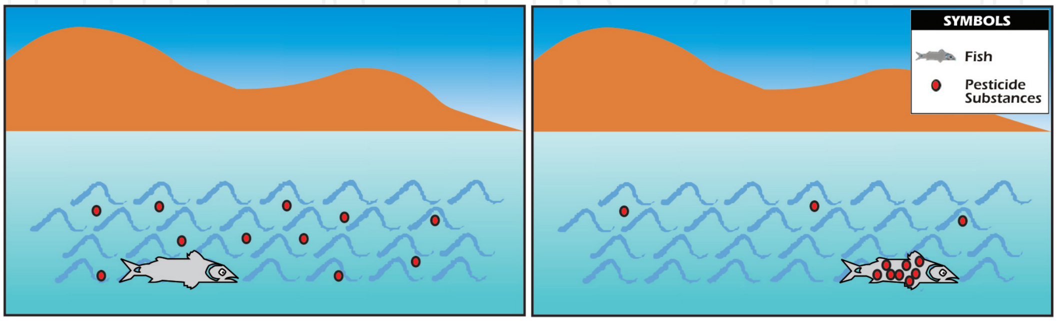

Figure 1. In aquatic systems the movement of lipophilic substance is unidirectional towards living forms, resulting in bioaccumulation

Despite enormous amounts of published scientific literature about bioaccumulation, the distribution of pollutants in the soil or biosphere is not well understood. Here the mechanisms of bioaccumulation in the soil environment will be discussed including the development of the proposed "preferential partition" concept.

2.1.1. Lipophilic molecule uptake by microorganisms

Soil microorganisms represent a large part of the living biomass but in general are not used for bioaccumulation studies since they cannot be separated from the soil to measure the pollutants. Nevertheless important information could be obtained from an experiment in which antibiotic resistant bacteria with bioaccumulated difocol were introduced into the soil [10]. Radioactive ^{14}C-dicofol was bioaccumulated during the incubation of *Pseudomonas fluorescens* (soil bacteria) resistant to kanamicyn and rifampycin. These bacteria can be measured in the soil using CFU counts with petri dishes containing the above mentioned antibiotics able to suppress all other soil microorganisms. ^{14}C-dicofol was incubated and bioaccumulated in Pseudomonas fluorescens strains after which it was poured on top of a soil and subjected to a succession of simulated rainfall events. At the end of the simulated rainy period of 24h, 95% of the radioactive labeled insecticide remained in the upper 1cm of the soil, whereas 60% of the microorganisms had been transported 10 cm through the soil and were recovered in the leachate. Only 7% of the bacteria poured onto the soil remained within the first 1 cm of soil. In this experiment the acaricide dicofol moved away from the bacteria toward the soil particles [10] showing that it was more strongly attracted to the soil matrix than to the living cells. Therefore in this case the soil acted as a filter/sponge, protecting microorganisms, mesofauna, plant roots and preventing ground water pollution. Molecules will move to the sites they find most attractive and in this case the soil matrix showed a higher uptake of the pesticide, thus reducing the dicofol content in the bacterial cell envelope. In organic matter rich soils, it is not uncommon for many POP´s to show **preferential partition** towards soil organic matter adsorption rather than to plants or other living forms [11]. A good parameter to evaluate **preferential partition** of pollutants between soil and biosphere is to compare octanol/ water (K_{ow}) ratios of each compartment. A higher octanol/water ratio (K_{ow}) for organic matter than for the soil bacteria explains why the dicofol moves out of the cell and into the organic component of the soil [12, 13].

2.1.2. Lipophilic molecule uptake by earthworms

Earthworms, as a "living system" model, facilitate bioaccumulation studies in soil since they can be collected easily and analyzed for pollutant uptake. Papini and Andrea [14] working with simazine, a relatively non-polar (K_{ow} 2-2.3) herbicide, [15, 16] and Paraquat, a highly polar herbicide, found that simazine did not bioaccumulate in the earthworm *Eisenia foetida* but Paraquat did. This result was the opposite of what was expected from the point of view that non polar substances bioaccumulate in the biosphere and polar substances do not. In a separate but similar study using an Argisol soil, the herbicide atrazine did not bioaccumulate in the earthworms *Pontoscolex corethrurus* either [17]. However, these results are not fully explained by the polarity of the pesticides. To interpret these results more precisely requires an understanding of K_{ow} as well as knowing the importance of organic matter in the soil. Soil organic carbon content (K_{oc}) correlates positively with soil K_{ow} and is an important factor to attract lipophilic substances [13, 18]. Given that K_{oc} and K_{ow} in general correlate positively, soil organic matter (OM) content can be used to select soils for study. Andréa and Papini used this method to compare how simazine and paraquat [19, 20] would behave in soil in the presence of the earthworm *Eisenia foetida* with different amounts of soil organic matter.

Two soils, one with 12 g. L^{-1} organic matter (pH 5.7) and the other with 93 g. L-1 organic matter (pH 6.4), were treated with simazine and paraquat. Soils were incubated for 90 days with *Eisenia foetida* [19, 20] and the bioaccumulation coefficient factor (Bcf.) was determined. Simazine did not bioaccumulate (Bcf. 0.9) in the earthworms in the high organic matter soil [19]; however, in the low organic matter soil it did (Bcf. 6.9). With simazine, it seems likely that molecular polarity controlled the different distribution of pesticides between soil organic matter and biota. In the soil with low organic matter, **preferential partition** was toward earthworms that provided more attractive sites for the pesticide than the soil matrix. In the high organic matter soil, **preferential partition** was toward the soil organic matter, less polar than the earthworms and therefore chemically more attractive to lipophilic pesticides (Figure 2). The results at first appear to be at odds with one another, in terms of where the pesticide accumulated, until we recognize that pesticide movement is not necessarily unidirectional.

2.1.3. Lipophilic molecule uptake between earthworms and plants

Experiments with p,p`-DDE in soils with the earthworms *Ersenia fetida, Lumbricus terrestris* or *Apporectodea caliginosa* in the presence of different plant subspecies showed that *Curcurbita pepo*

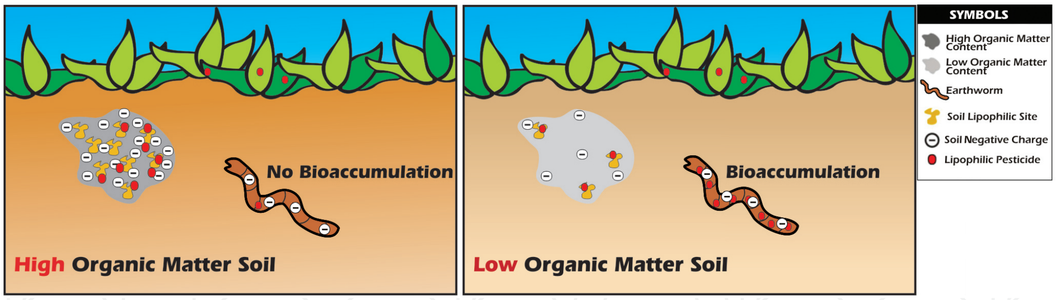

Figure 2. The movement of lipophilic pesticides in soil is influenced by the relative abundance of lipophilic sites in the living and non living soil components.

ssp. reduces bioaccumulation in the three species of earthworms. Similar experiments in the presence of *Curcurbita ovifera ssp.* showed a reduction as well as an increase of bioaccumulation in the different earthworm specie [21]. The authors observed that bioaccumulation in the plant C. pepo were enhanced with the three earthworm species which did not occur with *C. Ovifera* where only a slight increase was observed. In this set of experiments **preferential partition** occurs mainly toward plants and less to earthworms.

An increase in the bioaccumulation in plants indicates higher bioavailability of this residue due to presence of the earthworm [22] which through chemolysis is able to change humic acid and increase the protein and carbohydrate moieties and degrade the carboxylic and aliphatic groups. In consequence the hydrophobic index HI = 0.0433 – 0.0811 in the soil decreases in the presence of earthworms and by *C. pepo* to 0.0231- 0.0286, a condition that reduces soil adsorption and increases bioavailability and therefore bioaccumulation is enhanced in the plant [21]. Other data showed that the phytoextraction capacity of plants is related to the capacity of inorganic uptake from soil. Fertilizer amendment with N and P enhances phytoextraction and increases bioaccumulation in *C. Pepo* [23].

Bioaccumulation of lipophilic substances such as chlordane is quite different between plant species, as observed by zucchini with a low and pumpkin with a high uptake [24]. These lipophilic substances are normally bioaccumulated in roots and only a small amount is translocated in a decreasing sequence to stems, leaves and fruits [21, 24, 25]. When K_{ow} is higher than 5, plant uptake is considered to occur mainly via the air-to-plant route [26]. These data agree with the observations of Schnoor et al. [27] that plant uptake is very efficient for moderate hydrophobic organic chemicals with a K_{ow} of 0.5 to 3. For a K_{ow} higher than 3 these chemicals bind more and more strongly to the surface roots with decreasing translocation within the plant. However, translocation of chemicals such as terbuthylazine, with a K_{ow} of 3, and atrazine can occur in high amounts [28, 29, 30]. Fairly soluble chemicals with a K_{ow} lower than 0.5 are not sufficiently sorbed to roots and are not actively transported through plant membranes.

Soil amendment with manure compost may reduce bioavailability by retaining the toxic organic chemicals in the organic matter and therefore reduce the hazardous effects [31] but the literature shows controversy data in which organic amendment can reduce adsorption of pesticides by increasing the desorption effects [32]. The increasing addition of sludge as the final disposal on soil introduces POPs in much higher amounts than air deposition [33].

Nevertheless lipophilic substances with a high octanol-water partition coefficient (log K_{ow}) remain preferentially in soils and with little bioavailability they have low bioaccumulation in earthworms [8]. Radioactive atrazine applied on soil with low organic matter content previously covered by cattle manure, showed a slower leachate speed compared to control but with a low retention capacity in the soil [34]. Soils modulate adsorptions and bioavailability and an inverse correlation occurs with a decrease of bioaccumulation in earthworms when K_{ow} increases, which is different from an aqueous environment when there is a positive correlation between K_{ow} and bioaccumulation [6].

2.1.4. Cation bioaccumulation

Many evidences indicate that the lipophilic character of soil organic matter is one of the most important factors for **preferential partition** of lipophilic substances toward soil; nevertheless this process can be carried out by chemical bonds such as ionic charged bonds of organic toxic chemicals. Below is a description of how **preferential partition** works between the soil and the living biosphere with cationic charged molecules. As far as the author know bioaccumulation in terms of cationic charged molecules between the soil and biosphere has not been reported in the literature before.

Based on the hypothesis that polarity is the main factor controlling bioaccumulation, one would expect that a strongly polar pollutant, like paraquat, would be accumulated in the most polar parts of the soil. Thus in soils with low organic matter, one would expect no bioaccumulation in earthworms and paraquat would be bound within the soil matrix. Nevertheless, Papini and Andrea[14] found the opposite. **Preferential partition** moved this compound towards earthworms, depending on the amount of ^{14}C-paraquat (1.2; 12 and 120 μg. a.i.g^{-1}) applied to the soil [20]. To understand these results we have to note the importance of the relative abundance of charge-binding sites (attractive/exchange sites) in the biosphere and soil. In soils with low OM and low ion exchange capacities, the exchange sites, which sequester positive charged pesticides that gradually become saturated and consequently makes possible simultaneous available pesticides to bind anionic sites on or in earthworms [35]. This is a competition between the earthworms and attractive soil sites for paraquat. In this low SOM soil, paraquat bioaccumulation did not surpass Bcf 5 probably because the anionic sites on the surface of the earthworm cells were limited and already saturated (Figure 3).

In a high OM soil and with a low application of paraquat (1.2 μg a.i.g^{-1}), the bioaccumulation factor (Bcf.) was 1.1 and increased with higher concentrations of applied paraquat up to Bcf. 3.8. With increasing paraquat concentrations (12 to 120 μg a.i.g^{-1}) one would predict that as the soil charge sites gradually became saturated then gradually more paraquat would become attracted to the earthworms. From these experiments, we noted the predominance of electrostatic binding in the soil and the importance of an abundance of exchange sites. In comparison, lipophilic attraction is driven by affinity without limits of concentrations which are different from the electrostatic bonds were the charged sites involve higher bond energy and therefore are predominant but have quantitative limitations with pesticides up to saturation with consequences in bioaccumulation. The correlation between K_{oc} (soil organic matter) with K_{ow}

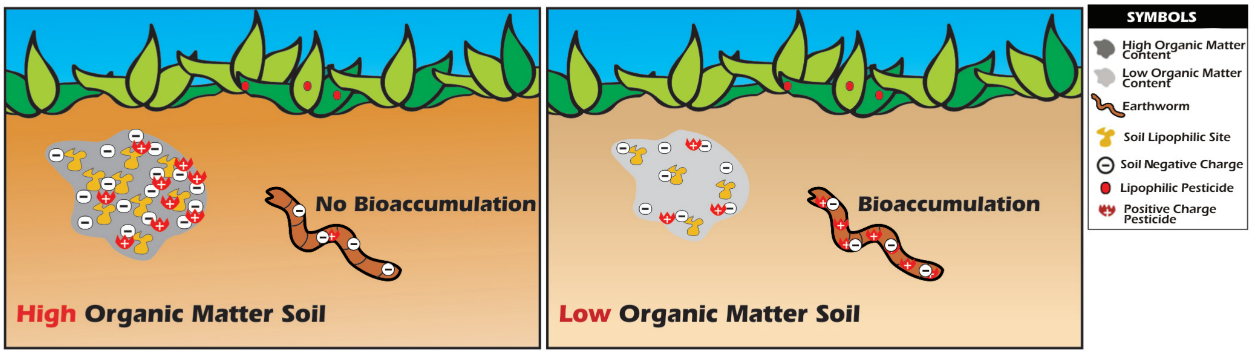

Figure 3. In preferential partition charged pesticides are attracted to anions between the abundance in soil and biosphere.

(molecular polarity) and availability of cation exchange sites (electrostatic bonds) in the soil shows that the **Preferential Partition** concept can explain pesticide bioaccumulation.

Ecotoxicology depends on soil organic matter. When the SOM is high the ecotoxicological effects are low and when the SOM is low the effects are high. In this latter case the residues remain bio-available and are intensely absorbed in the biosphere and therefore are hazardous to flora and fauna. Polarity and/or anion charge capacity of living organisms compete with the parameters in the soil organic matter. The highest attraction capacity of these different compartments defines the way in which molecules move in the environment. Molecules inserted in the soil matrix by "**Preferential Partition**" can be protected from hydrolysis, oxidation/reduction reactions as well escape enzymatic action.

2.2. Microbial constraints of biodegradation

All natural molecules can be biodegraded in the environment. An important constraint of xenobiotic biodegradation is the absence of microorganisms with efficient biodegradation capacity in a specific environment. Recently there has been an intense research effort to develop or transfer microbial efficient biodegradation genes to a microorganism that is adapted to a specific environment but lacks biodegradation capacity. Other constraints can occur when microorganisms do not enter in small soil microspores and therefore could not be present to promote biodegradation (Figure 4).

3. Movement of persistent molecules in the environment

The link between bioavailable persistent substances and the spread of these substances in the environment, causing dissemination of hazardous effects, will be discussed in this section. Desorbed or non sorbed molecules are bio-available and can move into the food chain and can also get into ground/surface water or reach the atmosphere through volatilization and are thus be randomly disseminated in the biosphere (Figure 5) [36]. When persistent molecules are adsorbed in the soil they cause less hazardous effects than when they are bioavailable.

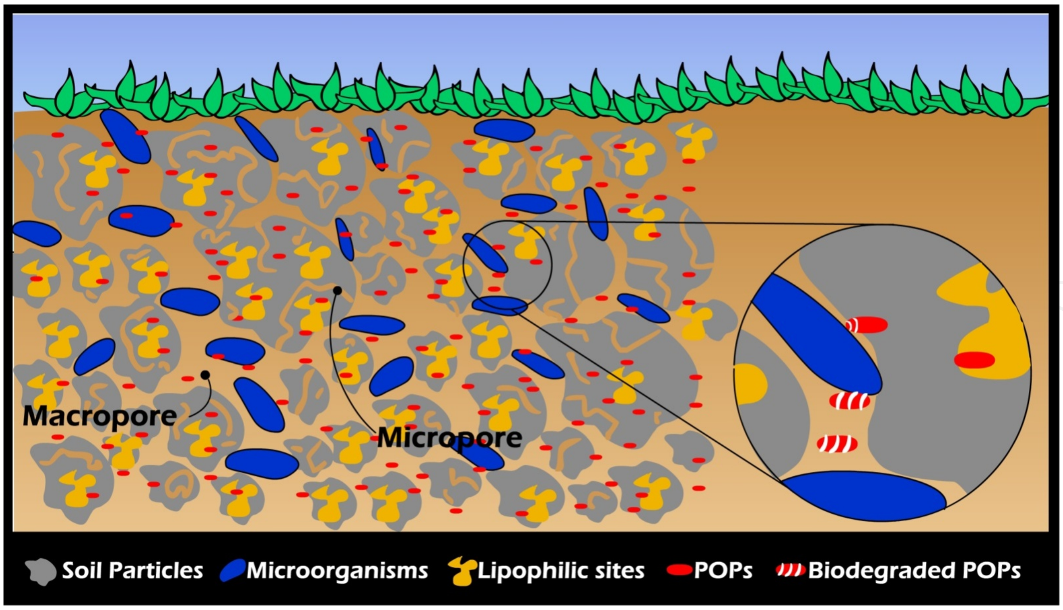

Figure 4. Restriction access of microorganism in the soil by micropores.

Biodegradable substances, differently from persistent molecules, cannot survive for a long time in the environment. The problem is not only the actual pollution of pesticide applications, which is strongly dependent on the climatic conditions [37, 38] but also the composts with the organic wastes containing POPs that are added to soils [39] as well the inadequate forms in which POPs used to be stored [40, 41].

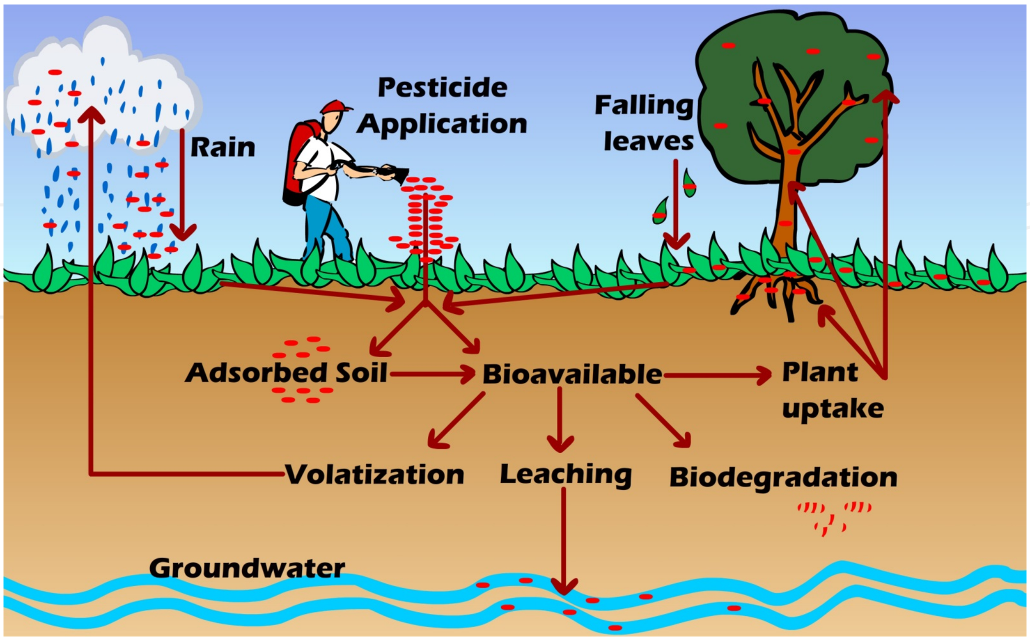

Figure 5. Overview of POP dispersion in the environment of air, water and biosphere.

3.1. Movement from soil to water

The vertical displacement of substances in the soil can leach from the surface through the unsaturated zone into deeper layers down to ground water [42]. It is well-known that the soil infiltration capacity depends on soil texture characteristics, porosity, and humidity [43]. Soils with a sandy texture are more susceptible to the process of leaching while clay soils have greater pesticide adsorption potential. Leaching can occur in an irregular manner known as preferential flow [44]. This is due to irregularities in the soil that facilitate an easy path for water and pollutants at specific points. These paths can be formed by soil cracks, worm trails, rotten roots, termites, and other biological activities [45]. Soil in which surface layer rich in organic matter was removed by flattened to built roads or courtyard enhance strongly the leaching process [34]. Water consumption from wells exposed to pesticide applications can be very dangerous for humans and cattle. Generally, ground water in the dry season drains to rivers and in the raining period receives water from rivers and pollutants follow these processes [46, 47].

Surface water contamination with persistent molecules occurs not only by the drainage processes from ground water but also strongly increases with runoff [48]. When the quantity of rainfall exceeds the soil infiltration capacity, superficial runoffs occur [49]. Runoffs begin with small lamina flows that build up until they form turbulent flows which cause pesticide losses and even gully erosion. This process has been shown to be an important source of pollution in surface waters [50]. Another source of pollution is the discharge of effluents from waste water treatment plants to surface waters [51]. Pollutant molecules can be distributed by rivers and affect different living forms in the water as well as the fauna that use it for drinking. Persistent molecules contaminating these waters are also spread to agriculture products through irrigation [51].

3.2. Movement in the air

The sources of POP in the air are pesticide applications, oil combustion, industries and indoors at home. During the application of pesticides a part remains in the air due to drift. Another very important source is volatilization of pesticides from soil or plant surfaces [52]. Pesticide dissipation occurs when the product is being sprayed. Droplets are aerially dispersed and reach non-target areas [53]. The spray drift of pesticides is influenced by the size of the pulverized droplets, application pressure, distance of the pulverizer nozzle to the target and the velocity of the wind during application [54]. By strong volatilization the relative loss of the applied amount can be very high [55].

These molecules contaminating the air are transported by air currents and redistributed globally, polluting all kinds of ecosystems [56]. Today we may find many such molecules in the Antarctic and in obscure ocean islands [57, 36]. This pollution affects man as well as many animal species [58]. Besides the adsorption capacity that is able to immobilize these molecules, another important variable is the molecular vapor pressure which is influenced by temperature – an increase of 10°C makes these molecules about four times more volatile [59]. This process is much greater in the tropics with higher temperatures than in temperate regions of the world.

Also these losses can affect people, domestic animals, pollinating insects as well as contaminating lakes, rivers, and fish or other aquatic plants and animals. Air pollution is quite difficult to control. Trees and forests can filter the pollution that is spread by horizontal wind but not by rainfall [60]. Air pollutants can move from rural areas to towns and can be present everywhere. This distribution is determined by the wind and physical barriers such as mountains etc. The challenge is how to reduce this process as much as possible considering that these molecules have been lost for the purpose that they were intended and non target flora and fauna are not able to escape from their hazardous effects efficiently.

Air pollution can also begin indoors and then move outdoors. Polybrominated diphenyl ethers (PBDEs) and phthalates among others are some examples. Brominated compounds make up an important group of flame retardants. Some of these products, such as Penta-BDE, seem to show toxicological effects at very low concentrations [61]. PBDEs are structurally similar to thyroid hormones acting as endocrine disruptors via alterations in thyroid hormone homeostasis [62] and demonstrate neurodevelopmental effects [64]. The most sensitive populations are likely to be pregnant women, developing fetuses, and infants [65].

In recent years, PBDEs have been recognized as significant pollutants of the indoor environment [66]. These additives are mixed into plastics and foams but do not form chemical bonds. This makes them much more likely to leach out of goods and products by volatilization. PBDEs are lipophilic compounds [67], and when released into the environment bioaccumulation can occur in living organisms and this is followed by biomagnification in the food chain. Bioaccumulation in wildlife has been reported in numerous studies, even in places with no local sources or industrial production [68] like the Arctic. Due to their high production volume, widespread usage, and environmental persistence, PBDEs have become ubiquitous contaminants in environmental media, biota and humans [69]. As their levels are rapidly increasing in the environment, these chemicals have evolved from ‘emerging contaminants’ to globally-distributed organic pollutants [70].

3.3. Movement in the food chain

Movement of persistent molecules in the biosphere toward soil microorganisms, mesofauna and plant uptake will be discussed in this section. Here some aspects of the way in which persistent molecules can be transferred from one life form to other will be emphasized, considering that the overall food chain sequence processes are well known [71].

3.3.1. Cell bioaccumulation

How do persistent molecules move into cells in higher concentrations than the surrounding environment [72]? “**Preferential partition**” describes the “choice” of the substance, due to affinity, between cell membranes or components of the environment. As mentioned earlier affinity is characterized mainly by lipophilicity and charge binding. With the photo-binding technique it is possible to identify in which cell component the molecule will preferentially bind. This technique preserves the binding when only weak bonds between the pollutant and cell are available. These weak bonds are not resistant to the harsh conditions of cell fractionation. The method establishes covalent bonds by UV irradiation only between pollutants containing aromatic structures and the cell component where weak bonding occurs and this covalent form of bonding can resist cell fractionation. Studies with the gram negative soil bacteria *Azospirillum lipoferum*, have shown that dicofol, which is easily hydrolyzed [73] turns persistence by becoming imbedded in the membrane [74]. In this case dicofol was found in the neutral lipids of membranes [75] where it influences the microdomain of membrane bound enzymes, as also occurs with other molecules [76]. This characterizes a non specific mode of action as seen with other molecules that interfere with different membrane bound enzymes such as ATPase [77] and nitrogenase [78].

3.3.2. Ecotoxicological effects in soil living organisms

The key message is that ecotoxicological effects are not only defined by the intrinsic chemical nature of each compound but also by the interaction of their effects properties within a given environment. Applying the concept of **"Preferential Partition"** helps us to understand conflicting reports about bioaccumulation and the ecotoxicological effects in soils. Bioaccumulation is the natural process that gradually concentrates non toxic levels of pollutants into toxic levels within a biota causing unpleasant side effects [72].

Different side effects have been described for the same pesticide by distinct authors. For example in the nitrogen cycle, some authors reported an inhibition effect of a pesticide while others reported, for the same molecule, an increasing or no effect on the ammonification, nitrification and nitrogen fixation processes. This depends mainly on the differences in the soil used and concentrations applied [79, 80, 77]. **"Preferential Partition"** explains why substances remain in the soil matrix, when they are likely to be bioaccumulated in living forms or move through the soil to pollute water resources or are suitable for biodegradation.

Non soil bound residues are an essential condition for biodegradation. Persistence occurs mainly when low numbers of or no biodegrading microorganisms are present or most commonly when despite the presence of biodegradation microorganisms, the residues are entrapped and not bioavailable.

Hazardous organic substances that are strongly adsorbed in soil organic matter pose less risk than those with low adsorbance. Sufficient soil organic matter reduces bioavailability and decreases bioaccumulation in the living biosphere but in turn results in persistence with long term pollution in soils [81, 74]. The balance between adsorbed and bioavailable molecules determines the ecotoxicity levels [2] and this is determined by the physic-chemical characteristics of the soil as well as the pollutant molecule. This balance is changed by the weathered pollutants in the soil that have a lower bioavailability than the recently applied products [1]. Therefore it is a pitfall to conclude that the hazardous effects are only caused by pesticide concentrations in the soil.

3.3.3. Plant uptake and food chain up to fauna

One of the most important sources of pollution in the food chain is soil contaminated with pesticides and other POPs mainly introduced by air deposition. Another way is the direct surface uptake mainly in leaves during application but also by plant uptake powered by plant evapotranspiration in which persistent molecules dissolved in soil water are moved from roots to shoots. From the roots the pesticides move by translocation to stems and then often a strong bioaccumulation occurs in the leaves [29, 30] or fruits. Crops where pesticides are used intensively are consumed by cattle, humans or wild life. A strong increase the of concentrations of these molecules can occur in this process called biomagnifications as described above (Figure 6).

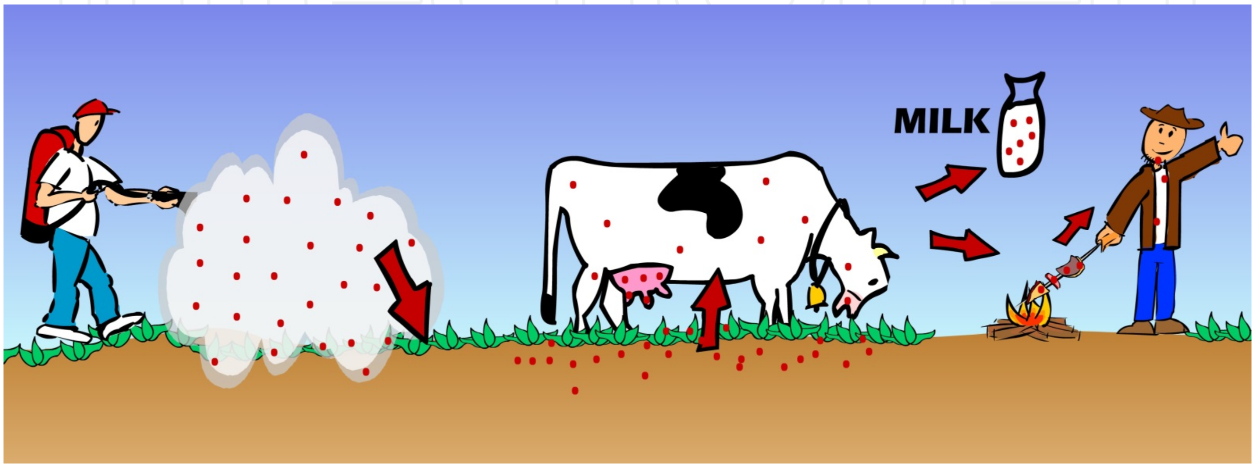

Figure 6. Human contamination with pesticide moved by food chain.

In order to minimize ecotoxicity we need to restrict the inappropriate use of pesticides and thereby remove them from the food chain and water reserves. **Preferential Partition** presents a concept - tool which is able to estimate what happens to pesticides in crop and fodder plants. In soils with high organic matter content, lipophilic and or charged pesticides are retained in the soil organic matter and the uptake into plants decreases [11, 82, 83]. The reverse occurs in low organic matter sandy soils with low cation exchange capacity CEC. Light textured sandy soils do not adsorb and retain in high amount hazardous products and will both bioaccumulate in living tissues and pollute water resources. In soils of this type, plants strongly adsorb pesticides resulting in enhanced contamination with subsequent phytotoxicity and toxicological effects on fauna [84]. This soil type would be a worst case scenario adequate to be the bench mark for pesticide registration. The pesticides that could be used under these conditions can be used generally in all soils. Registration based on strongly adsorbing soils needs to be avoided because it camouflages the eco-toxicological effects that occur when the pesticide is applied on less adsorbent soils.

3.3.4. Food chain up to fauna

The food chain sequence is where persistent molecules are first adsorbed by plants which are then consumed by animals that are in turn consumed by predatory species. In the first scenario, the animal serves as a filter with systemic eliminations and the concentration of a xenobiotic that remains present in the consumable product is much lower than the original concentration in a feed material. For meat (including adjunctive fatty tissue), this would mean that in many cases human exposure is very low or even negligible for almost all compounds. The second scenario addresses the accumulation of chemical residues in animal tissues such as liver and kidney with notorious examples including the accumulation of heavy metals, melamine and other nephrotoxins in the kidney, and dioxins and polyhalogenated persistent environmental pollutants (POPs) in the liver and fatty tissues [71]. Persistent molecules increase in each ingestion with the uptake of higher concentrations along the food chain that can result in very poisonous and hazardous concentrations for humans (Figure 6), cattle and wild life. The worst bioaccumulation seems to be salmon produced on fish farms [85].

The metabolic pathways of digestion in diverse animal species are different. Strict herbivorous species digest soluble fibers in their large caeca (the equivalent of the rumen) with the help of complex microbiological flora. This microbial fermentation may result in the release of bound (plant) toxic products which are often conjugated to sugars (glucosides) in plants and in this form are biologically inactive (or less active) [71]. The morphological and physiological characteristics of the gastro-intestinal tract in farm animal species largely determine the rate of absorption of a contaminant. The internal dose of a toxicant that reaches the post-hepatic circulation, the rate of excretion and subsequently the potential carry over and cumulative potential in tissues need to be considered. The most significant diversity in species is observed at the level of hepatic biotransformation expressed by cytochrome P450 enzymes and their polymorphisms [86]. Diversity can also be observed in all phase of enzymes such as glutathione-s-transferases, glycine conjugates, UDP-glucuronosyltransferases that are expressed in the intestinal wall and in the liver [87].

The choice of toxicity endpoints may differ between animal health and human risk assessments. Hence, clinical reports from intoxications in different animals when available may partly provide a basis for hazard characterization whereas other important endpoints maybe applied to human risk assessment as an extrapolation of the dose response from laboratory animal species to humans or using the dose response provided by human epidemiological data [88]. This is typically illustrated with genotoxicity and carcinogenicity data, which are prominent endpoints in human hazard characterization, but which are not commonly used in farm animal health risk assessment considering their relatively short lifespan [71]. The quantitative transfer of a substance from feed to an animal-derived product is commonly expressed as the carry-over rate and serves as a basis to establish maximum tolerable limits (MLs) in animal feed and animal-derived foods.

3.3.5. Chronic toxicology for animals and humans

Bioaccumulation is the natural process that gradually concentrates non toxic levels of pollutants into toxic levels within a biota causing unpleasant side effects [72, 5]. Bioaccumulation involves silent natural processes which stealthily and inevitably affect all biota. Today hazardous substances are ubiquitous, albeit mainly in low concentrations, and for the majority of us they are an unconscious part of our daily diet. The regular intake of sub toxic levels of persistent pollutants can gradually bioaccumulate up to toxic levels and after time produce chronic effects which today are recognized and understood as such.

More recently low concentrations have been shown to cause effects such as endocrine disruptors (EDs) quite different from those observed by high concentrations [89]. EDs are recognized as being partly responsible for a global reduction in male fertility [90], sexual abnormalities [91]), adrenal function disorders [92], human obesity [93] and other metabolic disturbances not to mention similar and worse effects on other living organisms [94, 95]. Recently new evidences have shown the effects of POPs (mainly pesticides) on metabolic disturbances related to obesity [96], insulin resistance promoting diabetes 2 [97] and the association of organochlorine with vitamin D deficiency [98].

The bioaccumulation of POPs by mothers, over many years, exposures the fetus to these pollutants during pregnancy [65]. Despite the difficulty of experimentation with POPs in humans, follicles could be analyzed when "induced reproduction" occurs and results have shown that contamination in the oocyte follicle can reduce human embryo quality with consequences for future generations caused by the harmful effects of these hazardous chemicals [89, 99].

Clearly, the threat to the environment and human health is reduced when pesticides are not bioavailable and cannot concentrate in the food chain. Food grown in soils where pesticides are strongly adsorbed has lower health risks.

3.3.6. Cell mortality and redistribution of persistent molecules

The presence of persistent molecules in different forms of life is temporary limited by plant senescence and/or microbial/fauna death. Two possible routes can occur; one following the food chain as described above and the other by a rotting process in which recalcitrant molecules can be released. In plants the rotting process of wood and straw [100] is a complex process in which the twisted lignin/hemicellulose/cellulose fibers follow a cascade where the first step is the "loosing" of the cell wall. This occurs by non enzymatic peroxidation (Fenton reaction) [101] that changes the lignin structure and reduces the barrier effect of the cell wall allowing the second step of enzyme diffusion of ligninase peroxidase, Mn peroxidase and laccase into areas where polysaccharides can be hydrolyzed [102]. Laccase is a phenol oxidase that has the ability to degrade many persistent xenobiotics [103, 104]. Other lignolytic enzymes could be released and are also able to biodegrade many persistent molecules [105, 106].

Nevertheless in this rotting process many recalcitrant substances are not biodegraded or only partially and therefore these molecules follow the normal distribution: adsorption in the soil, free moving molecules that can be removed by runoff, leaching, volatilization and uptake in plants, mesofauna or soil microorganisms [48, 37].

4. How to control hazardous effects of persistent molecules

The rules that enhance molecular persistence and the parameters that make the wide spread distribution of POPs possible are driven by natural factors, out of human control. Nevertheless recently remediation technology has been developed and in many cases has shown good results to remove pollutants. The approach in this text is to point out different possibilities with reference to some excellent reviews. The technology used was based on physical, chemical and biological methods.

The first step of POP remediation is to promote desorption [107]. Physical methods need to remove the pollutants from soils or water in order to destroy the molecules completely by burning [107]. This has a high cost as the incinerator plant needs filter systems to eliminate other pollutants such as dioxins. Physical methods such as electro kinetic (EK) remediation technology use a low-level direct current as the ''cleaning agent'', inducing several transport mechanisms (electro-osmosis, electro-migration and electro-phoresis) and electrochemical reactions (electrolysis and electrodeposition). This technology has already proven its value, especially in contaminated fine-grain soils [108].

Ozon can be used for chemical remediation of pollutants and there are other methods currently being researched [109]. Chemical degradation reactions in the environment depend on water content, pH, temperature and oxygen reduction potential. These conditions are normally not optimum in nature and therefore degradation is frequently low. Physical and chemical remediations are powerful technologies to remediate small areas that have been polluted by industry or transport accidents. For large areas these process are generally considered too expensive.

Biological degradation processes are promoted by living organisms such as animals, plants but mainly microorganisms. The advantages of microbes are the ubiquitous distribution in normal and extreme environments, fast biomass growth, easy manipulation and high diversity of catabolic enzymes. Bioremediation using microorganisms compared to the other methodologies can be used in polluted soils and waters and is less expensive than all other methods. Nevertheless the high costs are limitations for large polluted agricultural areas. One of the most powerful approaches is phytoremediation as some plants have a strong capacity to extract pollutants from the soil and incorporate these molecules into their own biomass [29, 30]. Nevertheless in phytoremediation of hydrocarbon pollutants (HCs) the accumulation between roots and shoots is quite low compared to plant-promoted biodegradation in the rhizosphere [110]. Root exudation stimulates microorganisms in the rhizosphere resulting in enhanced mineralization [111].

Today efforts are being made to identify the most adequate alternative remediation in a framework of possibilities considering parameters that characterize cost-risk tradeoffs and uncertainty impacts [112].

5. Conclusions

Two points related to persistent molecules need to be emphasized. The first is the limits of biodegradation of persistent molecules as reported here in which the best microorganism to degrade a given molecule can not be efficient if the molecule is entrapped in the soil. The second point is that there is no technology available to clean the environment considering the large dispersion of persistent substances.

The relationship between molecular characteristics and environmental conditions that determine persistence as described here can be helpful to understand what happens to other polluting molecules like non biodegradable plastic materials, bioactive products discharged by sewage treatment plants and nano-molecules. Many of these molecules get into the environment on a global scale and in fact this is due to a lack of regulatory rules such as those used for the registration process of pesticides. Little is known about what happens to many of these new molecules in the environment.

As shown here, to clean the environment of persistent products that were applied over large areas has limited possibilities. Prevention by only using biodegradable products is the best approach. However, the solution for the sustainable use of chemicals in the environment is to ban persistent molecules and substitute them for others with a high biodegradation capacity and less non-target effects.

Acknowledgements

The author thanks Prof. Andrew Macrae for his valuable contributions to the text. Financial support was provided by PRONEX – FAPERJ/CNPq and fellowship CNPq.

Author details

Tomaz Langenbach*

Address all correspondence to: tomazlange@yahoo.com.br

Department of Civil Engineering, PUC – Rio, Rio de Janeiro, Brazil

References

[1] Pignatello J.J., Frin, R., Mari, P.A. Drost, E.X. Field-observed ethylene dibromide in an aquifer after two decades. Journal of Contaminat Hydrology 1990;5 195-214.

[2] Vasseur P., Bonnard M., Palais F., Eom I. C., Morel J. L. Bioavailability of Chemical Pollutants in Contaminated Soils and Pitfalls of Chemical Analyses in Hazard Assessment. Environmental Toxicology 2008;23 652-656.

[3] Wang X., Guo X., Yang Y., Tao S., Xing B. Sorption mechanisms of phenanthrene, lindane, and atrazine with various humic acid fractions from a single soil sample. Environ Sci Technol. 2011;45(6) 2124-2130.

[4] Dörfler U., Scheunert I., Viswanathan R., Zsolnay A. Physikalisch- Chemisches Verhalten von s-Triazinen im Boden. In: Dörfler U., Scheunert I., Viswanathan R., Zsol-

nay A. (eds.) Standortgerechte Bewertung von s-Triazinen in Böden. GSF: Bericht 22/97; 1997 p99-123.

[5] Connell D.W. General Characteristics of Organic Compounds which Exhibit Bioaccumulation. In: Connell, D.W. (ed.) Bioaccumulation of xenobiontic Compounds. CRC Press; 1990. p47-57.

[6] Saarikoski J., Viluksela M. Relations between physichochemical properties of phenols and their toxicity and accumulation in fish. Ecotoxicology Environmental Safety 1983;6 501.

[7] Randall R.C., Lee I., Ozretich R.J., Lake J.L., Pruel RJ. Evaluation of selected lipid methods for normalizing pollutant bioaccumulation. Environmental Toxicology Chemistry 1991;19 1431-1436.

[8] Matscheko N., Tysklind M., De Wit C., Bergek S., Anderson R., Sellström U. Application of sewage sludge to arable land-soil concentrations of polybrominated diphenyl ether and polychlorinated dibenzo-o-dioxin, dibenzofurans, and biphenyls and their accumulation in earthworms. Environmental Toxicology Chemistry 2002;21 2515-2525.

[9] Cornelissen G., Gustavson O., Bucheli T.D., Jonker M.T.O., Koelmans A.A. Van Noort P.C.M. Extensive sorption of organic compounds to black carbon, coal, and Kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. Environmental Science and Technology 2005;39 6881-6895.

[10] Brunninger B.M., Mano D.M.S., Scheunert I. Langenbach T. Mobility of the Organochlorine Compound Dicofol in Soil Promoted by Pseudomonas fluorescens. Ecotoxicology and Environmental Safety 1999;44 154-159.

[11] Scheunert I. Aufnahme von s-triazinen in Planzen. In Dörfler U., Scheunert I., Viswanathan R., Zsolnay A. (eds.) Standortgerechte Bewertung von s-triazinen in Böden. GSF: Bericht; 1997(222) p173-183.

[12] Steen W.C., Karickhoff S.W. Biosorption of hydrophobic organic pollutants by mixed microbial populations. Chemosphere 1981;10 27-32.

[13] Karickoff S.W. Semi-empirical estimation of sorption of hydrophobic pollutants on a natural sediments and soils. Chemosphere 1981;10 833-846.

[14] Papini S., Andrea M.M. Ação de minhocas Eisinia foetida sobre a dissipação dos herbicidas simazina e paraquat aplicados no solo. Revista Brasileira de Ciências dos Solos 2004;28 67-73.

[15] Dörfler U. Anwendung, Eigenshaften und Wirkungen der s-Triazinen. In: Dörfler U., Scheunert I., Viswanathan R., Zsolnay A. (eds.) Standortgerechte Bewertung von s-triazinen in Böden. GSF: Bericht 22/97; 1997 p2-19.

[16] Perkow W. Wirksubstanzen der Pflanzenschutz und Schädlings-bekämpfungsmittel 2. In: Perkow (ed.) Verlag Paul Parey. 2 Auflage; 1988.

[17] Langenbach T., Inácio M.V.S., Aquino A.M., Brunninger B. Influência da minhoca Pontoscolex corethrurus na distribuição do acaricida dicofol em um Argissolo. Pesquisa Agropecuária Brasileira 2002; 37 1663-1668.

[18] Baker J.R., Mihelcic J.R., Shea, E. Estimating K_{oc} for persistent organic pollutants: limitations of correlations with K_{oc}. Chemosphere 2000;41 813-817.

[19] Andréa M.M., Papini S. Influence of soil properties on bioaccumulation of ^{14}C-simazine in earthworms Eisenia foetida. Journal of Environmental Science and Health Part B 2005;40 55-58

[20] Papini S., Langenbach T., Luchini L.C., Andréa M.M. Influence of substrate on bioaccumulation of ^{14}C-paraquat in compost earthworms Eisenia foetida. Journal of Environmental Science and Health 2006; 41(B) 523-530.

[21] Kelsey J. W., Slizovskiy I. B., Petriello M. C., Butler K. L. Influence of plant–earthworm interactions on SOM chemistry and p,p0-DDE bioaccumulation. Chemosphere 2011;83 897–902.

[22] Mangrich A.S., Lobo M.A., Tank C.B., Wypch F., Toledo E.B.S., Guimarães E. Criterious preparation and characterization of earthworms-compost in view of animal waste recycling. Part 1. Correlation between chemical, thermal and FTIR spectroscopic analysis of four humic acids from earthworm-composted animal manure. Journal of Brazilian Chemistry Society 2000;11 164-169.

[23] White J.C., Parrish D., Isleyen M., Gent M.P., Ianucci-Berger W., Eitzer B.D., Mattina M. I. Influence of nutrient amendments on the phytoextraction of weathered 2, 2-Bis(p-chlorophenyl)-1,1-dichloroethylene by cucurbits. Environmental Toxicology and Chemistry 2005;24 987–994.

[24] Mattina M. I., White J. C., Eitzer B. D., Iannucci-Berger W. Cycling of weathered chlordane residues in the environment: Compositional and chiral profiles in contiguous soil, vegetation, and air compartments. Environmental Toxicology and Chemistry 2002;21 281–288.

[25] Mattina M. I., Eitzer B. D., Iannucci-Berger W., Lee W. Y., White J. C. Plant uptake and translocation of higly wethered, soil-bound technical Chlordane residues: data from field and rhizotron studies. Environmental Toxicology and Chemistry 2004;23 2756-2762.

[26] Fries G. F. Transport of organic environmental contaminants to animal products. In: Ware G. W. (ed.). Reviews of environmental contamination and toxicology. Springer Verlag 1995; 41 p71-109.

[27] Schnoor J. L., Licht L. A., McCutcheon S.C., Wolfe N.L., Carreira L. H. Phytoremediation of organic and Nutrient contaminants. Environmental Science and Technology 1995;29 318-323.

[28] Schroll R., Bierling B., Cao G., Dörfler U., Lahaniati M., Langenbach T., Scheunert I., Winkler. Uptake pathways of organic chemicals from soil by agricultural plants. Chemosphere 1994;28 297-303.

[29] Marinho D.A., Bicalho S.T., Ferreira E.M., Langenbach T. Distribution and Mineralization of 14C-Hexazinone in Soil-Plant Microcosm with the Riparian Forest Specie Cecropia Hololeuca. Special Issue Article J Bioremed Biodegrad 2011; S1-002

[30] Bicalho S.T.T., Langenbach T. Distribution of the herbicide atrazine in a microcosm with riparian forest plants. Journal of Environmntal Science and Health Part. B 2012;47(6) 505-511.

[31] Jiang L., Ma L., Sui Y., Han S. Q., Wu Z. Y., Feng Y. X., Yang H. Effect of manure compost on the herbicide prometryne bioavailability to wheat plants. Journal of Hazardous Materials 2010;184 337-344.

[32] Celis R., Barriuso E., Houot S. Sorption and desorption of atrazine by sludge-amended soil: dissolved organic matter effects. Journal of Environmental Quality 1998;27 1348-1356.

[33] Sellström U., De Witt C. A., Lundgren N., Tysklind M. Effect of sewage –sludge applications on concentrations of higher-brominated diphenyl ethers in soils and earthworms. Environmental Science and Technology 2005;39 9064-9070.

[34] Langenbach T., Correia F.V., Macrae A., Vargas E.A., Campos T.M.P. Atrazine leaching through surface and subsurface of a tropical Oxisol. Journal of Environment Science and Health 2008;(B) 43 214-218.

[35] Rytwo G., Nir S., Margulies L.. A Model for Adsorption of Divalent organic Cations to Montmorillonite. Journal of Colloidal and Interface Science 1996;181 551-560.

[36] Weber J., Halsall C.J., Muir D., Teixeira C., Small J., Solomon K., Hermanson M., Hung H., Bidleman T. Endosulfan, a global pesticide: a review of its fate in the environment and occurrence in the Arctic. Sci Total Environ. 2010;408(15) 2966-84.

[37] Langenbach R., Schroll I., Sheunert. Fate of herbicide 14C-terbuthylazine in Braxzilian soils under various climatic conditions. Chemosphere 2001; 45 387-398

[38] Kookana R., Holz G., Barnes C., Bubb K., Fremlin R., Boardman B. Impact of climatic and soil conditions on environmental fate of atrazine used under plantation forestry in Australia. J Environ Manage Dec 2010;91(12) 2649-56

[39] Cañero A.I., Becerra D., Cornejo J., Hermosín M., Albarrán A., Piñeiro A., Cox, L. Transformation of organic wastes in soil: Effect on bentazone behavior. Science of the Total Environment 2012; 433 198–205

[40] Östereicher-Cunha, P., Langenbach, T., Torres, J.P., Lima, A.L.C., Campos, T.M.P., Vargas E.A.Jr. and Wagener, A.R.. HCH distribution and microbial parameters after liming of a heavily contaminated soil in Rio de Janeiro. Environment. Res 2003;93 316-327.

[41] Dvorská M. Šír, Honzajková Z., Komprda J., Čupr P., Petrlík J., Anakhasyan E., L. Simonyan, Kubal M. Obsolete pesticide storage sites and their POP release into the environment—an Armenian case study. Environ Sci Pollut Res. 2012;19 1944–1952.

[42] Jørgensen L.F., Kjær J. a, Olsen P. b, Rosenbom A. Leaching of azoxystrobin and its degradation product R234886 from Danish agricultural field sites. Chemosphere 2012;88 554–562.

[43] Correia F.V., Langenbach T., Campos T.M. Avaliação do transporte de atrazina em solos sob diferentes condições de manejo agrícola. R. Bras. Ci. Solo 2010;34 525-534.

[44] Vryzas Z., Papadakis E. K., Papadopoulou-Mourkidou E. Leaching of BrL, metolachlor, alachlor, atrazine, deethylatrazine and deisopropylatrazine in clayey vadoze zone: A field scale experiment in north-east Greece. Water Res. 2012;46 1979-1989.

[45] Reichenberger S.; Amelung W.; Laabs V.; Pinto A.; Totsche K.U.; Zech W. Pesticide displacement along preferential flow pathways in a Brazilian Oxisol. Geoderma 2002;110 63-86.

[46] Winter, T. C., Harvey, J.W., Franke O.L.Alley W.M... Ground Water and Surface Water. A Single Resource. U.S. Geological Survey. 1998 Circular 1139. Ed. U.S. Governmment Printing Office.

[47] Belamie R., Gouy V. Introduction des pollutants dans le milieu fluvial. Influence du ruissellement des sols. Oceanis 1992;18 505-521.

[48] Carluer N.; Gouy V.E., Grill J.N. Contamination des eaux de surface par dês produits phyosanitaires et modelisation. Ingenieries-EAT 1996;6 19-30.

[49] Correia F.V., Macrae A., Guilherme L.R.G., Langenbach, T. Atrazine sorption and fate in a Ultisol from humic tropical Brazil. Chemosphere. 2007; 67 847-854.

[50] Sangchan W., Hugenschmidt C., Ingwersen J., Schwadorf K., Thavornyutikarn P., Pansombat K., Streck T. Short-term dynamics of pesticide concentrations and loads in a river of an agricultural watershed in the outer tropics. Agriculture, Ecosystems and Environment 2012;158 1– 14.

[51] Fenet H., Mathieu O., Mahjoub O., Zhi L., Buys D., Casellas C., Gomez E. Carbamazepine, carbamazepine epoxide and hydroxycarbamazepine sorption to soil and occurrence in a wastewater reuse site in Tunisia. Chemosphere 2012;88 49–54.

[52] Rudel H. Volatilization of pesticides from soil and plant surfaces. Chemosphere 1997;35 143–152.

[53] Ganzelmeier H., Rautmann D., Spangenberg R., Streloke M., Herrmann M., Wenzelburger H.J. Studies on the spray drift of plant protection products. Mitteilungen aus

der Biologischen Bundesanstalt fur Land-und Forstwirtschaft. Berlin-Dahlem: Heft; 1995; 305 111.

[54] Arvidsson T. Spray drift as influenced by meteorological and technical factors. A methodological study. Swedish University of Agricultural. Sciences, Acta Universitatis.Agriculturae Sueciae; 1997. 71. 144.

[55] Willis G., Mcdowell L., Harper L., Southwick L., Smith S. Seasonal disappearance and volatilization of toxaphene and DDT from a cotton field. J. Environ. Qual. 1983;12 80–85.

[56] Lohmann R., Breivik K., Dachs J., Muir D. Global fate of POPs: Current and future research directions. Environ. Pollut. 2007;150(1) 150-165.

[57] Taylor A. Post-application volatilization of pesticides under field conditions. J. Air Pollut. Con. Ass. 1978;28 922–927.

[58] Jasma J., Linders J. Volatilization of pesticides from soil and plants after spraying, Report no. 679102030. National Institute of Public Health and Environmental Protection Bilthoven: The Netherlands; 1995.

[59] Lyman W.J., Reehl W.F., Rosenblatt D.H. Handbook of Chemical Property Estimation Methods. American Chemical Society: Washington, DC. 1990.

[60] Mast MA, Foreman WT, Skaates SV. Current-use pesticides and organochlorine compounds in precipitation and lake sediment from two high-elevation national parks in the Western United States. Arch Environ Contam Toxicol. 2007;52 294-305.

[61] Darnerud, P.O., Eriksen, G.S., Jóhannesson, T., Larsen, P.B., Viluksela, M. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. Environmental Health Perspectives 2001;109 49-68.

[62] Tseng, L.H., Li, M.H., Tsai, S.S., Lee, C.W., Pan, M.H., Yao, W.J., Hsu, P.C. Developmental exposure to decabromodiphenyl ether (PBDE 209): effects on thyroid hormone and hepatic enzyme activity in male mouse offspring. Chemosphere 2008;70 640-647.

[63] Meeker J.D., Johnson P.I., Camann D., Hauser R. Polybrominated diphenylether (PBDE) concentrations in house dust are related to hormone levels in men. Science of the Total Environment 2009;407 3425-3429.

[64] Caserta D., Mantovani A., Marci R., Fazi A., Ciardo F., La Rocca C., Maranghi F., Moscarini M. Environment and women's reproductive health. Human Reproduction Update, 2011;17 418–433.

[65] McDonald, T.A. A perspective on the potential health risks of PBDEs. Chemosphere 2002;46 745e755.

[66] Besis A., Samara C. Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments and a review on occurrence and human exposure. Env. Pol. 2012;169 217-229.

[67] Li L., Xie S., Cai H., Bai X., Xue Z. Quantitative structure property relationships for octanol water partition coefficients of polybrominated diphenyl ethers. Chemosphere 2008;72 1602-1606.

[68] Beyer W.N., Heinz G.H. Redmon-Nordwood, editor. Environmental Contaminants in Wildlife. In CRC Lewis Publisher; 1996.

[69] Wang Y.W., Jiang G.B., Lam P.K.S., Li A. Polybrominated diphenyl ether in the East Asian environment: a critical review. Environment International 2007;33 963-973.

[70] Ikonomou M.G., Rayne S., Addison R.F. Exponential increases of brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. Environ. Sc. and Technology 2002;36 1886-1892.

[71] Dorne J.L.C.M., Fink-Gremmels J. Human and animal health risk assessments of chemicals in the food chain: Comparative aspects and future perspectives. Toxicology and Applied Pharmacology (in press) 2012.

[72] Langenbach T. Bioaccumulation. In: Pimentel D. (ed.). Encyclopedia of Pest Management. Marcel Dekker Inc.; 2002. p50-53.

[73] Walsh P.R., Hites R.A. Dicofol solubility and hydrolysis in water. Bull. Environ. Contam. Toxicol. 1979;22 305-315.

[74] Mano D.M.S., Buff K., Clausen E., Langenbach T. Bioaccumulation and enhanced persistence of the acaricide dicofol by azospirillum lipoferum. Chemosphere 1996;33 1609-1619.

[75] Mano D.M.S., Langenbach T. [14C]dicofol Association to cellular components of Azospirillum lipoferum. Pest. Sci. 1998;53 91-95.

[76] Buff K. & Bernd J. Interaction of DDT (1,1,1-trichloro2,2-bisp-chlorophenyl)-ethane) with liposomnal lipids. Bioch. Biop. Actga (BBA) 1980;643 205-12.

[77] Lal R., Shivaji S. Effects of pesticides on asymbiotic nitrogen fixation. In: Lal R., Lal S. (eds). Pesticide and Nitrogen Cycle III. CRC Press; 1988. p1-46.

[78] Subramanian G. The effect of pesticides on nitrogen fixation and ammonia excretion bu Anabaena. In: national symposium biology of nitrogen fixation. Iari. New Delhi: 1982. p567.

[79] Rao V.V.S.N. Effects of pesticides on ammonification. In: Lal R., Lal S. (eds.) Pesticide and Nitrogen Cycle II. CRC Press; 1988. p1-41.

[80] Dhanaraj P.S. Effects of pesticides on nitrification and denitrification. In: Lal R., Lal S. (eds). Pesticide and Nitrogen Cycle II. CRC Press. 1988; p43-118.

[81] Afferden M.V., Beyer M., Klein J. Significance of bioavailability for the microbial remediation of PAH-contaminated soils. Preprints. International Symposium Soil Decontamination Using Biological Processes 1992 605-610.

[82] Bell R.M., Sferra P.R., Ryan J.R., Vitello, M.P. Studies of organic Pollutant uptake by plants. In: Wolf W., Van den Brink J., Colon F.J. (Eds.) Contaminated soil ’88. K. Kluwer Academic Publisher; 1988 1. p451-458.

[83] Trapp S., Mathies M., Scheunert I., Topp E. M. Modelling the bioconcentration of organic chemicals in plants. Environmental Science and Technology 1990;24 1246-1252.

[84] Covaci F. V., D’Havé A., Van den Brink H., Blust N. W., De Coen R. W., Bervoets L. Accumulation of background levels of persistent organochlorine and organobromine pollutants through the earthworm-hedgehog food chain. Environment International 2010;36, 721-727.

[85] EFSA (European Food Safety Authority). Opinion of the Scientific Committee on arequest from EFSA related to a harmonised approach for risk assessment ofsubstances which are both genotoxic and carcinogenic. The EFSA Journal 2005; 282(a) 1–31. (http://www.efsa.europa.eu/EFSA/Scientific_Opinion/sc_op_ej282_gentox_en3.pdf).

[86] Fink-Gremmels J. Implications of hepatic cytochrome P450-related biotransformation processes in veterinary sciences. Eur. J. Pharmacol 2008;585 502–509.

[87] Walton K., Dorne J.L., Renwick A.G., Uncertainty factors for chemical risk assessment: interspecies differences in glucuronidation. Food Chem. Toxicol. 2001;39 1175–1190.

[88] Schlatter J. Toxicity data relevant for hazard characterization. Toxicol. Lett. 2004;153 83–89.

[89] Petro Evi M.L., Leroy, J. L.M.R., Covaci, A., Fransen, E., Neubourg, D., Dirtu, A. C., Pauw, I. and Bols, P.E.J. Endocrine-disrupting chemicals in human follicular fluid impair in vitro oocyte developmental competence. Human Reproduction 1988;27 1025-1033.

[90] Saradha B., Mathur P.P. Effect of environmental contaminants on male reproduction. Enviromental Toxicology and Pharmacology 2006;21, 34-41.

[91] Whitehead S.A., Rice S. Endocrine-disrupting chemicals as modulators of sex steroid synthesis. Best Practice and Research: Clinical Endocrinology and Metabolism 2006; 20 45-61.

[92] Hinson J.P., Raven P.W. Effects of endocrine-disrupting chemicals on adrenal function. Best Practice and Research Clinical Endocrinology and Metabolism 2006; 20 111-120.

[93] Baillie-Hamilton P.M.B. Chemical Toxins: A hypothesis to explain the global Obesity. The J. Alternative and Complementary Medicine. 2002;82 185-192.

[94] Elango A., Shepeherd B., Chen T.C. Effects of endocrine disrupters on the expression of growth hormone and prolactin mRNA in the rainbow trout pituitary. General and Comparative Endocrinology 2006;145 116-127.

[95] 95] Walker A. N., Bush P., Puritz J., Wilson T., Chang E.S., Miller T., Holloway K., Horst M.N. Bioaccumulation and metabolic effects of the endocrine disruptor methoprene in the Lobster, Homarus americanus. Integrative and Comparative Biology 2005;45 118–126.

[96] Arsenescu V., Arsenescu R.I., King V., Swanson H., Cassis L.A. Polychlorinated biphenyl-77 induces adipocyte differentiation and proinflammatory adipokines and promotes obesity and therosclerosis. Environ. Health Perspect. 2008;116 761–768.

[97] Ruzzin J. Public health concern behind the exposure to persistent organic pollutants and the risk of metabolic diseases. Public Health 2012;12 298-306.

[98] Yang J.H., Lee Y.M., Bae S.G., Jacobs D.R. Jr., Lee D.H. Associations between Organochlorine Pesticides and Vitamin D Deficiency in the U.S. Population. Plos ONE 2012;7 30093

[99] Anway M.D., Cupp A.S., Uzumcu M., Skinner M.K. Epigenetic transgenerational actions of endocrine disruptors and mate fertility. Science 2005;308 1466–1469.

[100] Gutierrez A., Reconret, Cadena E. M., Rico A., Barth D., Río J. C., Martínez A.T. Demonstration of laccase-based removal of lignin from wood and non-wood; plant feedstocks. Bioresource Technology 2012;119 114–122.

[101] Hammel K.E., Kapich A.N., Jensen K.A. Jr., Ryan Z.C. Reactive oxygen species as agents of wood decay by fungi. Enzyme Microb Technol 2002;30 445–453.

[102] Arantes V., Jellison J., B. Goodell. MINI-REVIEW. Peculiarities of brown-rot fungi and biochemical Fenton reaction with regard to their potential as a model for bioprocessing biomass. Appl Microbiol Biotechnol 2012; 94:323–338.

[103] Thurston C.F.The structure and function of fungal laccases. Microbiology 1994;140 19–26.

[104] Baldrian P. Wood-inhabiting ligninolytic basidiomycetes in soils: ecology and constraints for applicability in bioremediation. Fungal Ecol 2008;1 4–12.

[105] Austin S.D., Benson J.T. The fungus among us: use of white rot fungus to biodegrade environmental pollutants. Environmental health perspectives 1993;101 232-233.

[106] Sinsabaugh R.L. Phenol oxidase, peroxidase and organic matter dynamics of soil. Soil Biol. Biochem. 2010;42 391–404.

[107] Tong M., Yuan S. Physiochemical technologies for HCB remediation and disposal: A review. J. of Hazardous Materials 2012;229–230 1– 14.

[108] Gomes H. I., Dias-Ferreira C., Ribeiro A. B. Review Electrokinetic remediation of organochlorines in soil: Enhancement techniques and integration with other remediation technologies. Chemosphere 2012;87 1077-1090.

[109] Ma J.W., Wang F.Y., Huang Z.H., Wang H. Simultaneous removal of 2,4- dichlorophenol and Cd from soils by electrokinetic remediation combined with activated bamboo charcoal. J. Hazard. Mater. 2010;176 715–720.

[110] Khan S., Afzal M., Iqbal S., Khan Q. M. Review: Plant–bacteria partnerships for the remediation of hydrocarbon contaminated soils. Chemosphere 2012; in press.

[111] Martínez Bueno M.J., Gomez, M.J, Herrera, S., Hernando, M.D., Agüera, A., Fernández-Alba, A.R. Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. Env. Pol. 2012;164 267-273.

[112] Yang A.L., Huang G.H., Qin X.S., Fan Y.R. Evaluation of remedial options for a benzene-contaminated site through a simulation-based fuzzy-MCDA approach. J. Hazardous Material 2012;213-214 421-433.

IntechOpen