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Pesticide Tank Mixes: An Environmental Point of View

Valdemar Luiz Tornisielo, Rafael Grossi Botelho,
Paulo Alexandre de Toledo Alves,
Eloana Janice Bonfleur and
Sergio Henrique Monteiro

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1. Introduction

During the last decades, human activity has affected the aquatic and terrestrial ecosystems' sustainability. None of these activities has damaged the environment as severely as agricultural practices.

Current agricultural practices have negatively affected aquatic and terrestrial ecosystems by destroying habitats, deforesting to increase cropping areas and applying pesticides.

Pesticides are a heterogeneous category of chemical products destined to pest, disease and weed control including several types, such as insecticides, fungicides, herbicides, nematicides and others.

Nowadays, such chemical product applications have been considered the most efficient plant protection procedures and have significantly contributed to the improvement of crop productivity.

Nevertheless, the claimed objective of supplying the population with enough food does not justify damaging the environment, just because small quantities of pesticides are known to efficiently control pests, diseases and weeds. However, most of them are rapidly spread out affecting all living beings (flora and fauna, including humans).

The use of chemical molecules in agriculture increased after the Second World War with the advent of DDT (dichloro-diphenyl-trichloroethane). DDT was discovered in 1939 by Paul Müller (Swiss entomologist) and its worldwide use was rapidly expanded due to its large

action range, low cost and efficiency in the control of tropical disease vectors, such as typhoid fever and malaria [1].

After the release of DDT, a large range of molecule groups destined to crop protection were developed and commercialized. In 1962, the book "Silent Spring" was the first act of environment manifest against DDT, describing the bird population decrease (from the top of the food chain) attributed to its indiscriminate use.

After the 1960's, the use of chemical products in agriculture rapidly increased and it was associated with the appearance of environmental and human health problems.

The frequent and incorrect use of pesticides have caused soil, atmosphere, food and water resource (superficial/underwater) contaminations, negatively affecting aquatic and terrestrial organisms as well as frequently causing toxicity to the human population.

Therefore, studies are urgently needed to make environmental monitoring procedures viable in order to detect potential contamination risks and give support to public actions for environmental safety and agriculture sustainability.

Currently, product mixtures (associations between one or more molecules) are applied in agriculture instead of individual molecules; therefore, previous studies that focused on only one molecule should now consider molecule mixtures.

The existence of such a large variety of pests, diseases and weeds affecting yields have led farmers to use product mixtures, aiming at efficiently managing crop protection. Such mixtures, also called product associations, enter the environment in a different way compared to the individual product application. Thus, more studies are required about these mixture-environment interactions and possible interactions between molecules and consequent interferences in the environment.

Although mixtures have been intensively studied concerning their agronomic efficacy, little information is found about their implications on environmental safety.

In this chapter, the tank mixture subject is approached from an environmental point of view, explaining the chemical product mixture interactions and the possible contaminant effects. Studies on the product-environment interactions are presented to provide the main available information as support to future studies and decisions in environmental sustainability and safety.

2. Agronomic characteristics of tank mixtures

Tank mixtures are associations among two or more chemical products (pesticides) or among chemical products and fertilizers in a unique tank for application in crops. This practice is common in Australia, Canada, U.S.A and United Kingdom, where there are recommendations on application procedures, incompatibilities, and safety [2].

Concerning agricultural practices, the tank mixture of two or more chemical products might be a good application strategy, saving fuel and labor-hours, causing less soil compaction, and

possibly providing a larger pest control range and efficacy, when compared to the single product application. For these reasons, this technique is preferred by farmers [3].

Nevertheless, the herbicide mixture might induce, for instance, interactions before or after reaching the target-plant, by altering the product action in synergistic, antagonistic or additive ways. One common practice is the simultaneous application of herbicides with and without residual effect in order to increase the weed species control range and/or the control period. Another practice is the addition of adjuvants to improve herbicide performance to control weeds. The simultaneous application of pesticides (concerning the species-target to be controlled) might induce undesirable (antagonistic, synergistic or additive) reactions, depending on the herbicide type and plant species [4]. When the mixture induces an antagonistic reaction, it means that a lower weed control action than expected is observed. When the mixture induces a synergistic reaction, it means that a higher weed control than expected is observed. And, finally, when the mixture induces an additive reaction, it means that no change in weed control is observed.

Several studies have elucidated the questions about synergistic and antagonistic effects of active ingredient mixtures on weed control, for instance, the studies with glyphosate reported by Vidal et al. [4], Shaw and Arnold [3], Selleck and Baird [5].

The application of pesticides plus adjuvants has also been a usual practice. The adjuvant enhances the active ingredient action [6]. In other words, the adjuvant substance induces the herbicide molecule uptake by leaf tissues, by accelerating the product penetration through plant cuticles. The most common types are the biosurfactants, mineral or vegetal oils, synthetic or natural polymers, humectants, organic salts, buffer solutions, and others [7].

The tank mixture practice or different individual pesticide applications at short intervals might result in multiple pesticide residues on foods, as observed by Gebara et al. [8], when monitoring food samples in São Paulo metropolis, Brazil, during the period between 1994 and 2001. The authors found multiple pesticide residues in 5.8% of vegetable samples analyzed and 11.4% of fruit samples.

Gebara et al. [9] alerted for the violation risk of the Theoretical Maximum Dietary Intake (TMDI), which is calculated by the relationship between the Limit of Maximum Residues (LMR, mg kg^{-1}) established for a pesticide in a food and the daily consumption (DC, kg day^{-1}), based on the individual diet. The presence of multiple pesticide residues in foods due to the use of tank mixtures, might lead to the extrapolation of toxicological parameters for the acceptable daily intake (ADI), mainly for children and nursing women.

3. Pesticide tank mixtures environmental effects

3.1. Soil

Weed control with pesticide tank mixtures has been widely studied concerning mixture effectiveness, component antagonism and/or synergism. However, there is little information on environmental issues.

Knowledge on soil-herbicide interactions when herbicide mixtures are applied is extremely relevant. However, few studies on herbicide associations and their soil interactions can be found, because most studies are restricted to the individual molecule behavior.

When a pesticide is released in the environment, it will probably enter the soil by direct application, or indirectly, by crop residue incorporation into the soil and molecule transport by spraying derivation. In the soil, several processes might occur, that is, molecule retention (adsorption, absorption), transformation (decomposition, degradation) and transport (spraying derivation, volatilization, lixiviation, superficial runoff). Such processes will determine the molecule destiny, persistence and agronomic efficiency. The main factors influencing those processes are the climatic conditions, the pesticide physical-chemical properties and the soil physical-chemical attributes. According to Oliveira [10], the complex molecule retention process by soil sorption/desorption directly or indirectly influences other factor activities.

Knowledge on pesticide physical-chemical properties is fundamental to predict soil interactions, potential contamination and transport risks when in the soil solution or associated to sediments. Studies on pesticide mixtures have been restricted to their phytotoxicity effects and few were dedicated to the interactions between two or more associated molecules.

Alves [11] demonstrated that ametryn mineralization half-life is longer when associated to glyphosate than when applied alone; but there was a synergistic effect in the soil, because ametryn half-life was 15 days for the ametryn + glyphosate mixture and 20 days for isolated ametryn in the soil. In the same study, the author observed increased glyphosate mineralization half-life from 55 to 119 days, when comparing single glyphosate and glyphosate + ametryn treatments, respectively; the glyphosate soil half-life could not be determined due to its strong soil sorption during extractions.

Yet in studies of soil microbial activity, Alves [11] observed that glyphosate (at a higher rate) enhanced microbial activity; meanwhile isolated ametryn (at a lower rate) negatively affected microbial activity, but a less negative effect of ametryn + glyphosate mixture (at a lower rate) was observed compared with single ametryn at the same rate. The ametryn + glyphosate mixture (at a higher rate) increased the microbial activity, evidencing a stronger mixture synergistic effect.

Alves [11] also studied the herbicide sorption/desorption in a red Ultisol. High glyphosate and low ametryn sorption were observed when herbicides were applied alone. Higher soil sorption was observed for both herbicides in mixture than for the single molecules. Low glyphosate desorption occurred at all rates in both application procedures (alone or in mixture), but ametryn desorption decreased when applied in mixture.

White et al. [12] studied the effects of chlorothalonil, tebuconazole, flutriafol and cyproconazole fungicides on the metolachlor herbicide dissipation kinetics. Significantly lower metolachlor dissipation was observed with chlorothalonil, when compared with soil treatments without chlorothalonil or with other fungicides. The authors observed significant reduction in metolachlor metabolites probably attributed to the fungicide effect on glutathione S-transferase enzyme activity. Overall, chlorothalonil fungicide induced a two-fold increase in metolachlor persistence.

Ke-Bin et al. [13] observed that atrazine and bentazon herbicides showed longer lag-phase and lower degradation rate when applied in tank mixture in a maize crop. Therefore, the association of atrazine-bentazon had longer soil persistence which means that higher environmental potential contamination risks might be expected.

The effect of glyphosate on atrazine degradation was studied by Krutz et al. [14] in a silt clayey soil (pH 8.3 and 10.6 g kg⁻¹ of organic-C) from the Texas region in USA. Atrazine degradation was inversely related to glyphosate rate and microbial activity during an eight-day period, evidencing that glyphosate enhanced microbial activity and inhibited atrazine degradation. The authors discussed that atrazine degradation, when in association, is mainly a microbial mechanism, and the degradation reduction might be explained by a lower enzymatic activity and/or by microbial population suppression by glyphosate.

Similar results were reported by Haney et al. [15] for the same soil type, demonstrating the atrazine and glyphosate effects on soil microbial activity evaluated through the soil carbon (C) and nitrogen (N) mineralization. Soil plots treated with the herbicide mixture showed higher microbial activity than plots treated with single atrazine. The evaluated soil C and N flows allowed understanding of the microbial preference for glyphosate because this herbicide's complete mineralization occurred in 14 days, followed by fast atrazine degradation.

Zablotowicz et al. [16] studied the effects of glufosinate (herbicide), ammonium sulfate (fertilizer) and both products in mixture on atrazine mineralization. The authors observed decreased atrazine mineralization when the product mixture was applied. The authors explained that an alteration in ¹⁴C-atrazine molecule partition into its metabolites and residues would occur caused by ammonium sulfate that would restrict the triazine ring cleavage. Such results evidenced that the application of glufosinate combined to a mineral N source might increase soil atrazine persistence, increasing its residual effect.

Lancaster et al. [17] observed that glyphosate increased soil C mineralization and fluometuron microbial degradation. The authors suggested that the increasing C mineralization might be related to the increasing fluometuron degradation or to a priming glyphosate effect.

Concerning the glyphosate and diflufenican association, Tejada [18] observed longer degradation periods for both herbicides in mixture than for the individual molecules. Furthermore, the glyphosate-diflufenican association increased both herbicide toxicities to the soil biological activity (measured by the microbial C biomass and enzyme activities - dehydrogenase, urease, β -glycosidase, phosphatase and arylsulfatase) and the individual herbicide persistence.

Pereira et al. [19] evaluated the application of isolated glyphosate and associated to endosulfan on the soil microbial activity in soybeans and observed reduced microbial activity and biomass, and also, reduced metabolic quotient.

In genetically modified glyphosate-tolerant maize cultivars, it is possible to mix glyphosate and atrazine. In the USA, there are a number of commercially available associations, among them, glufosinate or glyphosate mixed with atrazine [20]. Bonfleur et al. [21] observed that glyphosate mineralization was not affected by atrazine presence in a tropical soil. However, increased atrazine mineralization (measured by the ¹⁴CO₂ release) was observed with increas-

ing glyphosate rates. The authors observed a 100-day variation in the atrazine half-life when associated with a two-fold glyphosate rate. Therefore, the glyphosate-atrazine tank mixture allowed atrazine persistence reduction in the soil. The authors said that a possible explanation is the glyphosate contribution to the microorganisms as source of N, and this N supply might decrease the initial atrazine immobilization when this is the only substrate, and then, increasing its mineralization.

Fogg and Boxall [22] observed inhibitory effects of an isoproturon-chlorothalonil mixture on the isoproturon degradation in soils. Isoproturon half-life (DT50) values varied from 18.5 to 71.5 days when combined with chlorothalonil. This might be explained by the TPN-OH chlorothalonil metabolite inhibition and the reduction in the soil microorganism population involved in isoproturon degradation.

The soil degradation of pendimethalin (herbicide) was significantly reduced when mixed with mancozeb (fungicide) or mancozeb+thiamethoxam (insecticide) [23]. Pendimethalin herbicide half-life increased from 26.9 to 62.2 days when in single and combined (mancozeb + thiamethoxam) applications, respectively, in a sandy soil. On the other hand, the same authors observed that pendimethalin degradation is not affected by the presence of isolated metribuzin or thiamethoxam.

Several studies have pointed out the adjuvant influence on pesticide destiny in the environment, specifically their persistence and bioavailability. Cabrera [24], in laboratory studies, affirmed that metazachlor herbicide added to oil and surfactant showed reduced degradation rates and increased residues in the soil. Similar results to other pesticides were reported by Kucharski and Sadowski [25] and Rodríguez-Cruz et al. [26]. In a field experiment, Kucharski et al. [27] observed a 43% increase in lenacil herbicide residues in the superficial soil layer, with the addition of adjuvants (oil and surfactant).

High mobility pesticides used together with adjuvants present decreased movement along the soil profile. Reddy and Singh [28] evaluated bromacil and diuron herbicides lixiviation in soil columns. In treatments with adjuvant addition, the authors observed significant lower bromacil vertical movement and no effect on diuron movement. These two herbicides present distinct physical-chemical characteristics that explain their differential movement abilities in the soil. Thus, bromacil is an acidic molecule with high water solubility (815 mg L^{-1}); meanwhile diuron is a non-ionic herbicide of low water solubility (42 mg L^{-1}). From the environmental point of view, the adjuvant effect was positive in the case of bromacil, but the agronomic efficacy was restricted.

The results found in the literature have highlighted the interactions existing among several molecules, especially in the soil, but such interactions might be different under other environment compartments. For this reason, studies on environmental pesticide behavior and destination must include all aspects, bringing together laboratory and field approaches.

3.2. Water: An ecotoxicological approach for pesticide mixtures

According to Botelho et al. [29], water resource contamination has currently been considered one of the greatest environmental problems on Earth.

Pesticides applied to field crops are released in the environment mainly through lixiviation (when molecules move into the soil and reach the underground waters), superficial runoff (when molecules move together with soil and water runoff), and spraying derivation (when molecules are carried by wind during pesticide spraying).

The situation is complex once crop diversity allied to the high number and diversity of pesticide products usually applied to field crops, and the short distances between fields and aquatic areas have exposed the water resources not only to individual products but also to all their associations [30].

Several products, mainly herbicides and insecticides, are common superficial water contaminants, due to their large application in agriculture and residential areas. Therefore, there is an increasing concern about superficial and underground water contamination, due to the lack of information on pesticide impacts mainly in aquatic systems.

In Brazil, several studies have been carried out to determine the presence of pesticides in aquatic ecosystems. Armas et al. [31] evaluated the presence of herbicides in the superficial water and sediments of Corumbataí River (State of São Paulo, Brazil). The authors found several herbicides - ametryn, atrazine, simazine, hexazinone, glyphosate and clomazone – and triazines were specifically found in higher levels, above the limits allowed for potable water by Brazilian legislation. Dores et al. [32] found herbicide residues from the triazine group and their metabolites, as well as metribuzin, metolachlor and trifluralin residues. Among the Brazilian literature, the research works of Caldas et al. [33], Lanchote et al. [34], Filizola et al. [35], Laabs et al. [36], Dores et al. [37], Jacomini et al. [38] are pointed out.

Other interesting results can be found in the literature: Benvenuto et al. [39] determined the presence of eleven pesticides in superficial waters of Italy and Spain and observed concentration values varying between 0.002 and 0.087 $\mu\text{g L}^{-1}$. Yu et al. [40] determined the presence of nine (among eleven pesticides evaluated) herbicides of the triazine group in all water samples analyzed. Similar determinations were made by Ma et al. [41], Palma et al. [42], Balinova and Mondesky [43] and Segura et al. [44].

Understanding of how pesticides affect aquatic environments has been a challenge to researchers, and the science of ecotoxicology has helped to answer many questions on this subject.

The “ecotoxicology” term was first suggested by the French toxicologist René Truhaut, during the *Committee of the International Council of Scientific Unions (ICSU)* meeting, in June 1969, in Stockholm (Sweden) [45]. According to this author, Ecotoxicology is the science that studies the effects of natural or synthetic substances on living beings, populations and communities, animal or vegetal, terrestrial or aquatic, constituting the biosphere, including the substance interaction with the environment where they live in an integrated context [46].

Usually, ecotoxicological experiments follow standardized protocols developed by international organizations, for example, the Environmental Protection Agency (EPA); the Organization for Cooperation and Economical Development (OCDE); and the Brazilian Agency of Technical Norms (ABNT).

The toxicity tests allow evaluating the environmental contamination by different pollutant sources, such as agricultural, industrial and domestic residues, sediments, medicines and chemical products overall, as well as the results of their synergistic and antagonistic effects [47-48]. The ecotoxicological tests can also detect the toxic agent or mixture capacity of causing deleterious effects on living organisms, allowing determination of the harmful concentration ranges, and how and where the effects are expressed [49].

Several parameters have been used to determine the xenobiotic effects in different organisms. Among these variables, the lethality [50-51], immobility [52], gill alterations [53-56], and reproduction [57-59] are pointed out.

The ecotoxicological experiments consist of exposing living organisms to several concentrations of a specific product and evaluating the results that might be expressed according to the test type. For instance, the acute test consists of short-term exposure of organisms to several product concentrations, and then, the species life cycle is evaluated; the toxicity indicative parameters more frequently used are: lethality (expressed by the average lethal concentration - LC_{50}), and immobility (expressed by the observable toxic concentration effect - EC_{50}). It is important to highlight that both parameters take into consideration the effects for 50% of the organisms tested under the specific experiment conditions [60-61]. In the case of a chronic test, the organism is submitted to long-term product exposure and the observable effects are usually focused on organism reproduction, behavior, morphology, and size, among others.

Water quality tests have been important tools aiming to minimize the pollution effects on aquatic ecosystems and to implement remediation and monitoring programs, and for that, the ecotoxicological tests have been used.

In the case of pesticide mixtures, the ecotoxicological tests to determine toxicity effects are difficult to interpret, because toxicity symptoms might depend on interactions occurring among different chemical molecules in solution and their accumulative quantities in organisms [61].

When analyzing mixture toxicity effects, some approaches and definitions must be established. In the aquatic ecotoxicology, two different models have been used to describe the relationships between single compound effects and their mixtures: concentration addition model (CA) and independent action model (IA) [62]. In the CA model, each mixture component toxicity effect is induced through a same mechanism, meanwhile in the IA model, the combined components show different actions, inducing a unique toxicological response, but via distinct reactions within the organisms [63]. Nevertheless, both models are used as references to predict the expected mixture toxicity effect, based on the known toxicity of the individual compounds [62].

For a long time, there has been concern about mixture impacts on aquatic ecosystems, not only from pesticides but also from other compound groups, and several discussions and reviews have been reported. In 1984, Hermens and collaborators investigated organic mixture effects on mortality and reproduction of *Daphnia magna* microcrustacean, after exposure to 14 products with different modes of action. The authors observed more severe toxicity effects on mixture-treated organisms than with individual products, although the chronic test results with the mixture showed less severe symptoms [64]. Strmac and Braunbeck [65] observed

several structure and biochemical alterations in rainbow trout hepatocytes submitted to a 20-component mixture, including pesticides. Delorenzo and Serrano [66] evaluated the effects of atrazine (herbicide), chlorpyrifos (insecticide) and chlorothalonil (fungicide) on the *Dunaliella tertiolecta* algae growth; the results of atrazine - chlorpyrifos mixture showed an additive toxicity pattern, meanwhile atrazine - chlorothalonil mixture showed a synergistic effect. Yet, the authors observed a two-fold higher toxicity effect of atrazine – Chlorothalonil mixture than the individual products. Choung et al. [67] observed that relatively high atrazine rates increased the terbufos (insecticide) toxicity to *Ceriodaphnia dubia* microcrustacean.

4. Final remarks

Pesticide tank mixtures are currently and frequently used not only in developed countries with specific regulatory legislation for the practice, but also in all agricultural countries where information on harmful effects do not directly reach farmers.

From the agronomic point of view, an effective pest control with pesticide mixtures will depend on the molecule compatibility and also on specific control tests. When the farmer uses two chemically incompatible substances in tank mixture, high losses in crop yield and equipment problems might occur, for example, sprayer nozzle obstruction due to chemical reaction between molecules and subsequent compound precipitation.

Although the pesticide tank mixture may appear to be an efficient pest control practice with synergistic results, the aspects concerning environmental safety must be considered. Little specific information on associated pesticide residues is available in the literature concerning withholding periods and overall environmental behavior.

When a single pesticide is applied, the expected environmental results should be similar to previous results reported for the pesticide registration and before its commercial release. The environment (mainly aquatic and soil medium) is a large contaminant reservoir, where the chemical compounds used in agriculture can be found together. In spite of that, it is important to reinforce that a single pesticide interacts quite differently with the medium, compared to the mixture interaction, as already discussed in this chapter.

In light of the large global demand for food and the increasing crop productivity in the same cropping area, it is imperative to consider the environmental safety questions concerning tank chemical mixture applications in agriculture.

This is a relatively new science area that demands urgent studies on environmental safety, ecotoxicology and toxicology, in order to make highly prevalent the declaration of the United Nation Organization about the planet environment: “*The man has the fundamental right to liberty, equality and enjoyment of adequate life conditions, under an environment of such quality that allows him living a dignifying life and well-being, and he is carrier of the solemn duty of protecting and improving the environment for the present and future generations*” [68].

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Author details

Valdemar Luiz Tornisielo, Rafael Grossi Botelho, Paulo Alexandre de Toledo Alves, Eloana Janice Bonfleur and Sergio Henrique Monteiro

Laboratory of Ecotoxicology, Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba, SP, Brazil

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