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Environmental Risk assessment of Chlorpyrifos and TCP in Aquatic Ecosystems

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Abstract

Chlorpyrifos is a commonly used pesticide that belong to the organophosphorus pesticides (OPPs) group. Chlorpyrifos is widely used in residential environments and agriculture for pest control. As many OPPs, Chlorpyrifos degrades faster to more complex and toxic compounds under natural conditions, thus diverse effects of these compounds over aquatic species are unknown. Due to the risk that pesticides as Chlorpyrifos, which mainly breaks down to 3,5,6- trichloro-2-pyridinol (TCP) on the ecosystems, there is an increasing need to intensify the environmental monitoring and ecotoxicological risk assessment for both substances. Risk assessment provides a systematic approach for characterizing the nature and magnitude of the risks associated with environmental health hazards. However, in countries like Colombia, where the use of Chlorpyrifos is widespread, the number of investigations on the dynamics and risk involved in the presence of this class of substances in water bodies is limited.

Keywords: Chlorpyrifos, Risk Assessment, Aquatic ecosystems, Degradation products, Organophosphorus pesticides, Colombia.

Evaluación de Riesgo ambiental de Clorpirifos y TCP en Ecosistemas Acuáticos

Resumen

El clorpirifos es un plaguicida de uso común que pertenece al grupo de compuestos organofosforados (OPP). El clorpirifos se usa ampliamente en entornos residenciales y agrícolas para el control de plagas de insectos. Como muchos de los OPP, El clorpirifos se degrada rápidamente a compuestos más complejos y tóxicos en condiciones naturales, por lo que se desconocen los diversos efectos de estos compuestos sobre las especies acuáticas. Debido al riesgo de que los plaguicidas como el Clorpirifos, que se descompone principalmente en 3,5,6-tricloro-2-piridinol (TCP) en los ecosistemas, existe una necesidad de intensificar y ampliar los datos de monitoreo ambiental y la evaluación de riesgo ecotoxicológico para ambas sustancias. La evaluación de riesgos proporciona un enfoque sistemático para caracterizar la naturaleza y la magnitud de los riesgos asociados con los peligros para la salud ambiental. Sin embargo, en países como Colombia, donde el uso del Clorpirifos está muy extendido, el número de investigaciones sobre la dinámica y el riesgo que implica la presencia de esta clase de sustancias en cuerpos de agua es limitado.

Palabras clave: Clorpirifos, evaluación de riesgos, ecosistemas acuáticos, productos de degradación, pesticidas organofosforados, Colombia.

1. Introduction

Since the prohibition in the production and use of organochloride pesticides in the 1970s, due to their high bioaccumulation and toxic biological effects, organophosphorus pesticides have increased, especially in developing countries, where agriculture is the main economic activity(Moussavi *et al.*, 2014). This is due to the proven high-efficiency of these substances to control pests at competitive costs. Even though pesticides offer economic benefits to the agricultural sector, the relationship between agricultural production and its environmental impact could be described as negative since the interaction between pesticides components also affects other populations in addition to the target population. Furthermore, due to their persistent nature, pesticides with high half-life ($t_{1/2}$) remain in the ecosystem longer periods and enter into the food chain (Chawla *et al.*, 2018), affecting the vegetation cover, soil quality and aquatic systems (Burgues *et al.*, 2012).

Factors such as land use and pesticide application pattern, rainfall intensity and irrigation strategy, soil type, landscape and field slope, physicochemical properties such as adsorption, absorption, solubility and Log $K_{ow,}$ and natural degradation processes are crucial to determine the environmental fate and persistence of pesticides, in surface water bodies, sediments and their own biota (Sabatier *et al.*, 2014)but the long-term fate, storage, and transfer dynamics of pesticides in a changing environment are poorly understood. Many pesticides have been progressively banned, but in numerous cases, these molecules are stable and may persist in soils, sediments, and ice. Many studies have addressed the question of their possible remobilization as a result of global change. In this article, we present a retro-observation approach based on lake sediment records to monitor micropollutants and to evaluate the long-term succession and diffuse transfer of herbicides, fungicides, and insecticide treatments in a vineyard catchment in France. The sediment allows for a reliable reconstruction of past pesticide use through time, validated by the historical introduction, use, and banning of these organic and inorganic pesticides in local vineyards. Our results also revealed how changes in these practices affect storage conditions and, consequently, the pesticides' transfer dynamics. For example, the use of postemergence herbicides (glyphosate.

In Colombia, by the first quarter of 2018 there were 444 companies registered as manufacturers, formulators, importers, exporters, packagers and distributors of chemical pesticides for agricultural use (Instituto Colombiano Agropecuario, 2018). In 2016, about 6,871.88 m^3 and 6,831.43 Tn of Chlorpyrifos were commercialized. This data suggests a significant consumption of agrochemicals in the country, where

Chlorpyrifos was the third most commercialized pesticide behind glyphosate and Mancozeb (Instituto Colombiano Agropecuario ICA, 2017).

Taking into account the lack of appropriate technology, situations arise where use and misuse of pesticides produce considerable waste, adding to the cost and contributing to the adverse environmental and health consequences. Inappropriate application of pesticides increase the available fractions which may be accumulated in the food chain and may be transferred to soil, air, ground, and surface water (Abhilash and Singh, 2009).

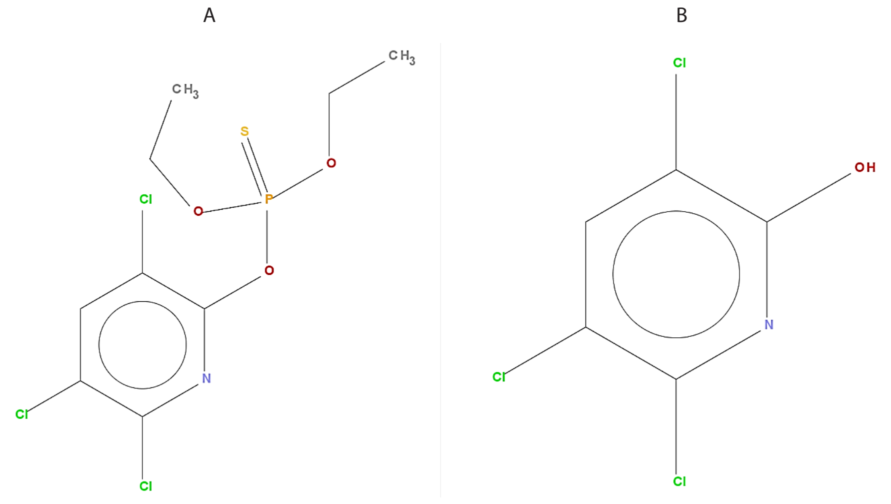
Due to the broad-spectrum insecticidal activity, OPPs are widely used in residential environment and agriculture for pest control(Jain, 2017). However, those substances from polluted environments lead to acute toxicity on aquatic organisms (especially fish) while excessive exposure makes humans prone to acute phosphorus poisoning through phosphorylation of acetylcholinesterase (AcHE) (Dahiya *et al.*, 2017), and cause cholinergic effects over different species exposed (Wu *et al.*, 2017). Furthermore, more chronic effects at low levels may arise on biota. Therefore, it is important to determine the effects that these substances generate in the ecosystems, which may be measured through different tools. Among these are Risk Assessments (ERA), which is a process to collect, organize, analyze and present scientific information to improve decision making (US EPA, 2018b), that use a formal process of problem formulation (PF) to narrow the focus of the assessment to address key questions and, from these, develop the risk hypotheses (US EPA, 1998). This methodology has been applied widely for a variety of substances such as Persistent Organic Compounds (POPPs) because it allows to determine levels of harm, prioritize issues, and inform policy for contaminated land management (Andres *et al.*, 2018).

2. Chlorpyrifos

Chlorpyrifos belong to the organophosphorus compounds which are part of a large group of synthetic chemicals that can be broadly classified as esters, amides or thioester derivatives from phosphoric, phosphonic, phosphorothioic or phosphonothioic acids. Hundreds of those chemicals have been synthesized and studied for biological activity and many have been used commercially. As OPPs Chlorpyrifos is characterized by its low solubility in water, a high water-oil partition coefficient (LogK_{ow}), and a low vapor pressure (Riches, 2014). Chlorpyrifos (**Figure 1**) is a widely commercialized insecticide used in rice, coffee, banana, among other crops; has a broad spectrum and moderate toxicity with a half-life (persistence) of 10–120 days in the environment (Maya *et al.*, 2011), while its main degradation product is the 3,5,6- trichloro-2-pyridinol (TCP), which is a broad-spectrum antimicrobial and toxic metabolite (Mauriz *et al.*, 2007), that is subsequently degraded to organochloride compounds and carbon dioxide (Testai, Buratti and Di Consiglio, 2010). Chlorpyrifos mechanism of action is to interfere with (AChE), that is essential for the proper working of the nervous system of humans among others (Xu *et al.*, 2008). The excessive use of chlorpyrifos and its inappropriate application significantly increase the risks to human health, animals and the environment (Agudelo C, Jaramillo and Peñuela, 2012).

TCP is considered as one of the major degradation product of Chlorpyrifos (Yang *et al.*, 2005) and exhibits a high degradation capacity, high water solubility and high migration capacity (Lei, Huo and Zhou, 2017), It is moderately mobile due to its greater water solubility, which causes the widespread contamination in soils and in the aquatic environment (Yang *et al.*, 2005). Also TCP has antimicrobial activity, and it has been classified as toxic, persistent and mobile by the US EPA with a half-life ranging from 65 to 360 days in soil (Maya *et al.*, 2011).

Figure 1. A) Chemical structure of Chlorpyrifos, **B)** Chemical structure of TCP (United States Environmental Protection Agency, 2018)



Physical and chemical characteristics of Chlorpyrifos and TCP (**Table 1**) are the principal factors that govern the fate in the different environmental matrices (Solomon and Giesy, 2014), towards the aquatic systems, as a result of transport phenomena as well as volatilization (Singare, 2016), diffusion (Giesy *et al.*, 2014), advection (Thibodeaux and Mackay, 2011), dispersion (Hemond and Fechner-Levy, 2015) and sorption (Gebremariam *et al.*, 2012). There, the rate of Chlorpyrifos degradation depends on environmental conditions, such as pH, temperature, UV radiation, and microbiota, therefore as being a xenobiotic that alters the quality of water and as a result of Chlorpyrifos presence and its degradation products, which may result even more hazardous than the parental compounds, affect the ecosystem (Ríos-González, 2010).

TABLE 1. PHYSICOCHEMICAL PROPERTIES OF CHLORPYRIFOS AND ITS DEGRADATION PRODUCT TCP(CHENG *ET AL.*, 2007; NATIONAL CENTER FOR BIOTECHNOLOGY INFORMATION, 2018; US EPA, 2018A).

	CHLORPYRIFOS	**TCP**
Chemical name	O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate	3,5,6-Trichloro-2-pyridinol
Molecular Weight (g/mol)	350.6	198.44
Empirical and Structural Formula	C9H11Cl3NO3PS	C5H2Cl3NO
CAS Registry Number	2921-88-2	6515-38-4
Melting point (°C)	41.5 – 42.5	208 - 209
Vapor pressure (mmHg)	2.03E-05 at 25°C	1.03E-05 at 25°C
Density (g/mL)	1.51 at 21°C	1.67 at 26 °C
Solubility in water (g/L) at 25°C	1.12	89
Partition coefficient (n-octanol and water)	$\log K_{ow}=5.1$	$\log K_{ow} = 3.21$

Chlorpyrifos in the aquatic environments and Its Risk Assessment

Acute and chronic exposure to common-use pesticides remains a considerable threat to non-target species, despite the continued effort to synthesize compounds with high target specificity and low environmental persistence (Simpson, Jeyasingh and Belden, 2017), in the case of Chlorpyrifos its behavior in surface water may be given by complex interactions of factors related to its application, agronomic practices, climatological conditions during and after the application, soil pedology and chemistry, hydrologic responses of drainage systems, and its physicochemical properties that affect mobility and persistence under those environmental settings (Williams *et al.*, 2014). Chlorpyrifos may cause acute toxicity effects by inhibition of AChE occurring at low-level exposure in organisms that lack the target enzyme (Giddings *et al.*, 2014); besides its long half-life in water, the effects of chlorpyrifos on aquatic ecosystems at different trophic levels are attracting more interest (Zhao and Chen, 2016). Chlorpyrifos is potentially toxic to most organisms that show differences in susceptibility, this is because of the differences in rates of adsorption, distribution, metabolism, and excretion among species (Solomon and Giesy, 2014).

Due to the threat that pesticides as Chlorpyrifos pose to the ecosystems, and owing to the growing public awareness on the need of protecting both ecosystems and human health from the risks related to chemical pollution (Kuzmanović *et al.*, 2015). There is an increasing need to intensify the environmental monitoring data and Ecotoxicological Risk Assessment(ERA) (Carazo-Rojas *et al.*, 2018). Recently, many monitoring programs and scientific studies have put more focus on the occurrence, distribution and fate of pesticides and their potential environmental effects in individual rivers, reservoirs and lakes (Chen *et al.*, 2018).

The ERA provide a systematic approach for characterizing the nature and magnitude of the risks associated with environmental health hazards (Department of Health and Ageing of Australia, 2004), and allow to estimate the likelihood that undesired effects might occur or are occurring as a result of exposure to one or more stressors (Guo *et al.*, 2013), in view of ecological risk assessments involving multiple chemical, physical and biological stressors are, by their very nature, complex (Moore, 2001).

Researchers have been developing different approaches for ERA in order to make more holistic assessments due to the complexity of the ecosystems and the substances in the aquatic systems (Tsaboula *et al.*, 2016); using tools such as multimedia fate, exposure and effects models (Guillén *et al.*, 2012)(Houbraken *et al.*, 2017); the influence of physicochemical factors such as temperature, volatilization, precipitation (Delnat *et al.*, 2019),(Beeck, Verheyen and Stoks, 2018),(Potter and Coffin, 2017),(Pereira, Cerejeira and Daam, 2017); ERAs based on the Ecosystem services (Raimondo *et al.*, 2019), and ecotoxicity assays (Janssens, Op De Beeck and Stoks, 2017).

Table 2 shows a summary of ERA conducted for some organophosphorus compounds including Chlorpyrifos in different environmental matrices and sample techniques, which found that Chlorpyrifos was systematically associated with hazard to the studied system.

In spite of the increasing number of ERAs made around the world, there is a limited number of investigations about OPPs pesticides in equatorial zones such as Colombia. In 2015 (Narvaez, 2015) conducted research about the occurrence and preliminary risk assessment of Chlorpyrifos and its principal degradation product TCP in a reservoir in Colombia, where the Risk Quotient was less than 0.1, which indicate a presumption of no danger to the population. Nevertheless, the preliminary results indicated that the TCP as a partial transformation of Chlorpyrifos leads to a product with possible impact on the population.

TABLE 2. RISK ASSESSMENTS RELATED WITH CHLORPYRIFOS AND OTHER ORGANOPHOSPHORUS COMPOUNDS

Assessment	Environmental Matrix	Country	Source
Framework For Ecotoxicological Risk Assessment, EPA method	Aquatic organisms	United States	(Giddings *et al.*, 2014)
Joint Probability Curve	surface waters	United States	(Wang, Singhasemanon and Goh, 2016)
Biological Response Indicator Devices Gauging Environmental Stressors (BRIDGES)	Passive Samplers in surface waters	United States	(Hillwalker *et al.*, 2010)
PRISW-1: Short- Term Pesticide Risk Index for Surface Water System	Polar Organic Chemical Integrative Sampler in surface waters	Lebanon	(Aisha *et al.*, 2017)
PRIMET model	Aquatic Ecosystems	Mexico	(Ríos-González, 2010)
Prospective Aquatic Environmental Risk Assessment	Aquatic Ecosystems	The Netherlands	(Rico *et al.*, 2016)
Ecotoxicological essays	Aquatic Ecosystems	Spain	(Rivetti *et al.*, 2017)
The probabilistic cumulative risk assessment	Soil	United States	(Li, 2018)
First-Tier Risk Quotient (RQ) Approach	Aquatic Ecosystems	Bangladesh	(Sumon *et al.*, 2018)
Toxicity Units	Aquatic Ecosystems	Ghana	(Affum *et al.*, 2018)
ChimERA fate	Shallow Aquatic Ecosystems	Italy	(Morselli *et al.*, 2018)

Although there have been studies on the presence and monitoring of organophosphorus pesticides in aquatic ecosystems in latitudes close to the tropics (Carro *et al.*, 2012; Singare, 2016; Huang, Tornero-Velez and Barzyk, 2017; Bedoya-Ríos *et al.*, 2018; Moncaleano-Niño *et al.*, 2018), it is necessary to do more research about the dynamic, and impact of the OPPs, because in equatorial regions like Colombia, due to its distinctive climatological conditions processes such as occurrence, distribution and fate of organophosphorus compounds as Chlorpyrifos and its degradation products are still poorly known (61).

Quantitative Structure Activity Relationship (QSARs) models of Chlorpyrifos and TCP for Ecological Risk Assessment

Although Daphnia magna, an important freshwater invertebrate species in aquatic food webs, has been used worldwide for many years as a representative test species for the ecotoxicological evaluation of chemicals, this approach is expensive and time-consuming (Toropova *et al.*, 2016). Also, based on the reduction in the use of living organisms to carry on test, QSAR models appear as an alternative, since for ethical reasons, such as avoiding animal testing, QSAR methods may be also preferable

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(Guillén *et al.*, 2012).. Another factor that explain why QSAR models are popular is because they can be developed using experimental data of a small data set, which can be used to get predictions for a large dataset provided they fall inside the applicability domain of the models (Khan, Roy and Benfenati, 2019).

QSAR, sometimes defined as "*in silico*" computational models, enable the prediction of physicochemical or biological properties of the compound by comparing them to other known molecules. In QSAR, different types of descriptors associated with chemical structures are quantitatively correlated with their physicochemical properties as melting point, water solubility, etc., environmental fate, ecotoxicity and other effect end points related to human health (Guillén *et al.*, 2012) (Hamadache *et al.*, 2014). These QSAR models have proven to be very valuable as prioritization tools to classify compounds according to their toxicity and, as more information becomes available, to predict toxicity (Benfenati *et al.*, 2017), and because of that utility the use of QSAR is recommended in early detection of environmental hazards by several regulatory agencies like European Centre for the validation of Alternative Methods (ECVAM) of the European Union, United States Environmental Protection Agency (US EPA), European Union Commission's Scientific Committee on Toxicity, and the Agency for Toxic Substances and Disease Registry (ATSDR)(Khan, Roy and Benfenati, 2019).

In the specific case of Chlorpyrifos and its principal degradation product, preliminary QSAR models indicate that the anaerobic conditions in reservoir sediments favor the reductive dehalogenation mechanisms of CPF and TCP, which could carry out the formation of pyridine, a compound with high carcinogenic activity (Narvaez V *et al.*, 2014).

3. Conclusion

The environmental risk assessment has proven to be an appropriate tool for the estimation of environmental health hazards and therefore the well-being of the human being. This is why ERA it's widely used by government regulatory agencies around the world as the basis for decision making for the management of resources. Risk assessments associated with the exposure of organophosphorus pesticides such as chlorpyrifos have helped the authorities to restrict the use of these substances in their territories, however, these investigations have been carried out in latitudes with climatic and geomorphological characteristics different from those of Colombia, where the use of this pesticides is common in agriculture and livestock.

Due to the limited number of investigations on the dynamics of organophosphorus pesticides, such as chlorpyrifos and its degradation products in Colombian ecosystems, the number of associated ecological risk assessments has also been limited. That is why it is necessary to conduct future researches using tools such as QSAR models that are low cost and with easy access to information in order to predict the toxic effects of these substances widely used in the agricultural sector of Colombia and with this, present scientific bases that allow Colombian governmental entities to manage policies for the regulation of the use of these chemical compounds.

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Conflict of interest

The authors declare no conflicts of interest.

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