CHAPTER 4

Impacts of Agricultural Pesticides on Terrestrial Ecosystems

Francisco Sánchez-Bayo^{*}

Centre for Ecotoxicology, University of Technology Sydney, Australia

Abstract: Pesticides are toxic chemicals used to control pests, weeds and pathogens. Three quarters of all pesticides are employed in agricultural production, particularly in developed countries, in an effort to mitigate crop damage endured by intensive agriculture. However, after more than 60 years of worldwide usage, their side-effects on terrestrial ecosystems - even when applied as recommended - are obvious. This chapter examines the ecological problems caused by specific chemicals/groups, so that this awareness may help improve agricultural practices through appropriate risk management. Fungicides alter the microbial-fungi communities responsible for the recycling of nutrients in the soil, and copper fungicides are toxic to earthworms and other animals. The routine application of herbicides has produced a net loss of plant biomass and biodiversity in many landscapes, which indirectly reduces the associated arthropod communities and leads to population declines in many species of birds, and possibly amphibians too, due to lack of food. Insecticides are very toxic to most invertebrates in the soil, birds and small mammals, causing significant reductions in their populations and disturbing the trophic structure of their communities. Persistent pesticides accumulate in soil and concentrate through the trophic chain, causing a plethora of sublethal effects which are negative for the survival of individuals as well as the viability of their populations; the long term effects of DDT and cyclodiene poisoning in birds is still an ecological issue despite more than 30 years of not being applied in most developed countries. While pesticides have increased our agricultural productivity and helped feed the current human population, the price of this productivity is being paid by the Earth's ecosystems at large.

INTRODUCTION

Since Neolithic times, humanity has learnt to use agriculture to supply the food needed for its own sustenance. Agricultural practices first started with cereal crops in the Fertile Crescent about 11,000 years ago, and subsequently developed in other regions of the world, although a rather small suite of 35 domesticated plants and seven animals ended up established over the world because of their yield and nutrient characteristics [1]. For centuries, most of the staple plant foods have been cultivated as monocultures: unusual ecosystems in which no diversity of plants other than the crop is allowed to grow on the same land in order to maximize crop yields, and where all means possible are used to ensure this is the case; the unwanted, competing plants are called weeds. Because of this feature, monocultures are ideal targets for specialized consumer animals (usually insects, birds and rodents) that feed on them. Once such animals find a crop that suits them, they multiply explosively and become pests. With the exception, perhaps, of locust plagues all other agricultural pests are a product of monocultures, and from early times humanity has struggled to keep at bay the pest species that decimated our crops.

As with agriculture, the story of pesticides – the substances used to control and kill pests – started in the Middle East. The Persians found that the extract of certain chrysanthemum flowers (known as pyrethrum) was very effective in killing flies and other insects, so they used it to control agricultural pests [2]. Late in the 18th century, Erasmus Darwin found nicotine (the extract of Nicotiana tabacum) to be a powerful insecticide, and early in the 1900s arsenic salts were also used to control a wide range of pests, particularly in orchards. However, it wasn't until the 1940s that a revolution in pesticides took place, when the chemical industry started to mass-produce synthetic toxic substances that were effective, not only in killing insects (insecticides) and other animal pests (rodenticides), but also weeds (herbicides) and fungal diseases (fungicides). The rapid development that ensued, especially in North America, Europe and Asia-Pacific, led to the establishment of a new kind of agriculture based on chemistry. The so-called Green Revolution involves the use of chemical pesticides and fertilizers together with increased irrigation and genetic improvement for agricultural production. Hailed as the saviour of human starvation, the Green Revolution practices were quickly adopted worldwide, particularly in densely populated countries of South East Asia such as Indonesia and the Philippines, where food shortages were soon replaced by bumper crop yields [3]. Indeed, the use of pesticides in agricultural production became so widespread that the term 'conventional agriculture' indicates a cropping system where the Green Revolution tools are applied routinely.

Francisco Sánchez-Bayo, Paul J. van den Brink and Reinier M. Mann (Eds) All rights reserved - © 2011 Bentham Science Publishers Ltd.

^{*}Address correspondence to Francisco Sánchez-Bayo: Centre for Ecotoxicology, University of Technology Sydney, NSW 2007, Australia; Department of Environment, Climate Change & Water NSW, 480 Weeroona Road, Lidcombe NSW 2141, Australia; Email: sanchezbayo@mac.com

While the Green Revolution was producing 'miracles' everywhere, the newly developed pesticides applied to an increasing variety of crops started to have side effects in the surrounding natural ecosystems. Bioaccumulation of DDT and cyclodiene insecticides was first noticed in bird predators like the peregrine falcon (*Falco peregrinus*) despite the fact they had little relation to the sprayed crops [4]. Through a long and painstaking research that involved many experts in the areas of environmental chemistry, toxicology and agriculture [5], it was eventually revealed how these chemicals had secondary and indirect effects on non-target organisms, and their impacts on the structure and functionality of natural ecosystems rang the alarm in environmental circles. Even the direct effects of insecticides on arthropod communities, and the birdlife that depended on them, was brought into question by Rachel Carson as early as 1962. The birth of the environmental movement and ecotoxicology was thus linked from its very beginnings to the widespread use of synthetic pesticides in agriculture, forestry, and urban pest control. It was realised that all pesticides are toxic to a greater or lesser degree, so their release could not be without risks to some kind or other of organisms.

Pesticides are the only man-made contaminants released into the environment deliberately, for a purpose; whereas industrial chemicals, mining wastes, pharmaceutical residues and the large list of pollutants that humanity produces find their way into the air, rivers and oceans either unintentionally or because our technology is still unable to reduce their emissions, avoid accidents, and too inefficient to recycle the wastes.

PESTICIDES IN AGRICULTURE

There are currently 835 chemical compounds used in all sorts of agricultural enterprises [6], comprising some 1300 registered products, of which 31% are herbicides, 21% insecticides, 17% fungicides, 9% acaricides and 2% rodenticides; the remaining 20% of products include a plethora of biocides for control of snails (molluscicides), algae (algicides) and nematodes (nematicides) as well as plant growth regulators (6%) and natural or artificial pheromones (5%). In addition, 610 products, including most of the infamous organochlorine (OC) insecticides, were used in the past but not nowadays – they were banned for safety and environmental reasons or because they were no longer efficient (due to resistance) and have been replaced by newer products. Despite using so many chemicals, world crop losses are estimated at 37% of agricultural productivity: 13% due to insects, 12% to weeds and 12% to diseases [7].

The toxicity and specificity of pesticides depends on the mode of action of the active ingredients (a.i.), while the effects on organisms depend on the dose they are exposed to (see Chapter 1). Thus, organochlorine, cholinesterase inhibitors (organophosphorus (OP) and carbamates), synthetic pyrethroid and neonicotinoid insecticides are neurotoxic substances that disrupt the nervous system of arthropods and other animals. Given the similarities in neuronal physiology among all kinds of animals, it is not surprising that insecticides are also toxic to aquatic and terrestrial arthropods and, to a lesser extent, vertebrates, whereas they are harmless to plants and the majority of microbial organisms. Other insecticides affect cellular or physiological mechanisms of animals (e.g. chlorfenapyr, arsenic salts). Herbicides are very toxic to plants and algae, as they target physiological pathways specific to plants such as the photosynthesis; however, herbicides can interfere with metabolic and reproductive processes in animals as well, often in ways that are unrelated to their specific mode of action in plants. Fungicides are considered in some countries to be medicine for the crops as they control fungal infections of the roots or other parts of the plant; many of them are antibiotics or metabolic inhibitors of certain fungi, while organomercurial compounds are neurotoxic and poisonous to many animals. Rodenticide poisons are usually anticoagulants, and consequently are very dangerous to humans and all vertebrates alike. Thus, the specificity of action of pesticides is not restricted to the target pest or weed species, but it is rather general, affecting large taxonomic groups often at the order or class level, even though within the same class of organisms some species are more susceptible than others due to differences in body size and/or physiological traits [8].

Pesticide Usage

Global pesticide usage is estimated at 4 million tons per year [9], although its distribution throughout the world is very uneven [10], with Europe using one third and North America a quarter of the total market until recently (Table 1). Herbicides account for nearly half of the pesticides used in North America, insecticides 19%, fungicides 13%, with the remaining 22% including a variety of other products [11], whereas insecticides are prevalent in developing countries. Agricultural industries, i.e. crops and livestock, are the main users of pesticides in the USA and other countries (74% of

Impacts of Agricultural Pesticides on Terrestrial Ecosystems

the annual consumption), with gardening, golf courses, industry and urban uses making up 25% of the total amount whilst only 1% is being used in forestry [7], mainly in Canada and Scandinavian countries. DDT and lindane are still used in countries like India [12]; by necessity most of the DDT is to control mosquito-vectors of malaria and tse-tse fly in tropical countries and South Africa, where no other cost-effective chemicals are available. The distribution of pesticide types among crops differs widely: corn, soybean and cotton crops are the main users of herbicides in the USA (75%); orchards use mainly insecticides, while vineyards and vegetables use most of the fungicides [7].

Table 1: Annual pesticide usage in the world up to 1996. Source: [10]

	Millions of kg	% Total
Europe	800	32
Asia-Pacific	800	32
North America*	600	24
South America	200	8
Africa	100	4
Total	2500	100

* USA and Canada only

Average pesticide application in developed countries is 4.4 kg/ha per year. Since almost one fifth of the Earth's land area is dedicated to agriculture (12% as cropland and 6-8% as pastureland [13]), the impact of agrochemicals on ecosystems is quite significant at a global scale. However, not all agricultural land is treated with pesticides: in the USA, for instance, some 38% of the acreage is not treated with chemicals [7].

Application of Pesticides

Agricultural pesticides are typically applied directly on to the crop plants or fruit trees by spraying them in a liquid carrier (oil or water mixed with surfactants) that can be delivered by plane, helicopter, ground machinery or simply by hand-operated sprayer-guns. Some pesticides are applied as granules buried in the soil, or as seed-dressings to protect the growing seedlings.

The method of application greatly determines the exposure of non-target organisms to pesticides. For instance, 25-50% of the pesticide sprayed from aircraft reaches the crop, or 65-90% if sprayed with ground machinery [14]; the remainder is scattered around the target crop/orchard, with the spray droplets reaching distances up to 1.5 km under established conditions for application, *i.e.* low flying path, wind speeds between 3 and 15 km/h and no air inversions. Further drift can occur whenever these requirements are not met, as often happens with inexperienced personnel especially in developing countries. Not surprisingly, wildlife populations are systematically being affected every year by direct exposure to insecticide sprays, specially birds that are present in agricultural areas at the time of insecticide spraying [15] and receive a high dose *via* droplets or concentrated toxic vapours [16]. Exposure of terrestrial animals to herbicide sprays is less hazardous because of their lower toxicity. However, aquatic ecosystems and susceptible crops in nearby land can be affected as well, so the adoption of buffer zones around the crops can substantially mitigate the drift onto surrounding areas. For example, unsprayed strips 3 m wide around agricultural fields in the Netherlands reduced drift onto irrigation ditches by 95% [17]. Under present management practices in that country using narrow unsprayed buffer zones and other measures, the impact of sprays on non-target insects are down to 41% for herbicides, 21% for insecticides and 14% for fungicides compared to impacts in the past [18].

Granular pesticides are designed to avoid the risks of spray drift to farmers/applicators and wildlife. Also, the granules release the active ingredient over time, thus increasing the efficacy of the product. Many water soluble herbicides and fungicides are applied as granules, as well as some OP (fensulfothion, terbufos, parathion, fonofos, disulfoton, phorate, diazinon) and systemic insecticides (aldicarb, bendiocarb, carbofuran, imidacloprid). Special

machinery is used to bury the granules in the soil, but inevitably some granules remain exposed on the surface (from <1 to 50% depending on conditions), where birds and other animals may ingest them [19]. Birds are particularly fond of such granules, which they take as grit for their gizzards or simply mistake them as food, and consequently are more at risk from this formulation than small mammals [20]. In the case of insecticides, a single granule may contain a lethal dose (up to 20% a.i.), so the consequences are often dramatic: in North America, waterfowl were poisoned by eating fonofos granules they sifted from waterlogged fields six months after they were applied [21]. Seed-dressing was a common practice with OC insecticides such as aldrin, dieldrin and lindane, as well as organomercurial fungicides, and it poses similar risks as the granules, *i.e.* granivorous birds and mammals ingest the treated seeds often spilt around the edges of the crop and farm buildings. Poisoning incidents with seed dressings of cholinesterase inhibitors are still relatively frequent, especially in Europe [22]. The systemic insecticide is still present at concentrations ranging from 4.1 mg/kg in stems to 2.1 mg/kg in pollen, thus causing a great risk to honeybees [23]. Rodenticides are applied as baits spread around the farm buildings or near the crops where pest mice or voles congregate, posing a risk to other non-target vertebrates.

In irrigated crops, herbicides are often poured into the water channels either to allow an even distribution of the chemical throughout the irrigated field or simply to eliminate aquatic plants that may clog the channels and use up the water. Treated waters such as these invariably affect aquatic communities in agricultural landscapes (see Chapter 6), and are a constant source of contamination for many birds, frogs and mammals that bath in or drink from them.

Finally, some insecticides are used to control ectoparasites in domestic animals. In the 1950-60s it was common practice in many places to drench farm animals with solutions of DDT to combat cattle ticks. Today, the OC insecticides have been replaced by OPs (e.g. famphur), pyrethroids (e.g. cypermethrin), spinosad, cyromazine, avermectins and insect growth regulators (e.g. fluazuron) to control ticks, lice and blowfly maggots. Despite their lesser persistence and greater specificity, residues of the latter chemicals in dung from treated livestock affect dung-breeding insects and the degradation of faeces [24].

EXPOSURE OF ORGANISMS TO AGRICULTURAL PESTICIDES

Animals and plants are exposed to all these toxicants in a variety of ways. It is important to realise that just as the target pests and weeds are killed by the pesticides, all other non-target organisms may suffer deleterious or deadly consequences when exposed to the same doses of those chemicals.

Animal Exposure

The first route of pesticide exposure for most animals, vertebrates and invertebrates alike, is by direct deposition of the sprayed products on them, which is equivalent to a topical application on their skins/epidermis. Spray droplets are made of concentrated active ingredient in an oily or water-based carrier solution that sometimes contains an adjuvant. The tiny droplets (100-200 μ m in diameter [25]) deliver a concentrated dose of toxicant to the skin, hair and feathers of animals they fall upon. Thus, liphophilic insecticides are quickly absorbed through the skin, and the ensuing acute dermal toxicity is often enough to kill the animal. In fact, dermal deposition has been recognized as one of the most crucial routes of exposure in birds [26]. Animals that die as a consequence of direct pesticide spray deposition do so because they happen to be at the wrong place at the wrong time [15], but it is hard to imagine how this could be avoided since agricultural land and surrounding landscapes are the natural home to countless species of non-target organisms of all kinds. Inevitably, pesticides and fertilizers are applied during the crop growing season, which coincides with the breeding of insects, nesting of birds and breeding/metamorphosis of amphibians. Although application can have different impacts. For instance, the OP insecticide dimethoate applied early (spring) to barley crops at maximum rates (0.4 kg/ha) was very harmful to seven non-target soil-dwelling breeding beetles, but the same rate has a reduced impact on populations of old beetles when sprayed in autumn [27].

Concomitant with the deposition of spray droplets, inhalation of the misty and vaporized pesticides brings the active ingredients directly into the lungs and bloodstream of terrestrial vertebrates, even if they were initially sheltered from the spray deposits. Volatilisation of lipophilic insecticides from soil and other surfaces is a source of constant

air contamination in agricultural areas [15] even years after they were applied. For example, fluxes of DDE, toxaphene, dieldrin and trans-nonachlor from cotton soils in Alabama (USA) have been estimated between 325 and 7000 kg annually or 0.07-1.56 mg/kg per day for each of the respective chemicals [28]. Animals with a high rate of ventilation such as birds are at the highest risk. Nevertheless, it is difficult to separate the two kinds of exposure mentioned here – direct contact and inhalation – when an animal has been found paralysed or dead in the field. Most of the time it is the combination of several routes of exposure that accounts for the fatalities observed.

The third route of exposure is by direct consumption of contaminated plants, fruits, granules and coated seeds. This is known as primary poisoning to distinguish it from the secondary poisoning that occurs when a predator eats contaminated prey, insects or worms containing pesticide residues. Primary poisoning also occurs through drinking of contaminated waters from irrigation channels, drains, farm reservoirs, puddles, streams, rivers and lakes, which may contain high levels of pesticide residues, especially when they are in or near the agricultural fields that act as their source. A typical example is the case of DDT and cyclodiene insecticides used lavishly in the past; the persistence and lipophilic characteristics of these OCs resulted in their accumulation in granivorous birds and rodents that consumed seeds dressed with aldrin or dieldrin, in caterpillars that fed on leaves, and in worms of the treated soil - exposure through primary poisoning. In turn these animals were eaten by insectivorous birds and small predators, so the residues accumulated in their bodies as well. Larger predators such as falcons and eagles ate the contaminated prey and ended up with insecticide concentrations in their bodies which were several thousand times those found in the original seeds or treated plants - secondary poisoning. A parallel chain of contamination events occurred in the aquatic ecosystems where residues of these insecticides found their way through washoff from plants, runoff and drift [29]. Fortunately, most modern pesticides do not accumulate in organisms because they are either metabolized readily or eliminated in the urine and faeces. This does not mean they are all safe in regard to trophic contamination; *i.e.* woodlice consuming litter materials contaminated (0.1-500 µg/g food) with parathion-ethyl and endosulfan-sulfate take up these insecticides and experience their toxic effects [30]. Nor does it mean that secondary poisoning is a phenomenon relegated to past use of OC insecticides; it still occurs wherever the land was treated with arsenates [31] and OCs, as well as in tropical regions where they are still in use. Evidence of regular wildlife contamination by ingestion has been demonstrated by analyzing the gut contents of passerine birds in Australia during the agricultural season; sublethal levels of OC insecticides were found in 41-63% of the birds sampled, the OP parathion-methyl in 22% and the herbicide diuron in 78% of the birds [32]. The distribution of residues among trophic levels suggests that insecticides were obtained through ingestion of food whereas the herbicide was acquired by drinking from polluted waters. The highest residues were DDT (35-1980 μ g/L) and its metabolite DDE (2-21 μ g/L) even if it had not been used in that country for 20 years. Although the bioavailability of such old residues in soil and sediment decreases considerably with time [33], the fact that many animals continue to show DDT/DDE in their body tissues decades after they were applied indicates that the movement of this insecticide through the food chain is still a current issue in ecotoxicology.

Organisms exposed through primary consumption of highly toxic insecticides, rodenticides and fungicides usually experience acute effects, which may result in death if sufficient amounts are ingested. There are numerous examples of this, including the squirrels, raccoons and white-tail deer that have died over the years in the state of New York as a consequence of ingesting anticoagulant rodenticide baits [34], or the geese poisoned by ingesting heptachlor and chlordane treated seeds, and the countless songbirds killed in similar circumstances [15]. However, for the majority of pesticide products in the market, chronic and sublethal effects are more common because of the low level of residues (see Chapter 1). Secondary poisoning typically leads to chronic toxicity and unforeseen side-effects, as in the case of eggshell thinning in birds of prey and fish-eating birds contaminated with OC insecticides [35]. Nonetheless, secondary poisoning can be lethal to the predator even at normal rates of application if the chemical is very toxic (e.g. OP and carbamates) [36], or when the contamination is severe due to misuse; for example, the inappropriate spraying of monocrotophos over alfalfa fields to control voles in Israel resulted in the killing of hundreds of kites, eagles, buzzards and owls in a few days because they fed on voles that had been affected by this OP insecticide [37].

Exposure of Plants to Pesticides

Plants are affected by herbicides and fungicides only when these products are deposited directly onto them (contact) or are taken up through the roots. To avoid damaging the crop they intend to help, herbicides are usually applied prior to

planting. Herbicide drift on to non-target areas may affect other crops and wild plants alike, and is a common cause of economic injury to neighbouring farmers, which can reach up to 10% yield losses in the case of canola [38]. For this reason, aerial sprays of 2,4-D on fields of cereal crops must be carefully planned to avoid drift onto nearby sensitive crops like cotton [10]. Granular formulations of herbicides are otherwise preferred. Irrigation waters containing residues of unwanted herbicides and other pesticides may also affect the performance of rotational crops grown on the same fields. However, water-borne residues of herbicides in runoff are more likely to affect aquatic plant communities growing along streams, rivers and marshes since their levels are at most sublethal to animals.

Effects from Exposure to Pesticides

Toxicological effects depend on the doses exposed to, and such effects may occur at individual, population and community levels (see Chapter 1). The focus of this chapter is on the latter two effects, since they define the impacts on the ecosystem more clearly than any sublethal effect manifested on particular individuals. Besides, standard measurements of toxicity (e.g. LD50, EC10, NOEL) are determined with reference to populations. Community effects are typically described by the proportion of species eliminated or severely reduced in numbers within a collective group of species, but there is no standardized measurement to express this kind of impacts.

Dose is the amount taken up by the organism, which can be taken either all at once or through several episodic events. This distinction is important, particularly when dealing with pesticides, as most agrochemical products are recommended to be applied once or twice within the growing season of a crop; orchards usually require several applications. When a pesticide is applied only once, all non-target animals and plants that are directly exposed to it may experience short-term, acute toxic effects. In ecotoxicology this is called pulse exposure to distinguish it from constant exposure to pollutants in a given environment. After an initial shock, the affected organisms will be subject to decreasing exposure as the pesticide disappears progressively by natural decay, microbial degradation, and other dissipation routes (see Chapter 2). However, residues remaining in the plants, soil and water of the agricultural fields and surroundings can be taken up by animals moving into those areas any time after application. For non-persistent and biodegradable pesticides, those residual amounts are sufficiently low to ensure the LD50s for most species are not reached, although there is no guarantee they won't have any impact whatsoever – sublethal effects on some individuals may still take place.

In a different situation, when a pesticide persists in the environment for longer than one season (which occurs whenever half-lives are over 3 months) its residues are expected to build-up between consecutive annual applications. That is the case with most 'old' pesticides like OC insecticides and copper fungicides. In such circumstances, all organisms chronically exposed are at risk of accumulating the toxicant in their tissues, and with time the internal doses may be sufficient to cause either sublethal or lethal effects – the eggshell thinning due to DDE residues in birds is a classical example of this problem [5].

Mortality is the most obvious consequence of direct pesticide toxicity, reducing the populations of both target and non-target species affected. Such reduction in numbers is directly proportional to the toxic potency of the chemicals involved as measured by their LD50s. Since species live in communities rather than in isolation, the decrease in numbers of one species inevitably affects the other species with which it interacts. The resulting imbalance of populations is the most apparent direct effect of pesticides in biological communities. This usually takes place in the agricultural fields and small surrounding areas affected by drift and volatilization, whereas direct effects on aquatic ecosystems may take place beyond these boundaries since water-borne residues can be transported long distances (see Chapter 2). It is important to bear in mind that populations can recover once the toxicant levels drop or disappear, so the direct ecological disturbances caused by pesticides are temporary, not permanent.

It is also important to consider that organisms are not exposed to a single agricultural pesticide alone but rather to a suite of insecticides, herbicides and fungicides that are routinely applied to the crops, sometimes on the same day or even at the same time. Evidence that the combination of several toxic substances produces synergistic effects on the organisms exposed was first reported for mosquito larvae (Aeddes aegypti) and fruit flies (Drosophila melanogaster) exposed to the OP insecticide parathion and the herbicide atrazine [39]; the addition of the herbicide enhanced the lethal effect of parathion by a factor of 2 to 12 depending on the soil type used and other factors. The fungicide propiconazole enhances the activity of neonicotinoids [40], but the best known synergism is the enhancing effect of piperonyl butoxide on pyrethroids and cyano-substituted neonicotinoid insecticides, because the synergist inhibits the P450 enzymatic

detoxification mechanism. Estrogenic effects of mixtures of OC insecticides which are innocuous individually, are also examples of synergism that may have profound environmental implications [41]. The synergistic interaction of atrazine has also been proven in combination with some OP insecticides applied to house flies (Musca domestica), and other interactions between different types of pesticides are well documented in aquatic ecosystems (see Chapter 6); however, most of the mixture effects of pesticides are additive rather than synergistic [42].

Finally, sublethal doses of pesticides may cause enough stress in the organisms exposed so as to trigger anomalous behaviour. Examples are the reduced predatory skills in frogs exposed to malathion [43], negligence of female starlings exposed to OP insecticides in looking after their nestlings [44], as well as depressed immunological responses that may result in higher than normal rates of parasitic infection [45].

Persistence of Residues and their Bioavailability

Persistence indicates the ability of a toxicant to remain intact and active over long periods of time. The half-life is a useful measure of persistence: it is the time required for half of the chemical to disappear, usually by transformation into a non-active degraded product (metabolite). However, some metabolites can also be toxic (e.g. endosulfan sulphate, dieldrin, aldicarb sulfoxide and sulfone, heptachlor epoxide), in which case the total persistence of parent compound and metabolites should be considered in assessments of ecological impact.

Apart from a few exceptions, modern pesticides are not as persistent as those used in the past, and this together with specificity of action is a prominent feature of modern agrochemical products. Compared to the arsenates and OC insecticides of old, with half-lives in the environment of several years, most neurotoxic insecticides are easily degraded in the environment by chemical and biological processes. Modern herbicides and fungicides are also more degradable than their early products, even though these chemicals are generally more persistent than insecticides (Table 2). Currently, over 50% of pesticides have half-lives in soil under a month, with only 14-20% having half-lives over three months either in soil or water.

Table 2: Persistence of pesticides according to their average half-life in soil, and their proportion among the total number of registered products of the same type. Source [6]

Туре	Non-persistent	Moderate	Persistent	% products
Fungicides	64	31	20	59%
Herbicides	138	77	34	73%
Insecticides	82	41	19	58%
Rodenticides	1	1	1	18%

Non-persistent = half-life under 30 days, equivalent to 1% or less residues remaining after half a year

Moderate = half-life between 1 and 3 months, equivalent to 1-5% residues after 1 year

Persistent = half-life over 3 months, equivalent to 5% or more residues after 1 year

Persistent pesticides are more efficacious due simply to their prolonged action over time. From an environmental point of view this is undesirable because the longer the residues stay in the environment, the more chances of being dispersed and the higher risk they pose to organisms as a result of their prolonged exposure and accumulation. Indeed, persistence of agrochemicals poses as much concern as their acute toxicity. A highly toxic and degradable substance may have short-term lethal effects, but it usually allows recovery of populations after its disappearance, whereas a persistent substance of low toxicity will undoubtedly accumulate in the environment and in non-target organisms, in which case sublethal and unknown side-effects are likely to appear in the future. Obviously, when a pesticide is both persistent and very toxic the consequences can be disastrous, as happens with the 'old' OCs, arsenic insecticides and copper fungicides.

Residue accumulation in tissues of both plant and animals occurs whenever the degradation rate of a chemical is lower than its rate of uptake. Since toxic effects are related to the doses exposed, the bioavailability of the pesticide

residues is essential. For example, residues attached to soil particles may remain largely inaccessible to soil organisms, as if the residues were locked [33], and do not cause the effects one would expect. An extreme case is glyphosate: to be effective this herbicide must be absorbed by the plants, either by direct contact on the leaves or by uptake of the chemical in solution through the roots [46]. However, when glyphosate falls on bare ground it is immediately adsorbed onto the clay particles and humic substances in the soil, so it cannot be taken up by the plant roots – it remains effectively inactivated. In contrast, residues of most hydrophobic insecticides (e.g. pyrethroids, OCs and many OPs), systemic and soluble insecticides (e.g. imidacloprid; carbaryl) and herbicides (e.g. diuron) are adsorbed onto organic matter in the soil and remain available to earthworms and other soil microfauna even many years after being applied to the fields.

REVIEW OF PESTICIDE IMPACTS ON NON-TARGET COMMUNITIES

Soil Communities

The soil is a micro-ecosystem in its own right, and the organisms that make it or live in it play a crucial role in recycling nutrients, thus sustaining the soil fertility which allows ecosystem and agricultural productivity. Their diversity and heterogeneity are therefore necessary for long-term ecological resilience of the biosphere.

Micro-Organisms and Soil Metabolism

Fungi, bacteria and protists metabolize decaying plant and animal matter and convert it to either organic waste products (e.g. CO_2 , methane and others) or minerals (e.g. nitrates, phosphates), which constitute the nutrients of plants. In addition, white-rot fungi have evolved to degrade lignin, an ability that enables them to degrade recalcitrant chlorinated pesticides such as toxaphene, lindane and pentachlorophenol [47].

Pesticides can affect these processes by altering the microbial composition of the soil. For example, applications of the systemic fungicide benomyl over many years reduced mycorrhizal root colonization by 80%, thereby indirectly reducing the abundance of fungal-feeding and predatory nematodes by 33% while increasing microbial substrateinduced respiration by 10% [48]. Generally, fungicides eliminate pathogenic root-rot or dumping-off fungi (e.g. Pythium, Phythophthora, Rhizoctonia), thus fostering the growth of competing bacteria while surviving and resistant strains of fungi become dominant (Fig. 1). Among the latter are the actinomycetes Aspergillus, Penicillium, Mucor, Pyrenochaeta and Trichoderma, which are less susceptible [29]. Reduction of fungi affects negatively the decomposition of the surface litter by 25-36%, but increases the mineralization in the buried litter carried out mostly by bacteria [49]. This structural change is not always significant in single applications of chlorothalonil (15 g/kg soil) [50], and may be masked by quick recovery and other factors. Suppression of mycorrhizal symbiosis in crop plants treated with fungicides has been observed with normal rates of captan, carbofuran and mercury fungicides, resulting in stunted plant growth and yield reduction [51]. In contrast, typical application rates of some OP insecticides (trichlorfon, chlorpyrifos and quinalphos) may promote rhizosphere fungi temporarily until the suppressed bacterial populations recover in 45-60 days [52]. In soils contaminated with persistent arsenic and copper fungicides the regeneration of fungi is slow and takes many years [53], and this also reduces the ability of the indigenous soil microbial community to degrade DDT [54].

Soil basal respiration is generally reduced 30-50% after treatment with the fungicides benomyl and captan at field rates (51 and 125 mg/kg soil, respectively) [55], or under persistent residues (21-490 mg/kg) of copper fungicides [54], but carbendazim, even at dosages as high as 87.5 kg/ha, does not have significant impacts on soil nutrient cycling processes nor on soil microbial activity [56]. Suppressed basal respiration has also been observed after treatment with the herbicides 2,4-D, picloram and glyphosate, usually at concentrations higher than normally applied, whereas glyphosate applied at 2.2 mg/kg for several years in Brazil increased soil metabolism some 10–15% and fostered fungi while reducing bacterial counts [57]. Repeated application of the herbicides atrazine and metolachlor over 20 years altered the soil community structure in corn fields, in particular by reducing methanotrophic bacteria, but did not cause a decreased community function (methane oxidation) [29].

The mineralization of organic N to ammonium and then nitrate in soil, carried out by the nitrifying bacteria Nitrosomonas and Nitrobacter, is suppressed by the fungicide maneb and the herbicide picloram, but is unaffected by the continuous use of most pesticides either singly or in combination. However, the fungicides metalaxyl, mefenoxam,

mancozeb and chlorothalonil, and the herbicide prosulfuron, increase ammonium and nitrate levels by indirectly fostering nitrifying and denitrifying bacteria which inhibit N2O and NO production [29]. Nitrogen fixation in rice paddies by Azospirillum bacteria can increase following application of recommended doses of carbofuran insecticide (2-5 mg/L), but larger doses are inhibitory [58]. The herbicide glyphosate suppresses most soil bacteria, including nitrogen-fixing Rhizobium, because it inhibits the biosynthesis of aromatic amino acids. Susceptibility of plants to pathogens is also increased by glyphosate treatment as biosynthesis of the proteins phytoalexin and glyceollin, which normally block infection, is also inhibited. However, significant impairment is only observed at high concentrations, since glyphosate itself is completely degraded to CO2 by other micro-organisms living in the same soil [59]. A general inhibitory effect of phosphatase (5-98%) in the presence of glyphosate has also been observed [60], whereas the herbicides oxyfluorfen and oxadiazon at 0.4 and 0.12 kg/ha, respectively, stimulate the population and activities of phosphate solubilizing micro-organisms and also the availability of phosphorus in the rhizosphere [61].

Little is known about the impact of pesticides on soil protozoans, but it seems that they are just as sensitive as other soil micro-organisms, with insecticides being more toxic than herbicides. Soil protozoa can be critically disturbed as populations often do not fully recover within 60 days. Fungicides have rather varied effects: ciliates decrease slightly but testate amoeba species can be reduced by 50% in pesticide-treated agroecosystems, contrasting with the increased abundances and biomasses of soil protozoa found in ecofarming [62]. Transgenic Bt-crops, which produce the toxic Cry proteins from *Bacillus thuringiensis*, do not have much impact on microbial, nematodes and protozoan communities. Although some effects of Bt-plants on microbial soil communities have been reported, they were mostly the result of differences in geography, temperature, plant variety, and soil type and, in general, were transient and not related to the presence of the Bt-toxins [63].

Soil Mesofauna

The contribution of mesofauna to the recycling of total carbon has been estimated in the range 0.4-11% for surface litter from non-tillage fields and 6-22% in buried litter from pesticide treated fields [49]. Typical applications on crops, particularly of insecticides, can decimate the minute animals that carry out this essential task and disrupt the complex structure of the soil, which they effectively form. However, no matter how drastic their impact may be, all these effects can be reversed once the toxic activity has disappeared because populations of these small organisms recover very quickly [64]. The following is a summary of direct impacts on the most important taxonomic groups of soil fauna as affected by normal application rates used in agriculture, unless specified otherwise.

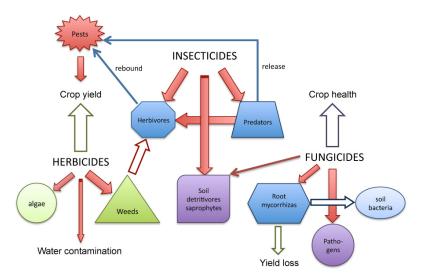


Figure 1: Diagram showing the main impacts of pesticides on soil, plant and arthropod communities. Red arrows indicate decreases and blue arrows indicate increases; empty arrows indicate indirect effects.

<u>Arthropods</u>

Since the early days of pesticide usage it was noted that OC insecticides had mixed effects on the animal communities of the soil [65]. On the one hand, aldrin, dieldrin, heptachlor, chlordane and DDT controlled well the insect pests of the

crops, but on the other hand their residues in soil greatly reduced most species of springtails (Collembola), saprophagous mites, symphylids and pauropods (Myriapoda). DDT was less toxic than aldrin and dieldrin but killed higher percentages of predatory mites than other insecticides, the destruction of the latter resulting in indirect increases of their Collembola prey species. All OC insecticides had little or no effect on earthworms, enchytraeid worms and nematodes at low application rates (*i.e.* aldrin 2.5 kg/ha), whereas five times that dose, as applied for the control of *Phyllophaga* larvae, affected several earthworm species. Many of these early reports refer to field observations that are difficult to evaluate, but proper assessments carried out later confirmed those findings [27].

Of special significance are the impacts on populations of mites because these tiny organisms are the most numerous arthropods in soil; many of them are predators, others are saprophytic while some Tetranychus are crop pests. Among the 84 studies in a variety of crops reported by Edwards and Thompson [66], 56 showed a decrease in mite densities, nine reported increases and 19 did not show significant changes. Impacts occur across all ecological types of mites, with populations of predatory mites being negatively affected more frequently when treated with OC insecticides (e.g. DDT, endosulfan, aldrin, chordane and heptachlor), most OP insecticides and carbamate biocides (i.e. aldicarb, carbofuran) [67]. Although mites recover within six weeks or a few months, a single exposure to aldicarb (25 kg/ha) resulted in different successional outcomes over the subsequent four years because of the elimination of many Gamasina predacious mites, which are often the most susceptible [68]. Even natural extracts like neem (from Azadirachta indica) are more detrimental to oribatid mites than other mites and spiders [69]. Fumigants (gaseous pesticides) have devastating effects: the D-D mixture eliminates all mite populations, does not allow their recovery until two years later and eventually decreases the soil biodiversity [66]. Some mites are susceptible to the herbicides simazine, atrazine, monuron and DNOC, but most of the population changes observed in fields treated with herbicides appear to be from indirect effects on the flora [70]. Apart from mites, predatory arthropods of the soil include carabid and staphylinid beetles, earwigs, centipedes and spiders, all of which control many pests and are, therefore, beneficial species to agriculture. Centipede populations were reduced by DDT and aldrin in the past, as subsequently did most OP insecticides and carbamates, but reports on impacts of modern pesticides on this group of animals are very few [71].

Saprophytic arthropods such as springtails (Collembola), Pauropoda, most millipedes (Diplopoda), woodlice (Isopoda), certain mites, symphylids and Diptera lavae help desintegrate plant material that many soil microorganisms are unable to process directly [66]. Although the role of these soil organisms is not as important in agricultural fields as it is in forests and other ecosystems, the current agronomic trend of no-tillage draws its benefits in soil fertility mainly from the role of these animals. For instance, an 80% reduction of springtail numbers after applications of lindane (0.5 kg/ha) to corn crops in Africa resulted in reduced breakdown of organic matter by 45% [72]. Collembola species are not as susceptible to pesticides as mites are; in fact, their numbers usually increase when fields are treated with normal doses of insecticides, as these kill the predatory mites that prev on them [73], thus altering the dominance structure of the springtail community even if the species composition remains unchanged. Springtails are very susceptible to fumigants, carbamates and many OP insecticides [74]. The arsenic herbicides reduced springtail populations in barley by half [75], while DNOC, paraquat, dalapon-sodium and several triazines also reduce their populations when applied in large doses [76], but most herbicides affect springtail communities indirectly [70]. Only a few fungicides (e.g. benomyl) appear to impact negatively on populations of springtails and woodlice [77]. Among the tiny Myriapoda of the soil, the pauropods seem to be most susceptible to all kinds of insecticides, and some populations are completely eliminated by OP insecticides. Symphylids, by contrast, do not suffer drastic effects because they live buried in the deep soil layers where they feed on plant rootlets. Thus, non-leaching, hydrophobic insecticides (most OCs, pyrethroids and some OPs) hardly affect their populations, whilst systemic, hydrophylic insecticides and fumigants deeply penetrate the soil and cause serious population reductions in all taxa [66]. Millipedes are more tolerant, and even if their populations are reduced temporarily by OC and OP insecticides, the herbicide monuron, or the fungicide carbendazim, they recover within a few months [78]. However, persistent residues of DDT in soil of cabbage plots can progressively accumulate in millipedes and reduce their populations over the years [29].

Larvae of many Diptera species are agricultural pests, but the majority of them are not. In any case, they all play an important role in breaking down dead plant/animal matter, so the repeated application of insecticides and herbicides like simazine leads to a significant loss of Diptera larvae and a potential accumulation of dead organic material on the surface [66]. Larvae of dung beetles and flies in pastureland are also affected by residues of parasiticides found

in the faeces of treated livestock. For example, emergence of the dung beetle *Liatongus minutus* and eight species of flies from cowpats in the first two weeks following ivermectin treatment at normal rates (0.5 mg/kg body weight) was significantly reduced, while Ceratopogonidae and Psychodidae species prospered [79]. These impacts occur while lethal levels of residues persist in the dung – usually 1-3 weeks for most pyrethroids and avermectins in cowpats [80] but shorter times in sheep dung [81]. By contrast, insect growth regulators like fluazuron and methoprene appear to have no such effects at normal rates of treatment [82, 83].

Other Invertebrates

Parasitic nematodes are regularly controlled with fumigants, lindane, some OP and carbamate insecticides applied directly into the soil, but depending on the doses applied, populations of saprophytic and beneficial nematodes are also reduced [29, 66]. Most OC insecticides and fungicides do not affect nematode numbers. Among the latter chemicals, carbendazim increases omnivorous species and benomyl reduces them [66]. Under field conditions, the risk of indirect effects from fungicide application is usually much greater than that of direct effects. For example, by reducing total fungal biomass and activity, captan decreases the numbers of fungal-feeding nematodes [84]. Herbicides have mixed effects, and this is believed to result from the complex interplay of top-down and bottom-up forces in soil food webs. Another example: plant-root parasitic species increased in rice paddy plots treated with a mixture of thiobencarb and simetryne (2.8 and 0.6 kg/ha, respectively) while predaceous mononchids, which mostly live on the surface, were drastically decimated when chlormethoxyfen at 2.8 kg/ha [85] was added to that mixture.

More important, particularly in tropical agroecosystems, orchards and vegetable patches with litter, are the impacts on detritivorous earthworms, because they remove large amounts of leaves and stubble material, and in doing so increase soil fertility and lessen the ability of certain pathogens to overwinter in the fields [66]. Past applications of copper fungicides and arsenates have led to the formation of mats of undecayed organic matter on the surface of many orchards, because these highly toxic and persistent compounds decimate earthworms populations [86], increase their avoidance behaviour [53], and negatively affect their burrowing rate. The latter sublethal effects have also been observed with the insecticide imidacloprid at 0.5-1.0 mg/kg dry soil [87]. The majority of OC, OP and carbamate insecticides do not cause significant reduction of earthworm populations at normal application rates [66], but chlordane, heptachlor, phorate and carbofuran are extremely toxic to all worms and eliminate them completely [88]. Recovery times from carbofuran treatments can last 90-105 days, and that from the OC insecticide butachlor can be longer than a season. Phorate can also foster enchytraeid worms indirectly by eliminating their predators [89]. All fumigants are deadly to earthworms because they penetrate the deep layers of the soil [66]. Among fungicides, carbendazim at 1 kg/ha decreased the abundance of several Lumbricus species in terrestrial model ecosystem (TME) studies, as well as *Fridericia* enchytraeid worms and native earthworms in rubber plantations of the Amazonia [78]. Some herbicides (e.g. DNOC, chlorpropham, atrazine, simazine, monuron) reduce earthworm populations slightly, and paraquat appears to increase them [70], but most have no direct effect on them. In general, conventional agronomic practices in orchards seem to affect negatively detritivores such as earthworms and woodlice. However, some long-term studies have shown that insecticide-treated fields had no ecologically significant impacts in earthworm populations when compared to untreated fields, the differences being largely consistent with the expected effects of climate, soil types, crop types and cultivation practices [90].

Vegetation and its Arthropod Communities

The soil is the substrate and nutrient source for the growth of plants, and the vegetation provides the basic structure on which most species of arthropods live. Both weeds and macro-invertebrates provide many valuable services to the agroecosystem – nitrification; soil aeration and water percolation; recycling of litter, dung and decay materials; pollination; and vectors of mycorrhizal spores, among others.

Impacts on Vegetation

Weeds are the competitors of the crop for water and nutrients, and can reduce crop yields significantly. Broadspectrum herbicides are toxic to all kinds of plants alike, usually by inhibiting the photosynthesis (e.g. urea herbicides, triazines) or any other essential plant metabolic pathway (e.g. glyphosate), but others inhibit seedling development from the seed (e.g. trifluralin and pendimethalin). Selective herbicides are designed to inhibit metabolic processes common to either grasses (monocotyledons) or broad-leaf plants (dicotyledons). This feature allows them to be used on certain crops to control weeds of the opposite type; for example, 2,4-D is used in cereal crops because it only inhibits growth of broad-leaf plants. The effectiveness of herbicides in reducing plant biomass is often underestimated. They effectively exclude many annual plants from being established, and although vegetation communities may recover in the following season, the constant application of herbicides year after year leads to the depletion of soil seed banks. For example, it has been reported that after many years of intensive agricultural practices using a range of herbicides, the Hilly Country of Saxony has lost many landscapes and their associated flora diversity [91]. It appears that the time of their application in relation to plant seed production influences more the nature of vegetation changes than does the soil seed bank type. However, individual herbicides have minimal impacts; a review of the impacts of the broad-spectrum herbicide glyphosate on a variety of ecosystems found the shifts in species floral composition and structure of habitats were within the normal range of variation in natural ecosystems [92].

Indirect impacts of herbicides on soil fauna are often reported. Long-term studies carried out over several years in vegetable crops have revealed that the soil arthropod community structure is positively correlated with the weed community biomass, which varies with the use of specific herbicides and other management practices [93]. For example, the abundance and diversity of rove beetles (staphylinids) is dependent on weed community composition as well as ploughing, with the highest biodiversity being observed on fields with no-tillage and less pesticide use [94], whereas use of paraquat and trifluralin herbicides in tomato plots result in significant reductions in the density of ground beetles. The unintended consequences of such indirect impacts are illustrated by the reduction of weeds in orange groves in Spain: many years of herbicide applications have reduced the abundance and biodiversity of consumer ants to the point that fewer ant colonies made the soil progressively less porous and more compacted, thus enhancing rainfall erosion and slowly depleting the orchard's soil fertility [95].

Plant biodiversity is not considered to be important in crop monocultures, but it is relevant to the establishment of stable arthropod communities in or around the crop. These play an essential role in effective crop protection and also sustain populations of birds and other vertebrates. In many cases, the losses in yield caused by weed competition can be offset by the benefits that predatory arthropods bring to the crop. For example, cane and sugar yields averaged 19% higher in weedy sugarcane plantations than in the weed-free plantations in Lousiana, because broadleaf weeds enhanced the populations of beneficial carabids, ants and spiders that control the sugarcane borer (*Diatraea saccharalis*) [96]. Similarly, the combined use of Bt-cotton, lucerne strips and a nuclear polyhedrosis virus in Australian cotton farms reduced the use of synthetic pyrethroid insecticides by 50% without sacrificing yield and profitability [97]. Experience over the years in these and other crops have demonstrated the benefits of the appropriately named integrated pest management (IPM) strategies that promote the conservation of existing natural biological controls through major reductions in insecticide and herbicide use.

The introduction of recent transgenic herbicide-tolerant crops (TGHT) may encourage no-tillage practices which are beneficial for soil fertility, but there is concern that such crops may lead to a more intensive use of herbicides and the removal of many weeds that support populations of pollinators [98]. Pollination by bees is a very important ecological service provided to agriculture, as 25% of tropical crops and possibly up to 84% of temperate crops [99] depend on insect pollination. Thus, management and protection of pollinator populations and habitats of nectar-producing plants can be essential for some crops, and for plant biodiversity in the environment at large. However, there are no clear examples of low crop yields resulting from the effect of pesticides or transgenic Bt-plants on pollinators [98]. Although agricultural intensification and habitat loss are the most frequent cause of pollinator impoverishment (64% of cases), direct bee mortality by insecticides is evident and cannot be ignored either [100].

Arthropod Communities

Insecticide sprays can wipe out 99% of the population of target pests as well as those of non-target species, just as chemotherapy kills both bad and good cells alike. Since the early years of the Green Revolution entomologists realized the limitations of this approach and looked for alternative methods of pest control. In nature, predatory arthropods keep the populations of phytophagous insects (most pests) in check: ladybird beetles, dragonflies, earwigs, some ants and crab spiders predate on eggs of pest species, while parasitic Hymenoptera play an essential part in controlling numerous pest larvae, so they are being used in biological pest control. A recent review of 39 ecosystems found that agrochemical pollutants negatively affect these parasitoids in 46% of cases [101], with

persistent and systemic insecticides (e.g. cartap and imidacloprid) having the greatest impacts [102]. However, predatory arthropods are less susceptible than parasitoids and more variable in response to pesticides [103]. Although some predatory species are very tolerant to pesticides (e.g. the spider *Lycosa pseudoannulata*, the coccinellid *Cryptolaemus montrouzieri*, and the lacewing *Chrysopa carnea*), their initial elimination by insecticides and their slower recovery than that of the pest species they control often results in rebounds of pests (Fig. 1) in the short and long term [104].

Early insecticide impacts in non-target arthropod communities were reported for orchards sprayed during three years with lead arsenate and nicotine. Ground-dwelling beetles, spiders and ants were reduced by 15%, and the proportion of eggs and larvae of the main apple pest – the coddling moth (*Laspeyresia pomonella*), which is parasitized by Hymenoptera species – decreased by 64-97%, allowing the moths to come back unopposed [29]. DDT sprays helped eliminate the coddling moth, but it created new pests among leaf-rollers, woolly aphids, red-spiders and *Tetranychus* mites that surged as a consequence of the lack of predators and the suppression of parasitism. Citrus orchards sprayed with DDT to control cottony-cushion scales and mealybug pests also eliminated the predatory ladybird beetles and parasites which control them – as a result, pest numbers not only did not decrease but rather surged exponentially [105]. Because of the persistence of DDT, restoration of a normal predator-prey relationship after cessation of sprays could take up to five years [106].

The annihilation of predatory and parasite arthropods in cotton, corn, rice and horticultural crops has created new community structures characterized by the absence of predator-prey relationships, one where pests species thrived for a while until the next insecticide spray decimates them, where resurgence became the norm and resistance to chemicals the final outcome [29, 107]. In America and Australia, early sprays of calcium arsenate to control the main cotton pest, the boll weevil (Heliothis spp.), boosted the populations of cotton aphids due to the elimination of predatory arthropods. Lindane was applied to control both the weevils and the aphids, but this resulted in outbreaks of Tetranychus mites, as more predators were also affected. To top it all, the application of OP and systemic carbamate insecticides to control leafworms (Spodoptera spp.) resulted in further outbreaks of boll weevils and mites due to a combination of two factors: total lack of predators and insecticide resistance developed within the pest species [29]. It is easy to understand that restoring these shattered communities usually takes a few years. Pest management plans in cotton agroecosystems continued to rely on the routinely, heavy use of pyrethroids, OPs, carbamates and new insecticides until the 1990s [108]. Recently, the introduction of transgenic Bt-cotton in some countries appears to have a positive effect on restoring the biodiversity of most predatory insects, spiders and birds in cotton fields, since insecticide applications are reduced 50% or more [109]. Similarly, the biodiversity of arthropods in Bt-corn crops is much higher than in fields treated with pyrethroids. Insecticide sprays on rice crops upset natural enemy control of pests such as plant hoppers (Nilaparvata lugens) and also create heavy selection pressure for strains of pests that can overcome previously resistant rice cultivars. Such circumstances create outbreaks of secondary pests and impair biological control of some key primary pests such as Pyralidae stem borers [104]. Typical applications of BHC and parathion significantly decreased densities of predatory dragonflies, spiders and parasitoids, thus increasing the herbivore:predator ratio among arthropods [110]. The insecticides imidacloprid and fipronil also change this ratio even if their main impact is on midge larvae (Chironomidae) [111]. In addition, herbicides applied to rice paddies foster the numbers of parasitic nematodes and alter the plankton communities [85]. Perhaps, the rich biodiversity of rice fields, with some 200 species of predatory arthropods, could be used in IPM programs to control the 55 species of pests found in this crop [112].

Ground-dwelling carabid beetles are essential in controlling many horticultural pests, and together with staphylinid beetles make up about 75% of the predaceous and/or parasitic insects on vegetable crops [113]. In the past, OC insecticides decimated their populations and allowed very slow recovery afterwards [29], whereas the OC endosulfan at 1 kg/ha appears not to cause major impacts on these arthropods [72]. The impact of cholinesterase inhibiting insecticides on carabid populations ranges widely among species [114, 115], but all allow their recovery within a few weeks [66], whereas pyrethroids and imidacloprid at recommended rates have minimal impacts in spite of their extreme toxicity to insects [72]. Most herbicides indirectly increase densities of carabids, ladybird beetles and linyphiid spiders [74], but 2,4-D and chlorpropham are toxic to carabids too [29]. TGHT sugar beet and Bt-canola crops do not appear to have any significant effect on carabids, staphylinids nor spiders, but rather reduce the overall arthropod abundance through indirect effects on weed biomass [116].

Spiders and phytoseiid mites are important predators in all kinds of crops. Applications of OP, carbamate and pyrethroid insecticides in vineyards, orchards and other crops usually result in increases of pest *Tetranychus* mites because of reductions in the more susceptible phytoseiid predators [117]. In experimental plots, spiders were three times less abundant in apple orchards treated with insecticides than in untreated ones, and spiders and ants were reduced in numbers in 53% of the corn crops in Africa treated with lindane (0.5 ka/ha), an effect that lasted 2-3 weeks [72]. Lycosidae and linyphiid spider populations undergo a similar pattern – they are initially eliminated from cereal fields treated with OP insecticides, but their abundance may increase subsequently in response to rebound densities of unaffected prey like springtails [29]. Indirect effects of herbicide application on field margins often reduces the habitat for lycosid and linyphiid spiders, as border crop fields and hedges act as refuges for these and many other beneficial predatory invertebrates [118]. No-tillage practices and TGHT crops enhance spider populations through a more heterogeneous and diverse vegetation structure [119].

The direct impact of insecticides on honey bees (*Apis mellifera*) was recognized a problem since the calcium arsenate dust sprays killed entire hive colonies in the past [29]. They also affect the performance of the colonies, with impacts ranging from odour discrimination to the loss of foraging bees due to disruption of their homing behaviour [120]. Pyrethroid and OP insecticides such as triazophos and dimethoate continue to be very toxic and hazardous to bees [121]. Spray drift and volatilization are responsible for most of the incidents reported on hives [100], while impacts on wild bumblebees (*Bombus* spp.) are likely underestimated and non-reported. All bees are also affected by the poisoned nectar and pollen taken from plants treated with systemic insecticides such as carbamates and imidacloprid. Typical concentrations of imidacloprid of 6 mg/kg in male flowers (panicles) and 2 mg/kg in pollen from maize, sunflower and rape plants are sufficient to decimate honeybee colonies [23], especially when the pollen contains higher residues of other pesticides that could act simultaneously or synergistically. Besides mortality, imidacloprid appears to affect the brain (memory) and metabolism in bees, with the resulting impairment in the workers activity [122].

Crop diversification in conventional farming can help increase the biodiversity of arthropods while significantly reducing the densities of phytophagous pests by 60-70% [123]. In tropical rice crops particularly, which sustain a large biodiversity [112], pest management is best achieved using natural controls rarely supplemented by insecticides [104]. In ephemeral annual crops such as cereals, sugar cane, alfalfa or even cotton, leaving strips of grass and weeds on field margins, woody borders and other practices that attract and provide refuge to many arthropods can increase both biodiversity and abundance of natural predators [118]. It should be borne in mind, however, that any efficiency in controlling the pest populations through natural enemies depends very much on the identity of both predator and prey species, not on the diversity of predators *per se* [124].

Vertebrates

Since invertebrates are small and not very mobile – except some insects –, pesticide impacts on their communities are restricted to the agricultural fields, orchards and the margins affected by spray drift. By contrast, vertebrates move around fields, nearby forests, wetlands, rivers, lakes and even far away places in the case of many bird species. Therefore, off-farm contamination is another source of exposure for vertebrates, even though it is much lower than on-farm exposure due to its lower residue levels [125]. For persistent chemicals, the possibility of bioaccumulation in the animal tissues introduces also a new and often unknown risk factor.

Direct Impacts

The susceptibility of vertebrates to agricultural doses of pesticides is typically lower than that of invertebrates simply because of their size difference. Vertebrates are more tolerant to synthetic pyrethroids, neonicotinoids and OC insecticides, but very susceptible to cholinesterase inhibitors, whereas amphibians are generally very sensitive to pyrethroids and more tolerant of cholinesterase inhibitors than birds and mammals [126]. Reptiles appear to have either less or similar sensitivities to mammals in regard to neurotoxic compounds [127]. Mammals are more tolerant to certain pesticide groups than other vertebrates because they posses active detoxification mechanisms. However, small insectivorous mammals, such as shrews and moles, are very sensitive to neurotoxic anti-cholinesterase insecticides because of their high feeding and metabolic rates. Birds are more tolerant of pyrethroid and neonicotinoid insecticides, but are very susceptible to chlorfenapyr.

Killing of non-target organisms such as birds, lizards and small mammals is often observed at the time of insecticide applications [128], but most incidents are probably not reported [129]. Bird mortalities from direct exposure to insecticides can range from a few birds to several hundreds. Indeed, OC insecticides were blamed for many bird fatalities in the past, and cholinesterase inhibitor insecticides were responsible for 25-50% of bird mortality observed in farmland of the United Kingdom between 1975-1990s, of 17% of all birds poisoned in agricultural lands of the Netherlands, and 3-12% of all birds of prey found poisoned in the USA [15]. Levels of inhibition of brain acetyl-cholinesterase in birds below 20% are associated with sublethal effects and levels above 70% result in death [130], whereas in lizards the levels are typically below 40% and above 50% for the respective effects [131]. In contrast to OC insecticides, carbamate and OP insecticides do not accumulate in vertebrates as they can be readily metabolized, so their potent effects are usually short-lived. Even so, mortality of magpies by direct poisoning with famphur, applied to cattle as parasitic treatment, has been reported [132]. Lizards suffer similar effects as birds and mammals when exposed to the latter insecticides, but impacts on their populations and ecology are unknown [127]. Frogs, toads and tadpoles are common inhabitants of rice paddies, irrigation ditches and farm ponds as well as in surrounding wetlands and riverbanks, and so are exposed to direct pesticide applications on farm and drift sprays into their habitats. Although pesticide concentrations in agricultural waters are insufficient to cause frog mortality, the development of tadpoles is usually affected by low concentrations of many OPs in water (e.g. 4-8 mg/L fenitrothion) and herbicides like triclopyr (2.4-4.8 mg/L) [133].

Apart from mortality, sublethal effects on birds and small mammals exposed to these insecticides are more common, including reductions in food consumption and drinking activity that leads to noticeable weight losses [44], lack of aggressive behaviour, memory impairment that can compromise their survival ability, immobility on the ground which puts them at risk of predation [134], apathy in bird hatching, nest defence and care for the nestlings [44] and reduced fertility [135]. In amphibians, stress [43], suppression of immunity, and susceptibility to parasite infections [45] have been reported. Most of these effects are transient, but those affecting reproduction impact on the long-term viability of a species, even if there might not be apparent short-term population reductions. For example, direct exposure to OC insecticides reduced the breeding success of songbirds in apple orchards [136] and the recovery of vole populations in experimental plots. This is of concern because wildlife species rely on tight net reproductive rates to maintain their populations and cannot cope with such adverse effects. Thus, it has been suggested that reduced egg weight and hatchling success in caimans as a result of typical exposures to atrazine (15 µg/egg) and endosulfan (0.15-1.5 mg/egg) may influence the populations of this species in the wild Amazon [137]. As the field assessment of such populations is difficult, models have been developed to predict the long-term effects caused by reproduction impairment. Balanced population densities are important in the case of rodents, where a delay in reproduction can give a competitive advantage to another species. In this regard, exposure to the OP azinphosmethyl applied on alfalfa at 0.9-3.6 kg/ha caused lower than normal pregnancy rates, or its delay, in both voles and mice [138], whereas similar rates on tall grasses did not have effect on populations of Microtus canicaudus voles [139]. Similarly, lack of aggressiveness after exposure to dimethoate (0.4-0.6 kg/ha) did not impede the populations of herbivorous prairie voles (Microtus ochrogaster) to increase five-fold because the survival of competitor, omnivorous deer mice (Peromyscus maniculatus) decreased significantly [140].

Endocrine disruption is another sublethal effect by which some pesticides and other contaminants may impair developmental growth and reproduction in vertebrates [141]. Altered thyroid hormone concentrations, which influence development and metamorphosis, have been observed in birds exposed to DDT, OP, carbamate and pyrethroid insecticides [142, 143], in goldfinches exposed to the herbicide linuron [144], in amphibians and fish exposed to endosulfan and other insecticides [145]. Abnormal sexual differentiation caused by herbicides like atrazine have been observed in frogs, although conflicting evidence also exists [146]. Confirmed cases of impaired reproduction refer to populations of bald eagles (*Haliaetus leucocephalus*) in the Great Lakes of North America [147] and alligators in Florida [148], both of them after many decades of exposure to DDE residues. In the second case, high residues of OC insecticides and other chemicals were found in alligator eggs from Lake Apopka, which was heavily contaminated by a spill of difocol and DDT in the nearby agricultural area, and though hatching success was lower than normal it appeared to be unrelated to the pesticide levels measured in eggs [149]. Subsequent studies found the levels of estrogen in female alligators from that lake were double than normal, while levels of testosterone in male alligators were three times lower than normal or similar to those found in females. In addition, males had poorly organized testes and abnormally small phalli and females exhibited abnormal ovarian morphology [148]. As a consequence, alligator populations in Lake Apopka are in decline.

Primary Poisoning

More common among vertebrates is the exposure to pesticide residues through ingestion of contaminated food. Granivorous birds and rodents often ingest large quantities of seeds that often contain pesticide residues; grazing mammals may consume pasture contaminated with herbicides or insecticide spray drift; and birds of prey and scavengers often consume the guts of their prey and/or carcass, so the undigested granules of cholinesterase inhibitors and rodenticides found in the prey can result in fatalities among raptors [150]. The extent of this contamination can be assessed by the relative amount of residues found in animal tissues. Based on the residue levels of mirex across a large number of non-target animals [151], we know that insects accumulate more residues than other invertebrates, and among the vertebrates amphibians and reptiles had lower levels than birds and mammals, which possibly reflect their differences in feeding rate and metabolism. While most residues are metabolized and/or excreted by the animals, persistent and recalcitrant chemicals may accumulate in organs such as the liver and kidney, whereas lipophilic residues usually are stored in fatty tissues. Modern biomarker techniques make it feasible to investigate the poisoning level of live animals in a non-destructive way, *i.e.* using small samples of blood serum from reptiles, birds and mammals [152, 153].

Secondary Poisoning

Insectivorous birds, frogs, lizards and mammals often consume insects contaminated with pesticides [32]. The ecological consequences of secondary poisoning differ markedly among vertebrate taxa and the role each species plays in the trophic structure of the ecosystem, and obviously depend on the chemical nature of the poison. Build-up of insecticide residues in primary consumers can make them more susceptible to predators and scavengers. Birds of prey feeding on these animals accumulate even higher residue levels and often die as a result [36]. Most of the fatalities in raptors due to secondary poisoning are associated with the illegal use of insecticides and rodenticides (e.g. to eliminate wild carnivores), but some result from the normal use of pesticides by farmers [154]. Indeed, secondary poisoning by non-persistent carbamate and OP insecticides has been attributed as the cause of mortality in barn owls (*Tyto alba*), American kestrels (*Falco sparverius*), red-tailed hawks (*Buteo jamaicensis*), great horned owls (*Bubo virginianus*) and bald eagles [36, 150], and it is probably more common than we think because most of the time the victims die without being noticed. The removal of vertebrate predators from an ecosystem leads to similar imbalances as described above for the insect communities in (Fig. 1), encouraging pest rodent species to multiply unrestrained.

Persistent OC residues bioaccumulate in the fatty tissues of all organisms, and are released slowly during periods of fasting or intense flying activity such as during migration [155]. As they are passed on from consumers to predators at the top of the trophic chain, the biomagnification factors can be staggering – up to 10,000 times or more [156]. Not surprisingly, consumption of invertebrates contaminated with OC insecticides causes the death of many insectivorous birds and bats [157], but the sublethal effects from this poisoning are more damaging in the long term. One of the first known impacts of OC insecticides was the reproduction impairment they caused in birds of prey and fish-eating birds, which was felt worldwide in less than two decades, and put some species on the brink of extinction [4]. The case is well documented for DDT, though cyclodiene insecticides like dieldrin produced similar effects [158]. Persistent residues in soil, plant forage, seeds, earthworms and other invertebrates accumulate up the trophic ladder because vertebrates consuming such contaminated foods cannot excrete them. Consequently, predators and scavenger birds concentrate large amounts of DDT in their bodies, where it is transformed into DDE, an equally recalcitrant compound which causes eggshell thinning by altering the calcium metabolism in birds [5]. This unforeseeable effect produced a high mortality of embryos and chicks in birds of prey such as the peregrine falcon (Falco peregrinus), sparrowhawk (Accipiter nisus), kestrels (Falco spp.), Spanish imperial eagles (Aquila adalberti) [159] and many fish-eating birds like herons, cormorants and pelicans [160]. Initially, the reduction in juveniles was compensated by higher reproduction rates because there was less competition for food, until the introduction of cyclodienes years later dealt a fatal blow and populations of raptors started to decline [161]. DDT and many other OC insecticides were banned in most countries during the 1970-80s, but their residues are still out there. Wildlife feeding in areas where DDT was applied for agricultural pest control continues to be affected by the persistent residues [32], which fortunately are now reduced to the point that raptor populations are no longer threatened with extinction and, on the contrary, are slowly recovering [162, 163].

Rodenticides are one of the most common causes of secondary poisoning in bird and mammal predators that feed on the target rodents. In particular the second generation of anticoagulant coumarin rodenticides are very persistent, and

residues ingested with the carcasses of poisoned animals accumulate in the predators' bodies, causing internal or external bleeding and eventually death. Some 70% of the owls collected in Canada between 1988-2003 had residues of at least one rodenticide at levels up to 0.93 mg/kg (brodifacoum) or 1.01 mg/kg (bromadiolone) in their liver [164]. Birds of prey are being increasingly reported dead as a consequence of coumarin poisoning in America [34].

Indirect Effects

Insecticides directly affect insectivorous vertebrates by reducing the insect prey base available to them, whereas herbicides indirectly affect their populations through a variety of pathways, including 1) the direct removal of the food base of granivorous species, 2) reduction in invertebrate abundance by removing the plants that invertebrates depend on for food or habitat, and 3) reduction in vegetative cover necessary for nesting/breeding and reproduction [165].

The best documented evidence of indirect pesticide effects on insects and bird populations is found in the United Kingdom, where declines of grey partridge (Perdix perdix) had been noticed by game hunters and ornithologists for some time - it was rightly attributed to the combined indirect effect of herbicides and insecticides that resulted in breeding failure as a consequence of chick starvation and low survival [90, 166]. Even if other contributing factors such as worm parasites have added to the partridge demise [167], the fact that pesticides are routinely sprayed on cereal and other crops everywhere has indirectly affected the populations of many other bird species as well, which are declining in European countries and North America [168]. Declining bird species (e.g. skylark, corn bunting, etc.) are not associated with particular foods, but with overall reductions in abundance and diversity of plants, seeds and insects [169, 170] resulting from intensive agriculture [171]. Granivorous species feed on cereal grain and seeds of many 'weeds' like knotgrasses (Polygonaceae), chickweeds (Stellaria spp.), goosefoots (Chenopodium spp.), and others, so their decline has been driven primarily by herbicide use and the switch from spring-sown to autumn-sown cereals [172], both of which have massively reduced the food supplies of these birds [173]. However, herbicides are not the only culprits, as other intensive management practices (including TGHT crops) also reduce farmland food and biodiversity. During the breeding season, grasshoppers, sawflies, spiders, leaf-beetles, weevils, butterflies/moths and their larvae, aphids, and crane-flies and their larvae are important foods for insectivorous and omnivorous birds; the first four taxa (which are sensitive to insecticides) are associated with the diet of most declining bird species [174]. Recovery of plant and insect densities can be achieved in a few years once the intensive management practices are abandoned [174], offering hope for the recovery of birds as well. Hedgerows with bushes and trees may also provide protection and nesting places for birds, but first the food supply needs to be restored to levels capable of sustaining their populations. Thus, bird densities and biodiversity can double in corn organic farms compared to conventional corn farms [175], despite some organic crops providing only slightly better food supplies.

It is reasonable to assume a similar fate in small insectivorous mammal and reptile populations, but at present evidence from field studies on these animal taxa is lacking. The fact that many amphibian population declines occur in intensive agricultural areas [176] has alerted some researchers. It appears that a combination of indirect effects from insecticides and herbicides, which introduce a cascade of events affecting negatively the feeding and growth of tadpoles, plus sublethal effects involving trematode infection [45] and other intensive farming practices, such as the use of fertilizers, may account for such declines [146]. However, pesticide-treated rice paddies continue to be a valuable haven for many species of frogs, since herons are not interested in preying in conventional fields because they have less foraging value than organic ones [111].

Apart from farmlands, indirect herbicide impacts are observed in wetlands that receive the outflows of agricultural waters, which often contain residual concentrations of atrazine, diuron and other persistent herbicides. For example, the constant use of herbicides for intensive rice production is thought to have contributed to the elimination of macrophyte vegetation in the lagoons of Ebro delta (Spain) during the 1980s, consequently reducing the populations of diving ducks and coot (*Fulica atra*) that depend on vegetative cover for nesting and feeding [177]. In a controlled experiment, density reductions of cattails (*Typha* spp.) after glyphosate sprays (5.8 L/ha) were well correlated with parallel reductions in the abundance of insectivorous and granivorous birds that depend on those plants for nesting [178]. Many wetland plants can take up and metabolize certain herbicide and insecticide residues found in waters (see Chapter 11), but they are still susceptible to the harmful effects of others. A recent study indicates that even if concentrations of individual herbicides may have a low risk to macrophytes, mixtures of bromacil, diuron, and norflurazon have a high risk [179]. At present, more field data are needed to assess the extent to which submerged

and emergent (cattails, reeds, rushes and sedges) macrophytes in wetlands are exposed to harmful concentrations of herbicide from aerial spraying, drift from ground application, runoff or soil erosion.

CONCLUSIONS

Although evidence indicates that 'conventional' chemically-based agriculture renders higher yields per area than 'organic' traditional practices, this has come at a price – high costs due to chemicals and fuel inputs to produce them [180], and multiple environmental impacts which in the long term can be detrimental [10]. Indeed the 'chemotherapy' applied to agriculture has had many side-effects and one wonders if it can go on forever without destroying the fabric of the biosphere. Here I have focused only on the problems, but an overall assessment must consider the benefits pesticides provide to humanity and the negative environmental consequences of not using them. The latter actions would reduce crop yields and lead to further deforestation in developing countries just to produce the ecological risks of pesticides is an urgent necessity [182, 183]. The use of pheromone traps is, for example, a very effective alternative to control most insect pests, one that does not impact on non-target organisms and cannot induce resistance [184, 185].

This review has shown that impacts of pesticides on soil fertility are almost neutral, although the long-term crop sustainability is questionable [7]. Truly, fungicides protect the crops against certain pathogens but may destroy the beneficial mycorrhizal symbioses that increase nutrient uptake by the plants. Copper fungicides and certain insecticides are detrimental to earthworms and reduce the recycling capacity of the soil; in the end, soil fertility decreases and yields drop slightly.

Impacts on the prevalence of weeds and pests are mixed and negative in many cases. On the one hand, herbicides increase crop yields, but on the other hand they indirectly reduce the biodiversity and abundance of beneficial arthropods that carry out pollination and keep most pest species at bay. Insecticides are then applied to decimate the pests arising naturally under these circumstances, but eliminate the predators and parasitoids; this causes serious destabilizing effects on invertebrate communities which result in the rebound, promotion and increased resistance of all pests. After a few years, such futile efforts to contain the pest populations reach an unbearable cost, which could be avoided if integrated management practices that rely on natural means of weed and pest control were put in place [184, 186]. On the positive side, these effects are short-lived for the majority of the agrochemical products currently in use, so the ecosystem can recover within a year or two following cessation of pesticide application.

Finally, the impacts on terrestrial wildlife vertebrates are clearly negative – the death toll that certain insecticides have annually on non-target bird and small terrestrial vertebrates cannot be overlooked, even if such mortality may not reduce their populations in the long term due to compensatory effects [187]. More serious is the indirect impacts of routinely applied herbicides that cause declining population densities and biodiversity of birds and possibly amphibians. Equally, the secondary poisoning of consumer and predatory birds, reptiles and mammals by ingestion of pesticide-contaminated food is a real and present worry affecting individuals in various ways; unfortunately, long-term impacts on their populations usually take years to be noticed. Significant changes in current policies, institutions and practices are necessary to reconcile biodiversity conservation and food security [183]. The contribution of DDT and other persistent OC insecticides to the local extinction of birds of prey is undeniable, and also a reminder that persistent toxic chemicals should have no place in this world. Indeed, the contamination of the planet's ecosystems with these and other persistent pesticides is an ecological tragedy that will take many decades to be cleaned up.

REFERENCES

- [1] Diamond JM. Germs, Guns and Steel. The Fates of Human Societies. Maryborough, Australia: Penguin; 1997.
- [2] Gabriel KL, Mark R. Environmental toxicology of pyrethrum extract. In: Casida JE, Quistad GB, Eds. Pyrethrum flowers: Production, chemistry, toxicology, and uses. New York: Oxford University Press; 1995. pp. 277-283.
- [3] Oka IN. Success and challenges of the Indonesia National Integrated Pest Management Program in the rice-based cropping system. Crop Protection 1991; 10: 163-165.
- [4] Ratcliffe DA. Decrease in eggshell weight in certain birds of prey. Nature 1967; 215: 208-210.
- [5] Peakall DB. DDE-induced eggshell thinning: an environmental detective story. Environ Rev 1993; 1: 13-20.

- [6] Tomlin CDS. The e-Pesticide Manual. 12 ed. Surrey, U.K.: British Crop Protection Council; 2001-2002.
- [7] Pimentel D, McLaughlin L, Zepp A, *et al.* Environmental and economic effects of reducing pesticide use. BioScience 1991; 41(6): 402-409.
- [8] Baird DJ, Brink PJvd. Using biological traits to predict species sensitivity to toxic substances. Ecotoxicol Environ Saf 2007; 67(2): 296-301.
- [9] Food and Agriculture Organisation of the United Nations. FAOSTAT. 2010 [cited 2010]; Available from: http://faostat.fao.org/site/424/default.aspx#%23ancor
- [10] Pimentel D. Green revolution agriculture and chemical hazards. Sci Total Environ 1996; 188: S86-S98.
- [11] Gianessi LP, Silvers CS. Trends in crop pesticide use: comparing 1992 and 1997: Office of Pest Management Policy, U.S. Department of Agriculture; 2000.
- [12] Voldner E, Li Y. Global usage of selected persistent organochlorines. Sci Total Environ 1995; 160-161: 201-210.
- [13] Vitousek PM, Mooney HA, Lubchenco J, Melillo JM. Human domination of Earth's ecosystems. Science 1997; 277: 494-499.
- [14] Hall FR. Pesticide application technology and integrated pest management (IPM). In: Pimentel D, Ed. Handbook of Pest Management in Agriculture. Boca Raton, FL: CRC Press; 1991.
- [15] Mineau P. Avian Species. In: Plimmer JR, Gammon DW, Ragsdale NN, Eds. Encyclopedia of Agrochemicals. 2003 ed: John Wiley & Sons, Inc.; 2003. pp. 1-27.
- [16] Siebers J, Binner R, Wittich K-P. Investigation on downwind short-range transport of pesticides after application in agricultural crops. Chemosphere 2003; 51(5): 397-407.
- [17] Snoo GRd. Unsprayed field margins: effects on environment, biodiversity and agricultural practice. Landscape Urban Plann 1999; 46: 151-160.
- [18] Jong FMWd, Snoo GRd, Zande JCvd. Estimated nationwide effects of pesticide spray drift on terrestrial habitats in the Netherlands. J Environ Manage 2008; 86(4): 721-730.
- [19] Jong FMWD, Snoo GRD. A comparison of the environmental impact of pesticide use in integrated and conventional potato cultivation in The Netherlands. Agric Ecosyst Environ 2002; 91: 5-13.
- [20] Wang G, Edge W, Wolff J. Response of bobwhite quail and gray-tailed voles to granular and flowable diazinon applications. Environ Toxicol Chem 2001; 20(2): 406-411.
- [21] Elliott JE, Birmingham AL, Wilson LK, et al. Fonofos poisons raptors and waterfowl several months after granular application. Environ Toxicol Chem 2008; 27(2): 452-460.
- [22] Greig-Smith PW. Hazards to Wildlife from Pesticide Seed Treatments. In. Surrey, UK: British Crop Protection Council Monograph; 1987. pp. 127-134.
- [23] Bonmatin JM, Marchand PA, Charvet R, *et al.* Quantification of imidacloprid uptake in maize crops. J Agric Food Chem 2005; 53(13): 5336-5341.
- [24] Floate KD, Wardhaugh KG, Boxall ABA, Sherratt TN. Fecal residues of veterinary parasiticides: non-target effects in the pasture environment. Annu Rev Entomol 2005; 50: 153-180.
- [25] Hewitt AJ, Johnson DR, Fish JD, Hermansky CG, Valcore DL. Development of the spray drift task force database for aerial applications. Environ Toxicol Chem 2002; 21(3): 648-658.
- [26] Driver C, Ligotke M, Van Voris P, *et al.* Routes of uptake and their relative contribution to the toxicologic response of northern bobwhite (*Colinus virginianus*) to an organophosphate pesticide. Environ Toxicol Chem 1991; 10(1): 21-33.
- [27] Gyldenkærne S, Ravn HP, Halling-Sørensen B. The effect of dimethoate and cypermethrin on soil-dwelling beetles under semi-field conditions. Chemosphere 2000; 41(7): 1045-1057.
- [28] Harner T, Bidleman TF, Jantunen LMM, Mackay D. Soil-air exchange model of persistent pesticides in the United States cotton belt. Environ Toxicol Chem 2001; 20(7): 1612-1621.
- [29] Brown AWA. Ecology of Pesticides. New York: John Wiley & Sons, Inc.; 1978.
- [30] Ribeiro S, Guilhermino L, Sousa JP, Soares AMVM. Novel bioassay based on acetylcholinesterase and lactate dehydrogenase activities to evaluate the toxicity of chemicals to soil isopods. Ecotoxicol Environ Saf 1999; 44: 287-293.
- [31] Green K, Broome L, Heinze D, Johnston S. Long distance transport of arsenic by migrating bogong moths from agricultural lowlands to mountain ecosystems. The Victorian Naturalist 2001; 118(4): 112-116.
- [32] Sánchez-Bayo F, Ward R, Beasley H. A new technique to measure bird's dietary exposure to pesticides. Anal Chim Acta 1999; 399: 173-183.
- [33] Ahmad R, Kookana RS, Megharaj M, Alston AM. Aging reduces the bioavailability of even a weakly sorbed pesticide (carbaryl) in soil. Environ Toxicol Chem 2004; 23(9): 2084-2089.
- [34] Stone W, Okoniewski J, Stedelin J. Poisoning of wildlife with anticoagulant rodenticides in New York. J Wildl Dis 1999; 35(4): 187-193.
- [35] Blus LJ, Gish CD, Belisle AA, Prouty RM. Logarithmic relationship of DDE residues to eggshell thinning. Nature 1972; 235: 376-377.

- [36] Mineau P, Fletcher MR, Glaser LC, et al. Poisoning of raptors with organophosphorous and carbamate pesticides with emphasis on Canada, the United States and the United Kigdom. J Raptor Res 1999; 33(1): 1-37.
- [37] Mendelssohn H, Paz U. Mass mortality of birds of prey caused by Azodrin, an organophosphorus insecticide. Biol Conserv 1977; 11(3): 163-170.
- [38] Sawchuk JW, Acker RCv, Friesen LF. Influence of a range of dosages of MCPA, glyphosate, and thifensulfuron: tribenuron (2: 1) on conventional canola (*Brassica napus*) and white bean (*Phaseolus vulgaris*) growth and yield. Weed Technol 2006; 20(1): 184-197.
- [39] Liang TT, Lichtenstein EP. Synergism of insecticides by herbicides: effect of environmental factors. Science 1974; 186: 1128-1130.
- [40] Iwasa T, Motoyama N, Ambrose JT, Roe RM. Mechanism for the differential toxicity of neonicotinoid insecticides in the honey bee, *Apis mellifera*. Crop Protection 2004; 23(5): 371-378.
- [41] Simons SS. Environmental estrogens: can two "alrights" make a wrong? (synergistic chemical reactions boost estrogenlike effects). Science 1996; 272: 1451.
- [42] Deneer JW. Toxicity of mixtures of pesticides in aquatic systems. Pest Manage Sci 2000; 56(6): 516-520.
- [43] Relyea RA. Synergistic impacts of malathion and predatory stress on six species of North American tadpoles. Environ Toxicol Chem 2004; 23(4): 1080-1084.
- [44] Grue CE, Powell GVN, McChesney MJ. Care of nestlings by wild female starlings exposed to an organophosphate pesticide. J Appl Ecol 1982; 19: 327-335.
- [45] Rohr JR, Schotthoefer AM, Raffel TR, et al. Agrochemicals increase trematode infection in a declining amphibian species. Nature 2008; 455: 1235-1239.
- [46] Wang Y-S, Yen J-H, Hsieh Y-N, Chen Y-L. Dissipation of 2,4-D, glyphosate and paraquat in river water. Water Air Soil Pollut 1994; 72(1-4): 1-7.
- [47] Stahl JD, Aust SD. Use of fungi in bioremediation. In: Kuhr RJ, Motoyama N, Eds. Pesticides and the Future. Amsterdam: IOS Press; 1998. pp. 189-194.
- [48] Smith MD, Hartnett DC, Rice CW. Effects of long-term fungicide applications on microbial properties in tallgrass prairie soil. Soil Biol Biochem 2000; 32(7): 935-946.
- [49] Beare MH, Parmelee RW, Hendrix PF, et al. Microbial and faunal interactions and effects on litter nitrogen and decomposition in agroecosystems. Ecol Monogr 1992; 62(1): 569-591.
- [50] Sigler WV, Turco RF. The impact of chlorothalonil application on soil bacterial and fungal populations as assessed by denaturing gradient gel electrophoresis. Appl Soil Ecol 2002; 21(2): 107-118.
- [51] Venkateswarlu K, Al-Garni SM, Daft MJ. The impact of carbofuran soil application on growth and mycorrhizal colonization by *Glomus clarum* of groundnut. Mycorrhiza 1994; 5(2): 125-128.
- [52] Pandey S, Singh DK. Total bacterial and fungal population after chlorpyrifos and quinalphos treatments in groundnut (*Arachis hypogaea* L.) soil. Chemosphere 2004; 55(2): 197-205.
- [53] Zwieten LV, Rust J, Kingston T, Merrington G, Morris S. Influence of copper fungicide residues on occurrence of earthworms in avocado orchard soils. Sci Total Environ 2004; 329(1-3): 29-41.
- [54] Gaw SK, Palmer G, Kim ND, Wilkins AL. Preliminary evidence that copper inhibits the degradation of DDT to DDE in pip and stone fruit orchard soils in the Auckland region, New Zealand. Environ Pollut 2003; 122(1): 1-5.
- [55] Chen S-K, Edwards C, Subler S. Effects of the fungicides benomyl, captan and chlorothalonil on soil microbial activity and nitrogen dynamics in laboratory incubations. Soil Biol Biochem 2001; 33(14): 1971-1980.
- [56] Van Gestel CAM, Koolhaas JE, Schallnass H-J, Rodrigues JML, Jones SE. Ring-testing and field-validation of a Terrestrial Model Ecosystem (TME) – An instrument for testing potentially harmful substances: effects of carbendazim on nutrient cycling. Ecotoxicology 2004; 13(1-2): 119-128.
- [57] Araújo ASF, Monteiro RTR, Abarkeli RB. Effect of glyphosate on the microbial activity of two Brazilian soils. Chemosphere 2003; 52(5): 799-804.
- [58] Kanungo P, Ramakrishnan B, Rao VR. Nitrogenase activity of *Azospirillum* sp. isolated from rice as influenced by a combination of NH4+-N and an insecticide, carbofuran. Chemosphere 1998; 36(2): 339-344.
- [59] Carlisle SM, Trevors JT. Glyphosate in the environment. Water Air Soil Pollut. 1988; 39: 409-420.
- [60] Sannino F, Gianfreda L. Pesticide influence on soil enzymatic activities. Chemosphere 2001; 45(4-5): 417-425.
- [61] Das AC, Debnath A, Mukherjee D. Effect of the herbicides oxadiazon and oxyfluorfen on phosphates solubilizing microorganisms and their persistence in rice fields. Chemosphere 2003; 53(3): 217-221.
- [62] Foissner W. Protozoa as bioindicators in agroecosystems, with emphasis on farming practices, biocides, and biodiversity. Agric Ecosyst Environ 1997; 62(2-3): 93-103.
- [63] Icoz I, Stotzky G. Fate and effects of insect-resistant Bt crops in soil ecosystems. Soil Biol Biochem 2008; 40(3): 559-586.

- [64] Straalen NMv, Rijn JPv. Ecotoxicological risk assessment of soil fauna recovery from pesticide application. Rev Environ Contam Toxicol 1998; 154: 83-141.
- [65] Ripper WE. Effect of pesticides on balance of arthropod populations. Annu Rev Entomol 1956; 1: 403-438.
- [66] Edwards CA, Thompson AR. Pesticides and the soil fauna. Residue Rev 1973; 45: 1-79.
- [67] Michereff-Filho M, Guedes RNC, Della-Lucia TMC, Michereff MFF, Cruz I. Non-target impact of chlorpyrifos on soil arthropods associated with no-tillage cornfields in Brazil. Int J Pest Manage 2004; 50(2): 91-99.
- [68] Koehler HH. The use of soil mesofauna for the judgement of chemical impact on ecosystems. Agric Ecosyst Environ 1992; 40(1-4): 193-205.
- [69] Stark JD. Comparison of the impact of a neem seed-kernel extract formulation, Margosan-O and chlorpyrifos on nontarget invertebrates inhabiting turf grass. Pestic Sci 1992; 36(3): 293-299.
- [70] Edwards CA. Effects of herbicides on the soil fauna. In: Proc. 10th Brit. Weed Control Conf. 1970; 1970. pp. 1052.
- [71] Epstein DL, Zack RS, Brunner JF, Gut L, Brown JJ. Effects of broad-spectrum insecticides on epigeal arthropod biodiversity in Pacific Northwest apple orchards. Environ Entomol 2000; 29(2): 340-348.
- [72] Wiktelius S, Chiverton PA, Meguenni H, *et al.* Effects of insecticides on non-target organisms in African agroecosystems: a case for establishing regional testing programmes. Agric Ecosyst Environ 1999; 75: 121-131.
- [73] Badji CA, Guedes RNC, Silva AA, et al. Non-target impact of deltamethrin on soil arthropods of maize fields under conventional and no-tillage cultivation. J Appl Entomol 2007; 131(1): 50-58.
- [74] Frampton GK. Spatial variation in non-target effects of the insecticides chlorpyrifos, cypermethrin and pirimicarb on Collembola in winter wheat. Pestic Sci 1999; 55(9): 875-886.
- [75] Southwood TRE, Cross DJ. The ecology of the partridge: breeding success and the abundance of insects in natural habitats. J Anim Ecol 1969; 38: 497-509.
- [76] Brooks DR, Clark SJ, Perry JN, et al. Invertebrate biodiversity in maize following withdrawal of triazine herbicides. Proc R Soc Lond B 2005; 272(1571): 1497-1502.
- [77] Martikainen E, Haimi J, Ahtiainen J. Effects of dimethoate and benomyl on soil organisms and soil processes a microcosm study. Appl Soil Biol 1998; 9(1-3): 381-387.
- [78] Foerster B, Garcia M, Francimari O, Roembke J. Effects of carbendazim and lambda-cyhalothrin on soil invertebrates and leaf litter decomposition in semi-field and field tests under tropical conditions (Amazonia, Brazil). European J Soil Biol 2006; 42(S1): S171-S179.
- [79] Iwasa M, Nakamura T, Fukaki K, Yamashita N. Nontarget effects of ivermectin on coprophagous insects in Japan. Environ Entomol 2005; 34(6): 1485-1492.
- [80] Krüger K, Scholtz CH. Lethal and sublethal effects of ivermectin on the dung-breeding bettles *Euoniticellus intermedius* (Reiche) and *Onitis alexis* Klug (Coleoptera, Scarabaeidae). Agric Ecosyst Environ 1997; 61: 123-131.
- [81] Wardhaugh KG, Mahon RJ. Avermectin residues in sheep and cattle dung and their effects on dung-beetle (Coleoptera: Scarabaeidae) colonization and dung burial. Bull Entomol Res 1991; 81(3): 333-339.
- [82] Kryger U, Deschodt C, Davis ALV, Scholtz CH. Effects of cattle treatment with a fluazuron pour-on on survival and reproduction of the dung beetle species *Onthophagus gazella* (Fabricius). Vet Parasitol 2007; 143(3-4): 380-384.
- [83] Niño EL, Sorenson CE, Washburn SP, Watson DW. Effects of the insect growth regulator, methoprene, on *Onthophagus taurus* (Coleoptera: Scarabaeidae). Environ Entomol 2009; 38(2): 493-498.
- [84] Ingham E, Parmelee R, Coleman D, Crossley DJ. Reduction of microbial and faunal groups following application of streptomycin and captan in Georgia no-tillage agroecosystems. Pedobiologia 1991; 35(5): 297-304.
- [85] Ishibashi N, Kondo E, Ito S. Effects of application of certain herbicides on soil nematodes and aquatic invertebrates in rice paddy fields in Japan. Crop Protection 1983; 2(3): 289-304.
- [86] Bünemann EK, Schwenke GD, Zwieten LV. Impact of agricultural inputs on soil organisms—a review. Aust J Soil Res 2006; 44(4): 379-406.
- [87] Capowiez Y, Bérard A. Assessment of the effects of imidacloprid on the behavior of two earthworm species (Aporrectodea nocturna and Allolobophora icterica) using 2D terraria. Ecotoxicol Environ Saf 2006; 64(2): 198-206.
- [88] Clements RO, Bentley BR, Jackson CA. The impact of granular formulations of phorate, terbufos, carbofuran, carbosulfan and thiofanox on newly sown Italian ryegrass, *Lolium multiflorum*. Crop Protection 1986; 5(6): 389-394.
- [89] Way MJ, Scopes NEA. Studies on the persistence and effects on soil fauna of some soil-applied systemic insecticides. Ann Appl Biol 1968; 62: 199-214.
- [90] Tarrant KA, Field SA, Langton SD, Hart ADM. Effects on earthworm populations of reducing pesticide use in arable crop rotations. Soil Biol Biochem 1997; 29: 657-661.
- [91] Schlueter H, Boettcher W, Bastian O. Vegetation change caused by land-use intensification examples from the Hilly Country of Saxony. GeoJournal 1990; 22(2): 167-174.

- [92] Sullivan TP, Sullivan DS. Vegetation management and ecosystem disturbance: Impact of glyphosate herbicide on plant and animal diversity in terrestrial systems. Environ Rev 2003; 11(1): 37-59.
- [93] Wardle D, Nicholson K, Bonner K, Yeates G. Effects of agricultural intensification on soil-associated arthropod population dynamics, community structure, diversity and temporal variability over a seven-year period. Soil Biol Biochem 1999; 31(12): 1691-1706.
- [94] Krooss S, Schaefer M. The effect of different farming systems on epigeic arthropods: a five-year study on the rove beetle fauna (Coleoptera: Staphylinidae) of winter wheat. Agric Ecosyst Environ 1998; 69: 121-133.
- [95] Cerdà A, Jurgensen MF. The influence of ants on soil and water losses from an orange orchard in eastern Spain. J Appl Entomol 2008; 132(4): 306-314.
- [96] Ali AD, Reagan TE. Vegetation manipulation impact on predator and prey populations in Louisiana (USA) sugarcane ecosystems. J Econ Entomol 1985; 78(6): 1409-1414.
- [97] Mensah RK. Development of an integrated pest management programme for cotton. Part 2: Integration of a lucerne/cotton interplant system, food supplement sprays with biological and synthetic insecticides. Int J Pest Manage 2002; 48(2): 95-105.
- [98] Richards AJ. Does low biodiversity resulting from modern agricultural practice affect crop pollination and yield? Ann Botany 2001; 88(2): 165-172.
- [99] Heard TA. The role of stingless bees in crop pollination. Annu Rev Entomol 1999; 44: 183-206.
- [100] Greig-Smith PW, Thompson HM, Hardy AR, et al. Incidents of poisoning of honeybees (Apis mellifera) by agricultural pesticides in Great Britain 1981-1991. Crop Protection 1994; 13: 567-581.
- [101] Butler CD, Beckage NE, Trumble JT. Effects of terrestrial pollutants on insect parasitoids. Environ Toxicol Chem 2009; 28(6): 1111-1119.
- [102] Kobori Y, Amano H. Effects of agrochemicals on life-history parameters of *Aphidius gifuensis* Ashmead (Hymenoptera: Braconidae). Appl Entomol Zool 2004; 39(2): 255-261.
- [103] Theiling KM, Croft BA. Pesticide side-effects on arthropod natural enemies: a database summary. Agric Ecosyst Environ 1988; 21(3-4): 191-218.
- [104] Way MJ, Heong KL. The role of biodiversity in the dynamics and management of insect pests of tropical irrigated rice a review. Bull Entomol Res 1994; 84: 567-587.
- [105] Griffiths JT, Thompson WL. The use of DDT on citrus trees in Florida. J Econ Entomol 1947; 40: 386-388.
- [106] Pickett AD. Pesticides and the biological control of arthropod pests. World Rev Pest Control 1962; 1: 19-25.
- [107] Hardin MR, Benrey B, Coll M, et al. Arthropod pest resurgence: an overview of potential mechanisms. Crop Protection 1995; 14: 3-18.
- [108] Fitt GP. An Australian approach to IPM in cotton: integrating new technologies to minimise insecticide dependence. Crop Protection 2000; 18: 793-800.
- [109] Wadhwa S, Gill RS. Effect of Bt-cotton on biodiversity of natural enemies. J Biol Control 2007; 21(1): 9-15.
- [110] Kobayashi T, Noguchi Y, Hiwada T, Kanayama K, Maruoka N. [Studies on the arthropod associations in paddy fields with particular reference to insecticidal effects on them. Part 3: Effect of insecticide application on the faunistic composition of arthropods in paddy fields]. Kontyuu 1978; 46(4): 603-623.
- [111] Mesléard F, Garnero S, Beck N, Rosecchi E. Uselessness and indirect negative effects of an insecticide on rice field invertebrates. Comptes Rendus Biologies 2005; 328(10-11): 955-962.
- [112] Bambaradeniya CNB, Edirisinghe JP, Silva DND, et al. Biodiversity associated with an irrigated rice agro-ecosystem in Sri Lanka. Biodiversity Conserv 2004; 13(9): 1715-1753.
- [113] Shelton AM, Andaloro JT, Hoy CW. Survey of ground dwelling predaceous and parasitic arthropod in cabbage fields in upstate New York, USA. Environ Entomol 1983; 12(4): 1026-1030.
- [114] Liang W, Beattie G, C. A, Meats A, Spooner-Hart R. Impact on soil-dwelling arthropods in citrus orchards of spraying horticultural mineral oil, carbaryl or methidathion. Aust J Entomol 2007; 46(1): 79-85.
- [115] Kennedy PJ, Conrad KF, Perry JN, et al. Comparison of two field-scale approaches for the study of effects of insecticides on polyphagous predators in cereals. Appl Soil Ecol 2001; 17(3): 253-266.
- [116] Gibbons DW, Bohan DA, Rothery P, et al. Weed seed resources for birds in fields with contrasting conventional and genetically modified herbicide-tolerant crops. Proc R Soc Lond B 2006; 273(1596): 1921-1928.
- [117] Prischmann DA, James DG, Wright LC, Snyder WE. Effects of generalist phytoseiid mites and grapevine canopy structure on spider mite (Acari: Tetranychidae) biocontrol. Environ Entomol 2006; 35(1): 56-67.
- [118] Tsitsilas A, Stuckey S, Hoffmann AA, Weeks AR, Thomson LJ. Shelterbelts in agricultural landscapes suppress invertebrate pests. Aust J Exp Agric 2006; 46(10): 1379-1388.

- [119] Drapela T, Moser D, Zaller JG, Frank T. Spider assemblages in winter oilseed rape affected by landscape and site factors. Ecography 2008; 31(2): 254-262.
- [120] Thompson HM. Behavioural effects of pesticides in bees-their potential for use in risk assessment. Ecotoxicology 2003; 12(1): 317-330.
- [121] Mineau P, Harding KM, Whiteside M, et al. Using reports of bee mortality in the field to calibrate laboratory-derived pesticide risk indices. Environ Entomol 2008; 37(2): 546-554.
- [122] Decourtye A, Armengaud C, Renou M, et al. Imidacloprid impairs memory and brain metabolism in the honeybee (Apis mellifera L.). Pestic Biochem Physiol 2004; 78(2): 83-92.
- [123] Tonhasca A, Byrne DN. The effects of crop diversification on herbivorous insects: a meta-analysis approach. Ecol Entomol 1994; 19: 239-244.
- [124] Wilby A, Villareal SC, Lan LP, Heong KL, Thomas MB. Functional benefits of predator species diversity depend on prey identity. Ecol Entomol 2005; 30(5): 497-501.
- [125] Sánchez-Bayo F, Baskaran S, Kennedy IR. Ecological Relative Risk (EcoRR): another approach for risk assessment of pesticides in agriculture. Agric Ecosyst Environ 2002; 91: 37-57.
- [126] Walker CH. Neurotoxic pesticides and behavioural effects upon birds. Ecotoxicology 2003; 12(1): 307-316.
- [127] Hall RJ, Henry PFP. Assessing effects of pesticides on amphibians and reptiles: status and needs. Herpetol J 1992; 2: 65-71.
- [128] Mineau P. Estimating the probability of bird mortality from pesticides sprays on the basis of the field study record. Environ Toxicol Chem 2002; 21(7): 1497-1506.
- [129] Snoo GRd, Scheidegger NMI, Jong FMWd. Vertebrate wildlife incidents with pesticides: a European survey. Pestic Sci 1999; 55(1): 47-54.
- [130] Ludke JL, Hill EF, Dieter MP. Cholinesterase (ChE) response and related mortality among birds fed ChE inhibitors. Arch Environ Contam Toxicol 1975; 3(1): 1-21.
- [131] Hall RJ, Donald R. Clark J. Responses of the iguanid lizard Anolis carolinensis to four organophosphorus pesticides. Environ Pollut A 1982; 28: 45-52.
- [132] Henny CJ, Blus LJ, Kolbe EJ, Fitzner RE. Organophosphate insecticide (famphur) topically applied to cattle kills magpies and hawks. J Wildl Manage 1985; 49(3): 648-658.
- [133] Berrill M, Bertram S, McGillivray L, Kolohon M, Pauli B. Effects of low concentration of forest-use pesticides on frog embryos and tadpoles. Environ Toxicol Chem 1994; 13(4): 657-664.
- [134] Galindo JC, Kendall RJ, Driver CJ, T.E. Larcher J. The effect of methyl parathion on susceptibility of bobwhite quail (*Colinus virginianus*) to domestic cat predation. Behav Neural Biol 1985; 43: 21-36.
- [135] Fry DM. Reproductive effects in birds exposed to pesticides and industrial chemicals. Environ Health Perspect 1995; 103(S7): 165-171.
- [136] Fluetsch KM, Sparling DW. Avian nesting success and diversity in conventionally and organically managed apple orchards. Environ Toxicol Chem 1994; 13(10): 1651-1659.
- [137] Beldomenico P, Rey F, Prado W, et al. In ovum exposure to pesticides increases the egg weight loss and decreases hatchlings weight of *Caiman latirostris* (Crocodylia: Alligatoridae). Ecotoxicol Environ Saf 2007; 68(2): 246-251.
- [138] Schauber EM, Edge WD, Wolff JO. Insecticide effects on small mammals: influence of vegetation structure and diet. Ecol Appl 1997; 7(1): 143-157.
- [139] Wang G, Edge W, Wolff JO. A field test of the quotient method for predicting risk to *Microtus canicaudus* in grasslands. Arch Environ Contam Toxicol 1999; 36(2): 207-212.
- [140] Barrett GW, Darnell RM. Effects of dimethoate on small mammal populations. Am Midland Nat 1967; 77: 164-175.
- [141] Manning T. Endocrine disrupting chemicals a review of the state of the science. Australas J Ecotoxicol 2005; 11(1): 1-52.
- [142] Jefferies DJ. Induction of apparent hyperthyroidism in birds fed DDT. Nature 1969; 222: 578-579.
- [143] Bishop CA, Boermans HJ, Ng P, Campbell GD, Struger J. Health of tree swallows (*Tachycineta bicolor*) nesting in pesticide-sprayed apple orchards in Ontario, Canada. II. Sex and thyroid hormone concentrations in testes development. J Toxicol Environ Health A 1998; 55(8): 561-581.
- [144] Sughrue KM, Brittingham MC, French JB. Endocrine effects of the herbicide linuron on the American goldfinch (*Carduelis tristis*). Auk 2008; 125(2): 411-419.
- [145] Sinha N, Lal B, Singh TP. Pesticides induced changes in circulating thyroid hormones in the freshwater catfish *Clarias batrachus*. Comp Biochem Physiol C 1991; 100(1-2): 107-110.
- [146] Mann RM, Hyne RV, Choung CB, Wilson SP. Amphibians and agricultural chemicals: review of the risks in a complex environment. Environ Pollut 2009; 157(11): 2903-2927.
- [147] Colborn T. Epidemiology of Great Lake bald eagles. Environ Health Perspect 1991; 33: 395-453.

- [148] Guillette LJ, Gross TS, Masson GR, et al. Developmental abnormalities of the gonad and abnormal sex hormone concentrations in juvenile alligators from contaminated and control lakes in Florida. Environ Health Perspect 1994; 102(8): 680-688.
- [149] Heinz GH, Percival HF, Jennings ML. Contaminants in American alligator eggs from Lake Apopka, Lake Griffin, and Lake Okeechobee, Florida. Environ Monit Assess 1991; 16: 277-285.
- [150] Elliott JE, Wilson LK, Langelier KM, Mineau P, Sinclair PH. Secondary poisoning of birds of prey by the organophosphorus insecticide, phorate. Ecotoxicology 1997; 6(4): 219-231.
- [151] Wheeler WB, Jouvenaz DP, D.P W, et al. Mirex residues in nontarget organisms after application of 10-5 bait for fire ant control, northeast Florida – 1972-74. Pestic Monit J 1977; 11: 146-156.
- [152] Walker CH. Biochemical biomarkers in ecotoxicology some recent developments. Sci Total Environ 1995; 171(1-3): 189-195.
- [153] Sánchez J, Fossi M, Focardi S. Serum B esterases as a nondestructive biomarker in the lizard *Gallotia galloti* experimentally treated with parathion. Environ Toxicol Chem 1997; 16(9): 1954-1961.
- [154] Tarazona JV. Geographical differences in the evaluation and protection of the effects of pesticides. In: Liess M, Brown C, Dohmen P, et al., Eds. Effects of Pesticides in the Field. Berlin: SETAC Press; 2005. pp. 102-104.
- [155] Kunisue T, Minh TB, Fukuda K, et al. Seasonal variation of persistent organochlorine accumulation in birds from Lake Baikal, Russia, and the role of the south Asian region as a source of pollution for wintering migrants. Environ Sci Technol 2002; 36(7): 1396-1404.
- [156] Hop H, Borgá K, Gabrielsen GW, Kleivane L, Skaare JU. Food web magnification of persistent organic pollutants in poikilotherms and homeotherms. Environ Sci Technol 2002; 36(12): 2589-2597.
- [157] Guillén A, Ibáñez C, Pérez JL, et al. Organochlorine residues in Spanish common pipistrelle bats (*Pipistrellus pipistrellus*). Bull Environ Contam Toxicol 1994; 52(2): 231-237.
- [158] Cooke AS. Shell thinning in avian eggs by environmental pollutants. Environ Pollut 1973; 4: 85-152.
- [159] Hernández M, González LM, Oria J, Sánchez R, Arroyo B. Influence of contamination by organochlorine pesticides and polychlorinated biphenyls on the breeding of the Spanish imperial eagle (*Aquila adalberti*). Environ Toxicol Chem 2008; 27(2): 433-441.
- [160] Albanis TA, Hela D, Papakostas G, Goutner V. Concentration and bioaccumulation of organochlorine pesticide residues in herons and their prey in wetlands of Thermaikos Gulf, Macedonia, Greece. Sci Total Environ 1996; 182: 11-19.
- [161] Sibly RM, Newton I, Walker CH. Effects of dieldrin on population growth rates of sparrowhawks 1963–1986. J Appl Ecol 2000; 37(3): 540-546.
- [162] Kirk DA, Hyslop C. Population status and recent trends in Canadian raptors: a review. Biol Conserv 1998; 83(1): 91-118.
- [163] Newton I, Wyllie I. Recovery of a sparrowhawk population in relation to declining pesticide contamination. J Appl Ecol 1992; 29: 476-484.
- [164] Albert CA, Wilson LK, Mineau P, Trudeau S, Elliott JE. Anticoagulant rodenticides in three owl species from Western Canada, 1988–2003. Arch Environ Contam Toxicol 2010; 58(2): 451-459.
- [165] O'Connor RJ. Indirect effects of pesticides on birds. In: Brighton Crop Protection Conference: Pest and Diseases, 1992; 1992.
- [166] Potts GR. The Partridge Pesticides, Predation and Conservation. London, UK: Collins; 1986.
- [167] Coghlan A. Killer pheasants. New Scientist 1999; 162(2180): 25.
- [168] Peakall DB, Carter N. Decreases in farmland birds and agricultural practices: a huge ecotoxicological experiment. Toxicol. Ecotoxicol. News 1997: 162-163.
- [169] Hart J, Murray AWA, Milsom TP, et al. The abundance of farmland birds within arable fields in relation to seed density. Aspects Appl Biol 2002; 67: 221-228.
- [170] Boatman ND, Brickle NW, Hart JD, et al. Evidence for the indirect effects of pesticides on farmland birds. Ibis 2004; 146(s2): 131-143.
- [171] Ewald JA, Aebischer NJ. Trends in pesticide use and efficacy during 26 years of changing agriculture in Southern England. Environ Monit Assess 2000; 64: 493-529.
- [172] Moreby SJ, Southway S, Barker A, Holland JM. A comparison of the effect of new and established insecticides on nontarget invertebrates on winter wheat fields. Environ Toxicol Chem 2001; 20(10): 2243-2254.
- [173] Newton I. The recent declines of farmland bird populations in Britain: an appraisal of causal factors and conservation actions. Ibis 2004; 146: 579-600.
- [174] Wilson J, Morris A, Arroyo B, Clark S, Bradbury R. A review of the abundance and diversity of invertebrate and plant foods of granivorous birds in northern Europe in relation to agricultural change. Agric Ecosyst Environ 1999; 75(1-2): 13-30.

- [175] Beecher N, Johnson R, Brandle J, Case R, Young L. Agroecology of birds in organic and nonorganic farmland. Conserv Biol 2002; 16(6): 1620-1631.
- [176] Davidson C. Declining downwind: amphibian population declines in California and historical pesticide use. Ecol Appl 2004; 14(6): 1892-1902.
- [177] Mañosa S, Mateo R, Guitart R. A review of the effects of agricultural and industrial contamination on the Ebro delta biota and wildlife. Environ Monit Assess 2001; 71(2): 187-205.
- [178] Linz G, Blixt D, Bergman D, Bleier W. Responses of red-winged blackbirds, yellow-headed blackbirds and marsh wrens to glyphosate-induced alteration in cattail density. J Field Ornithol 1996; 67(1): 167-176.
- [179] Schuler LJ, Rand GM. Aquatic risk assessment of herbicides in freshwater ecosystems of South Florida. Arch Environ Contam Toxicol 2008; 54(4): 571-583.
- [180] Pimentel D, Hepperly P, Hanson J, Douds D, Seidel R. Environmental, energetic, and economic comparisons of organic and conventional farming systems. BioScience 2005; 55(7): 573-582.
- [181] Brown LR. Outgrowing the Earth. New York: W.W. Norton & Company; 2004.
- [182] Rice PJ, Hapeman CJ, McConnell LL, et al. Evaluation of vegetable production management practices to reduce the ecological risk of pesticides. Environ Toxicol Chem 2007; 26(11): 2455-2464.
- [183] Brussaard L, Caron P, Campbell B, et al. Reconciling biodiversity conservation and food security: scientific challenges for a new agriculture. Curr Opin Environ Sustain 2010; 2(1-2): 34.
- [184] Witzgall P, Kirsch P, Cork A. Sex pheromones and their impact on pest management. J Chem Ecol 2010; 36(1): 80-100.
- [185] Yadav IS, Reddy PP, Rawal RD, Verghese A. Current pest problems in fruit crops and future needs. Indian J Plant Protection 1999; 27(1-2): 109-125.
- [186] Way MJ, Emden HFv. Integrated pest management in practice pathways towards successful application. Crop Protection 2000; 19: 81-103.
- [187] Forbes VE, Sibly RM, Calow P. Toxicant impacts on density-limited populations: a critical review of theory, practice, and results. Ecol Appl 2001; 11(4): 1249-1257.