Chapter

Why Airborne Pesticides Are So Dangerous

Tomaz Langenbach, Tácio M.P. de Campos and Luiz Querino Caldas

Abstract

More than four billion of tons of pesticides are used annually in agriculture worldwide. Part of it drifts down after pulverization, but a volatilized portion moves upwards. Pulverized pesticide applications are controlled by different parameters of fan and climate conditions. This can be mitigated with buffer zones, hedgerows and forest strips. Volatilization is determined by physicochemical parameters of the product and adsorption capacity to soils and leaves, and climate conditions. Prevention is the only efficient approach by banning high vapor pressure active ingredients. Volatilized pesticides are transported by air streams. Subsequently products are retained by mountains or eventually moved further by wind and descend in rain returning them to soil or vegetation. All regions of the planet are submitted to air pollution and nowadays pristine environments are very rare. These pollutants have hazardous effects on environment and toxic effects to skin and when they reach the blood stream directly via the lungs, are more intense to humans than from ingestion. The challenge of this overview highlights sustainability to avoid airborne pesticides by different strategies such as reduction of amounts sprayed through integrated pest management and mainly replacement of hazardous chemical pesticides by harmless ones or by biological control.

Keywords: pesticides airborne, air pollution, pulverization, volatilization, pesticide drift

1. Introduction

Before we trace the sinuous movement with hazardous effects of pesticides in the air, we need to take in account that humankind up to the twentieth century was threaten by hunger due to many factors including loss of agriculture production by pests [1]. Only by the control of essential factors of agricultural production as soil fertilization, dryness and pest management was it possible to get food security. Hunger today is addressed mainly to economic and political questions.

The first intensively used product was the insecticide DDT developed by Paul Muller at beginning of the 1940s, followed by new products applied as fungicides, acaricides, nematicides and bactericides [2]. Finally, the exclusion of herbs that compete for natural resources with crops, had changed from mechanical to chemical methods by herbicides. These processes dramatically increase productivity with less land used and resulted in intense migration of the rural population to the cities [3]. Herbicides in many countries now constitute about 50% of the amount of pesticide used.

The mechanism of action of insecticides [4] and fungicides [5] are highly active on animal cells and therefore the toxic effects are generally high in humans and fauna. Many of the active mechanisms of herbicides inhibition act on plant and algae physiology like photosynthesis, hormones, and others [6], but other molecules that inhibit electron chains in plants are also very dangerous to humans and other animals. Poisoning side effects have been identified for many pesticides. The criteria of mutagenicity and carcinogenic were more required. The toxic effects are more permanent from persistent molecules, so biodegradation is one of the most important parameters in ecotoxicology [7].

The hazardous effects of pesticides in the environment were first denounced by Carlson with publication of "Silent spring" in 1962 [8]. Their deleterious effects have been sensed dramatically and increasing along with the chaotic shifts provoked in nature, fauna, and flora. The repercussion and significance of its effects in the natural history of our planet remains to be assessed.

After 1970, in the USA the "Environment Protection Agency" (EPA) organized the first registration process to control all pesticides some of which were banned or restricted, particularly, the most hazardous [9]. Later many countries created similar agencies. The legal requirements include physical–chemical parameters of the active ingredients of the pesticides that give information about volatility capacity, an important tool to restrict the use of the worst of them. In this process many other parameters were considered such as biodegradation/persistence, effects on non-target forms of life, and acute and chronic toxicology.

The increase and decrease of airborne particles in the environment follow the history of the pesticides not only in quality but also in quantity. The figures of worldwide consumption have increased (**Figure 1**). This process was started in developed countries and followed in developing countries. Control by banning of many products has occurred differently among countries, but in the overall the amount increased about 80% between 1990 and 2018 [10]. We are far from reaching sustainability in the pest control even in the countries with the best management.

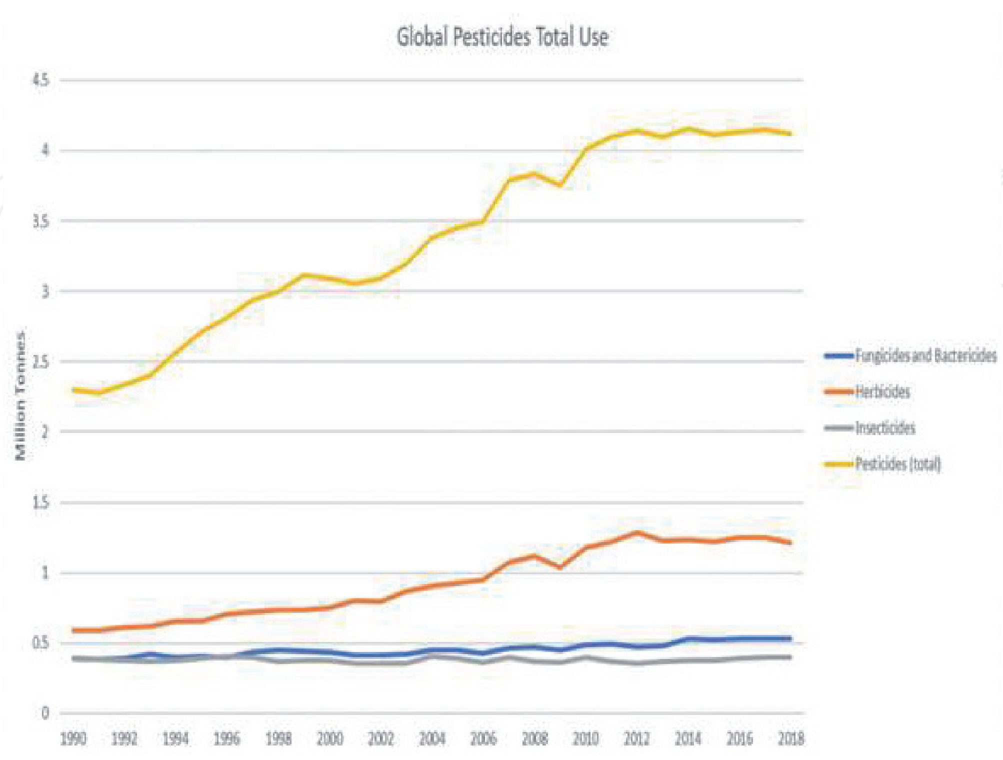

Figure 1.
Global pesticides use over 1990–2018.

The fate of airborne pesticides has some peculiarities: more disperse movement than those in polluting the whole world's water bodies [11, 12]; air movements are not under human control and the uptake by animals put them in direct contact with skin and blood. The purpose in this chapter is not only to describe airborne movement and the hazardous effects of pesticides, but also to identify new approaches in technical and management science that can overcome the bottlenecks toward sustainability.

2. How pesticides pollute air

Pulverization is a human decision of what, when, were and for what pests the pesticides will be applied. However, the step of volatilization in which molecules change to gas phase and are released into the air following application. Products with high volatilization are out of human control with scarce possibilities of mitigation.

2.1 Pulverization

Pesticides can be applied as dry powders that were mainly used in the past, as granules to control ants and other insects but the most frequent pesticide application is in water. In this form spraying can pollute air and is likely to drift to non-target areas. The modalities are wettable powder, emulcifiable concentrate and dilution of the commercial product in water for application.

Pulverization can be performed in different forms directly down to the soil, on the canopy of orchards or by floating for sanitary functions to control mosquitos. The efficiency of the methods used generally involves high amounts of loss to non-target forms of life in the environment. This process involves many parameters as fan position depending where the pests are in the soil, on upper leaf surface or on the underside of the leaves. The fan pressure is important for pesticide to arrive at the pest area and with high pressure directed toward the soil to reduce drift. Drop size higher than 5 u diameter weigh more than air and move down by gravity [13]. Smaller drops can float in the air. Climate conditions of wind speed and direction have important influence on the spraying through drift. All these parameters need to be considered for pesticide spraying.

The worst situation is of poor farmers using knapsack or pump with hose application in which the operator moves into the pesticide cloud with an enormous level of pesticide exposure [14]. Individual protection equipment in many instances are not used due to hot climate conditions and the protection itself has limits when using for longer periods. The use of tractors is much better because it moves away from the cloud and in tractors with a cabin the protection is quite good. The worst exposure to human populations that live in the countryside is spray from airplanes, forbidden in many countries or regions.

2.2 Volatilization

This process is when the active ingredient of the pesticide change to the gaseous phase and move upward into the atmosphere. Up to 0.5 cm above soil surface the molecules move only by dispersion while in the upper air layers gradual increase the wind speed and, in turbulence, mix this process these gases into the air [15]. Volatilization of each active ingredient depends on the physical–chemical conditions, mainly vapor pressure and Henri's Constant Law (partition of a substance between water and gas phase), strongly integrated with climate conditions. The highest volatilization rate occurs after rain followed by high temperatures due to Henri's Law. These conditions occur frequently in tropical areas.

Pesticide spraying is directed to soil or to vegetation for pest control. First, we begin with soil. In a report of different substances exposed under the same conditions shows that at low vapor pressure of less than 10^{-3} Pascals (Pa) no volatilization occurs, but after this value the increase is strong with amounts that can reach 90% of the pesticide sprayed. Volatilization on leaves with lower vapor pressure begins at 10^{-5} Pa and can arrive at high values from using higher Pa [15]. This parameter can be very useful to restrict dispersal of high volatile pesticides.

3. Factors influencing volatilization

Volatilization depends on the physical chemical properties of the active ingredient, climate, adsorption by surface, agriculture management and the interrelation between these factors. The humidity of the climate influences this residue adsorption, under dry conditions adsorption is more intensive and volatilization reduced [16, 17]. In **Table 1** climate and management factors influencing soil and leaf pesticide adsorption resulted in different amounts of volatilization [18].

Pesticide adsorbed on soil is a process in which aging is an important factor and this process can be reversible. Binding by entrapment and covalent bounding often occurs only after long contact time. Adsorption reduces the number of free molecules and therefore reduces the bioavailability that allows the molecule to eliminate pests. Likewise, adsorption can reduce the toxicity of the molecule and reduce free movement to leach or to volatilize. In practice, this is usually measured by adsorption of Freundlich isotherms or others [19]. The literature describes many different binding forms of pesticides depending strongly on the chemical characteristics of each product and soil composition as are mentioned below [20].

Covalent bonding – the pesticide reacts with some soil molecules resulting in a new substance that mischaracterize the pesticide. It is a strong chemical bounding.

Ionic charge - Compounds and their metabolites adsorbed by ionic bonding, or cation exchange, exist either in the cationic form in solution or can be protonated and become cationic.

Hidrogen bonding - Pesticide molecules compete with water for the binding sites on humic substances. H-bonding is suggested to play a vital role in the adsorption of several non-ionic polar pesticides,

Electron donor or acceptor complex - is a transfer of electron to acceptor pesticides with a part of humic substance that donated this electron. The resulting electrostatic attraction provides a stabilizing force for the molecular complex.

Climate conditions		**Pesticide on soil**	**Pesticide on leaves**
Temperature		10° C increase <3 to 4 times Pa > volat.	high temp. > volat.
Air humidity	Dry	> adsorption < volat.	> adsorption < volat.
	Dew	morning / late afternoon > volat.	
	Rain	leaching + enhanced > volat.	washout + penet. < volat.
Wind		> wind > volat.	> wind > volat.
		> turbulence > volat.	> turbulence > volat.
Pesticide management		**Pesticide in soil**	**Pesticide in leaves**
Small drop pulverization		less water < volat.	quick evaporation
Big drop pulverization		more water > volat.	faster adsorption

Table 1.
Parameters that influence pesticide volatilization from soil and leaves.

Van der Walls forces - is a distance-dependent interaction between atoms or molecules. Unlike ionic or covalent bonds, these attractions do not result from a chemical electronic bond; they are comparatively weak and therefore more susceptible to disturbance.

Hidrophobic partition - Hydrophobic retention need not be an active adsorption mechanism but can also be regarded as a partitioning between a solvent and a non-specific surface.

Pesticides in soil are adsorbed in part by strong binding energy different than for plants in which the main adsorption occurs by hydrophobic partition, a much weaker binding.

Most pesticide applications are on the plants which have quite different chemical composition than soil. Covering the epidermal cells of leaves, a domain called the cuticular layer is rich in polysaccharides (**Figure 2**) enriched with waxes (which are hydrophobic, *i.e.* repel water). These wax deposits inside the cutin matrix are called intracuticular. On the surface, the cutin is covered with a film and epicuticular wax crystals that give the leaf a glossy appearance [21].

Figure 3a shows the dynamics of the fate of parathion volatilization, leaf penetration, and photo-degradation after spraying. In **Figure 3b** the fate of chlorotanoyl during an experiment where rain washed it from leaves to the ground [22].

In experiments with parathion and chlorotanoyl pulverization the fate of these molecules on the leaves is traced (**Figure 3**) showing the residue amounts on the leaves, volatilized, penetration of the cuticle and the photo-transformed quantities. More than twenty percent of the applied amount of Parathion was volatilized with the vapor pressure of 8.9 x 10^{-4} Pa and chlorotanoyl with lower vapor pressure of 7.6 x 10^{-5} Pa volatilized about 5%.

Volatilization of parathion is fast with high volatilization in the first day and strong reduction in the following period (**Figure 4a**). For chlorotanoyl the amounts per day are much smaller and the volatilization process gradually reduces (**Figure 4b**). In both cases no volatilization occurs during the night and residue volatilization is higher than for commercial products showing that formulation can reduce volatilization [23].

In all the figures obtained by SURFATM-Pesticides volatilization did not occur at night. High sensitivity of the model was shown for vapor pressure to promote volatilization and the constant of the relation octanol/water K_{ow} for the penetration in the wax layer of the leave. More recently models were developed that integrate pesticide volatilization on leaves and soil [24].

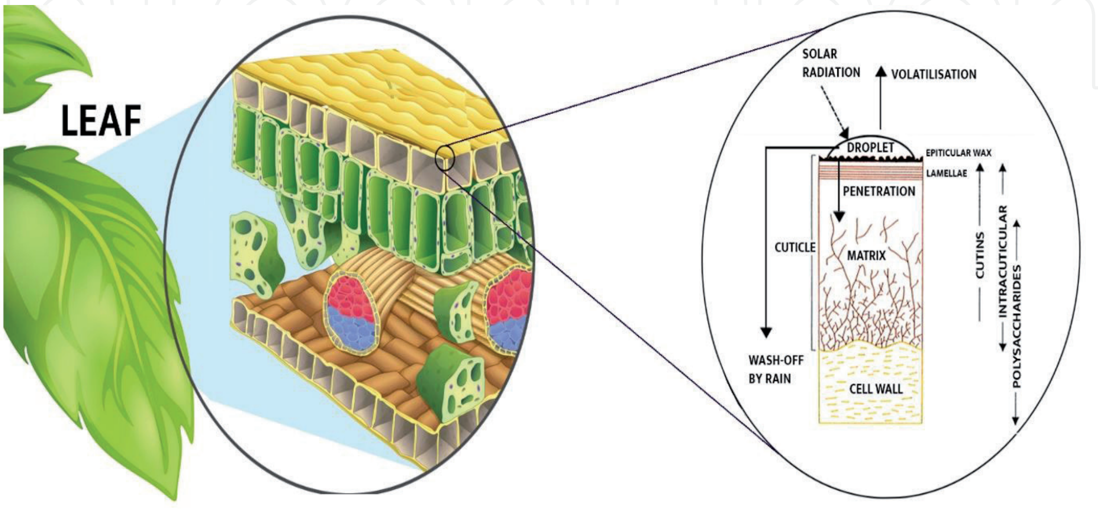

Figure 2.
The different process on fate of pesticide drops above leaves that are exposed to volatilization; photo-transformations; wash-off by rain and penetration on waxes. In focus is the cuticle with the wall (yellow) of upper epidermis.

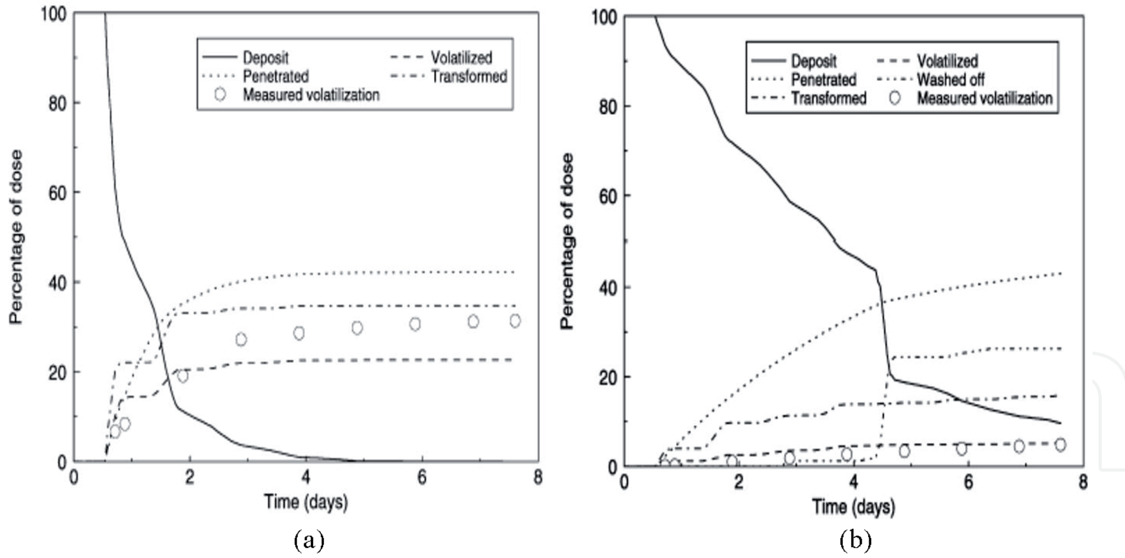

Figure 3.
(a) Decline of parathion and chlorotanoyl deposit on leaves, accumulation of volatilization, penetration into the plant and phototranformation in a computer program PEARL. The cumulative volatilization derived from measurements is plotted against (O). (b) Application was shortly after noon on the first day. For the chlorotanoyl experiment, the rain reduced residues by wash-off of 20% from the leaves.

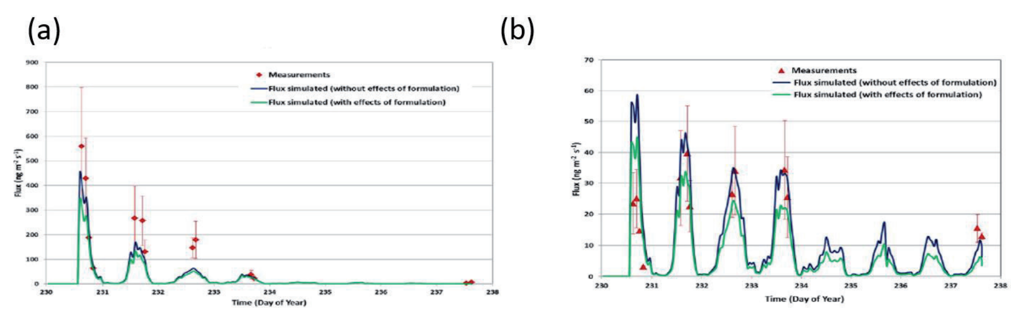

Figure 4.
Comparison of measured and modeled data by PEARL flux volatilization. Simulated without and with formulation: (a) parathion, and (b) chlorothalonil. The error bars represent the standard deviations based on the two measurement methods (AG and BR methods).

4. Prevention and mitigation of airborne pesticides

Many possibilities exist to mitigate pesticide pollution by spray drift. Directing the fan on the intended target to exclude as much general dispersion to non-target areas as possible. Some countries and in many cases, counties, cities and villages enforce buffer strips around the border in which spray is prohibited resulting in strong reduction of drift [25, 26]. This strip generally is about 10 m wide but can also be more. For small farms, these strips reduce the spraying area and land use. In such cases hedgerows of appropriate size can be used to mitigate drift pollution to neighbors or residential areas [27]. Every binding of residues can restrict volatilization. All wind break constructions as outdoor and indoor walls can retain pesticides [28]. Depending on the binding strength of the residues, they may escape to the air over time [29]. Indoor pollution with pesticides is a major problem by continuous exposure rural living habitants. In this case children are severely exposed by the hand to mouth movements [30]. Another possibility is to retain in hedgerows or forest strip to protect humans and environment [31].

Prevention of volatilization could be done by excluding all products with high vapor pressure. Mitigation can have some effects to preserve buildings and small villages when protected by a forest strip. Experiments have shown that riparian forest are able to retain volatilized pesticide residues on the canopy that by rain washing or leaf senescence move down to the soil [31, 32]. Phytoremediation with genetically modified poplar trees with introduction of Citochrome P450, shows that thrichloroethilene can be adsorbed by leaves and degraded efficiently [33]. In large scale pesticide dispersion up to remarkably high atmosphere altitudes are completely out of human control and no mitigation is possible. As a response to climate conditions, it is possible to change pesticide application management. Experiments in which sets of samples of the herbicide 2,4-D were applied in morning and then at 18 h in the evening showed samples from the afternoon volatilization were 9 to 30% less than when applied in the morning when measured 24 h after application [34]. These results suggest that dry soil in the afternoon adsorbed more residues yielding reduced volatilization as observed by others [35]. The best application management is to exclude loss factors as strong adsorption, photo degradation and volatilization mainly in the first period of application and this will occur at night [23, 36]. During this time residues need to have high bioavailability to act on the pest. Under these conditions it is possible to greatly reduce the amount of pesticide without efficiency loss.

5. Dynamics of pesticides in the air

After volatilization of pesticides from soil, leaves or water, these molecules move upward and through turbulence to arrive as a quite homogeneous mixture. Residues can move up and down powered by air streams following the directions of wind currents. The main deposition of pesticides are due to rain and snow. This occurs more frequently on mountains. When pesticides are airborne and arrive high altitudes, they can be transported for long-distances. Residues were found more than 50 years ago in the Antarctic [11]. This was due to wind and rain/snow deposits, but not from human activities. Pesticide residues coming from other regions were found recently on the top of the Itatiaia mountains in the State of Rio de Janeiro (Brazil) [12]. Much evidence shows that airborne pesticides arrive with impact in all environments around the world giving little chance of pristine environment without pesticides existing.

Photo-degradation occurs not only in the air but also on all kinds of surfaces exposed to solar irradiation. Many photo reactions are by direct action on molecules causing degradation while others have indirect effect in which some substances absorb photons and with this energy promote transformation reactions in other molecules. These processes have been shown to be a relevant pathway. The setup of laboratory conditions in which the experiments occur is very diversified and influence the reactions with different intensity [37].

Much of the airborne pesticide burden is removed from the atmosphere through deposit by rain in ocean and that could be considered as a sink. Nevertheless, the reverse movement in which pesticides volatilize to air occur also. The relative intensity of these two movements is expressed by the fugacity ratio $\left(\frac{fa}{fw}\right)$ of pesticide in air to the amount in the water. This define if the process is predominantly of deposition or volatilization [38]. Data show that some pesticides reduce fugacity rate with increase in surface water at higher latitudes (around 70° North) in the Arctic Ocean like a cold trap [39]. Persistent organochlorines compounds after long-range transport from the application site, pollute pristine environments as the artic in which the ecosystem is more vulnerable than those species on which risk assessment is based [40].

The fate of pesticides shows that all kinds of movements occur from air to soil/plants, to water and the reverse movement between all these environments. All flora and fauna are exposed to these residues in the air, but it is important to differentiate environments between high and low airborne pesticides as rural areas with intensive agriculture activity with cities and areas with little agriculture. In humans the toxicologic effects can be due to ingestion or to air pollution, but unprotected agricultural workers are exposed to high risk of acute toxic effects from pesticides.

6. Pesticides in environment and health

6.1 Air pollution in the environment

The potential degradation and accumulation of hazardous substances in the atmosphere of newly formed compounds within the environment are still quite unknown because of an enormous variety of possibilities generated by abnormal climatic conditions and anthropic actions around the globe [14]. When major, hard to predict, recurrent crucial environmental damages occur, they may irreversibly affect nature. Changes in its delicate balance that generally demand decades or centuries to recover, if they do at all. For instance, if the predator–prey relationship is severely disturbed due to the persistent exposure to airborne pesticides, it raises deep ecological changes in the local biota.

In humans, mammals, and reptiles we should pay special attention to the action of pesticides in two hormonal structures: gonadal and thyroid, because during the development, these glands (organs) are especially sensitive and, therefore, affected by exposure of low concentrations of sex steroids and thyroid hormones. It is recognized that there is a difference in the endocrine response of adults as compared to the embryonic/fetal/neonatal responses. Changes induced by exposure to these hormones during development are often irreversible, in contrast to reversible changes induced by exposure to transient hormones in adults [41]. Hayes and his coworkers [42–44], have studied isolated atrazine and a mixture of nine pesticides, on the impact in the environment, as an endocrine interfering factor. Examined larvae growth and development, sexual differentiation, and immune function in leopard frog found hormonal changes in sexual differentiation, body development and damage to the thymus resulting in immunosuppression. They concluded that the evaluation of each pesticide alone is inadequate to estimate the adverse impact on amphibian development or to link pesticides to the decline in the number of amphibians, as blends of pesticides provoked more effects than the isolated components.

In humans, apart from the bare skin exposure (explained further on), the lungs mainly of those occupationally exposed, usually remain the major cause of infirmities and the number of deaths among agricultural workers. Also, cancer and some effects in the endocrine system cannot be ignored [45–47].

6.2 Pesticides in the lungs

Inhalation of various volatile forms of aerosols, vapors, dust, or mist can be the source of respiratory diseases in agricultural workers, particularly for those without proper personal protective equipment or when they work in confined spaces. The main outcomes observed were bronchial asthma (BA), chronic obstructive pulmonary disease (e.g. emphysema) and lung cancer [48]. As explained below, the etiopathogenesis varies, some of them affecting the lung clearance by the mucocilliary tracheobronchial cells system, others affecting the bronchiolar smooth muscles physiology, or else destroying alveolar walls, burdening pneumocytes. Some pesticide molecules may deeply affect the oxygen supply and, therefore, will interfere with the exchange of carbon dioxide, the body's metabolic by-product. This, ultimately and decisively, will interfere in the metabolic turnover, and not rarely, leading to death.

In an average-sized person at rest, the O_2:CO_2 ratio is 1.25 (250 ml:200 ml/min) whereas when incrementing metabolic activity (e.g. exercise), the oxygen demand as well as concurrently its by-product CO_2 increases in order to preserve the body homeostasis. The bronchial ducts and alveolar sacs serve to conduct fresh air into the lungs (inhalation) where active gas exchange occurs between the environment and blood pressure gradients determine the gas exchange from the opposite direction, breathing out the body by-products. In the latter situation, the pulmonary ventilation rate may increase 20% with higher exposure to airborne pesticide.

Droplets larger than 10 μm are deposited in the upper respiratory tract (nose and mouth). The toxic effects of pesticides start as the air breathed in enters through the nose and contacts the sinus cavities where it irritates the fragile membranes and in response may lead to an inflammatory reaction with glands secreting significant mucous production which may ultimately become infected. When coarse particles (>5 μm) reach the upper respiratory tract, they are usually trapped into the conducting airways whereas fine (<0.2–5 μm) particles (such as pesticide drops) are deposited by impact and sedimentation (**Figure 5**). Other molecules may be adsorbed so that material dissolved in solvents or water vapor (hygroscopic) may get into contact with the airways ducts or alveolar septum with a 80–120-ml monolayer of blood.

That is, when these compounds provoke repeated cycle oxidation/reduction reactions generating toxic amounts of reactive oxygen species it can lead to diffuse pulmonary alveolitis culminating in a rampant acute or chronic fibrosis and, possibly, death [50].

This storm of clinical symptoms results in a profound change in the acid–base homeostatic mechanisms that lead to acidaemia, obnubilation culminating with convulsions and death. Supposedly, clean air, free from foreign substances, humidified and regulated to the body temperature must reach the alveoli where potentially injurious substances such as the airborne pesticides are in close contact with the alveolar system. In the tracheobronchial tree, smooth muscle spasms will resemble an asthmatic response.

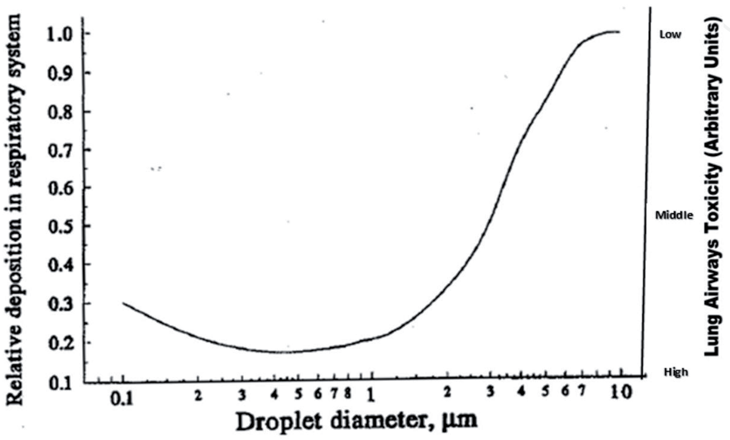

Figure 5.
Effect of aerodynamic diameter on deposition efficiency of inhaled droplets in human respiratory system and their reversal arbitrarily toxicity for the lungs adapted from Giles et al. [49].

6.3 Other systemic effects of airborne pesticides

The cutaneous hypersensitivity resulting from intimate contact of pesticides with the skin and/or the eyes since many spray adsorbent formulas can be seized and absorbed through the tissues.

Oxidative stress can be involved in many pathological conditions in the lungs and in the skin. It may alter irreversibly causing cell damage that evokes changes in proteins or DNA structures [51, 52] as well as mitochondrial disorders that lead to antioxidant enzyme suppression as dismutase and superoxidase [53]. Some compounds provoke repeated cyclic oxidation/reduction reactions generating toxic amounts of reactive oxygen species that can lead to diffuse pulmonary alveolitis culminating in a rampant acute or chronic fibrosis with possible, death [50].

7. Perspectives

Our focus here is on the future perspective of airborne pesticides. Airborne pesticide pollution can only be solved when sustainable products of pest control substitute harmful for harmless pesticides. The 1962 book Silent Spring of Carlson [8] was the first dramatic announcement of problems in flora and fauna due to pesticides use. After almost six decades no one, even the most pesticide-concerned countries, can commemorate agriculture with sustainable pest control [54]. In this period progress occurred with: the introduction of a registration process to ban the most hazardous pesticides worldwide; list of the worst products to be banned by the International conference of Stockholm 1972; introduction of the "International Code of Conduct on Pesticide Management" sponsored by FAO/WHO for a better practice of pesticide use; many scientific international conferences to improve technical advances and better policies of pesticide control and organic agriculture increased. It is difficult to know if the balance of these positive actions can overcome the hazardous exposure of environment and human health due to the enormous increase of pesticides used in the last decades. The conclusion is that we are far from the main target of sustainability in agriculture to avoid poisoning exposure but Improvement of sustainability would be a benefit in health, environment and social development [55].

The highly bureaucratic agencies of pesticide control together with the industrial interest shared with agricultural producers make the use of pesticides a steady state that does not promote progress toward sustainability due to the hegemonic economic interest. Approaching sustainability cannot achieved by banning of hazardous pesticides alone. Sustainability of pest control can be reached when applied pesticides are specific and not highly toxic to humans and to flora and fauna because of ecotoxic effects on non-target forms of life. An additional essential characteristic is to be completely biodegraded with no residue accumulation in the environment.

The new perspective for that is the intense use of recently developed biopesticides that can control insects, fungi, and nematodes efficiently. A lack of data makes it difficult to evaluate the intensity of use of these products up to now, but it seems that it was not very much. This demands a new specific policy to promote and push these changes to agriculture practice. To overcome the bottle neck of the few organic herbicides available, the most applied products, scientific advances with focus of new products with different approaches as allelopathic chemicals or development of reduction of herb populations by strategies of agriculture management or development of other solutions.

To arrive at sustainability all tools from restriction and banning of pesticides, integrated management supported by remote sensing [56] and the new approaches of nanotechnology [57], code of conduct of pesticide management and biopesticides, need to be used. This is a difficult task in which scientific development and information, creativity, flexibility and political will of the stakeholders, are essential.

Finally, a scenario in which hazardous chemical pesticides are substituted by non-hazardous organic control in a sustainable agriculture, would stop the introduction of more pesticides in the air. Nevertheless, to eliminate the huge amount of residual pesticides in the air, time would necessary to promote biodegradation, photo-transformation and covalent bounding to soil or other molecules, condition necessary to gradual elimination of these products from our environment.

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