Study of the Dynamics and Risk of the Organophosphate Pesticide Chlorpyrifos and its Degradation Product TCP in La Fe Reservoir, Antioquia

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Elija un elemento.

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List of Symbols and Abbreviations

μg/L	Micrograms Per Liter
A	Sampler Area
Å	Armstrong, 0.1 nanometers
AF	Assessment Factor
ASTM	American Society for Testing and Materials
ATSDR	Agency For Toxic Substances and Disease Registry
BW	Body Weight
C_0	Is The PRC Concentration in The Receiving Phase Before Exposure
CDI	Chronic Daily Intake
CPF	Chlorpyrifos
Cpw	Concentration in Pore Water
Cs	Analyte Concentration in Sampler
C_t	Residual Concentration (μg/g) of PRC
Cw	Analyte Concentration in Water
DIA-d5	Deisopropylatrazine-D5
DO	Dissolved Oxigen
DWTP	Drinking Water Treatment Plant
EBP	Reservoir - Pantanillo River Pumping
EBT	Uptake Tower Zone
ED	Exposure Time
EF	Exposure time
EFSA	European Food Safety Authority
EPE	Reservoir- Palmas-Espiritu Santo Tributario
ERA	Environmental Risk Assessment
ESB	Reservoir- San Luis Boqueron
f_{oc}	Fraction Of Organic Carbon
GC/MS	Gas Chromatography/Mass Spectrometry
GPC	Gel Permeation Chromatography

HQ	Hazard Quiotient
ICA	Instituto Colombiano Agropecuario
ISO	International Organization for Standardization
Kd	Sorption coefficient
ke	Elimination Constant
k_{ecal}	Calibrated Elimination Constant
$k_{ein\ situ}$	Elimination Constant Obtained In-Situ
K_{TW}	Triolein-Water Coefficient
ku	Uptake Constant
LC/MS	Liquid Chromatography/ Mass Spectrometry
LC_{50}	Lethal Concentration 50
LDPE	Low Density Polyethilene
$\log K_{oc}$	Organic carbon partition coefficient
$\log K_{ow}$	Octanol/water partition coefficient
$\log K_{sw}$	SPMD/water membrane partition coefficient
MAE	Median Absolute Error
MEC	Measured Environmental Concentration
Ms	Mass of the Analyte Acumulated in Passive Sampler
MTFBSTA	N-(Tert-Butyldimethylsilyl)-N-Methyltrifluoroacetamide
MW	Mega Watts
N	Analite Mass in SPMD After Exposure
N_0	Analite Mass in SPMD Before Exposure
ng/L	Nanograms per Liter
NOEC	No-Observed Effect Concentration
NTU	Nephelometric turbidity units
PES	Polyethersulphone Membranes
PNEC	No-Effect Predictive Concentration
POCIS	Polar Organic Chemicals Integrative Sampler
PRC	Performance Reference Compounds
R^2	Correlation Coefficient

RBCA	Risk-Based Corrective Action
R*f*D	Reference Dose
RQ	Risk Quotient
Rs	Sampling Rate
Rs_{cal}	Calibrated Sampling Rate
$Rs_{in\text{-}situ}$	Sampling Rate Obtained in-situ
SPE	Solid Phase Extration
SPMD	Semipermeable Membrane Devices
t	Deployment Time
TCP	3,5,6-Trichloro-2-Pyridinol
TPE	Palmas-Espiritu Santo Tributario
TSB	San Luis- Boqueron Tributary
TU	Toxic Units
TWA	Time-Weigthed Average Concentrations
US EPA	United States Environmental Protection Agency
V_s	Sampler Volume
WASP	Water Quality Analysis Simulation Program Model
wif.	Binary WASP Input File
XRF	X-Ray Fluorescence
ZF	Photic Zone

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Abstract

This doctoral thesis presents a study of the dynamics of Chlorpyrifos (an organophosphate pesticide) and its degradation product 3,5,6-trichloro-2-pyridinol in La Fe reservoir, an artificial tropical mountain reservoir. The main objective of this work is to contribute to a deeper scientific understanding of the degradation pathways, fate, and associated risk of the organophosphate pesticide Chlorpyrifos and its degradation product 3,5,6-trichloro-2-pyridinol in shallow freshwater bodies in tropical latitudes, through the application of passive sampling. Passive sampling with Semipermeable Membrane devices allowed estimating Chlorpyrifos concentrations in a range of 0.002-0.31 µg/L in the reservoir, while for estimating 3,5,6-trichloro-2-pyridinol concentrations, an in-situ calibration was carried out using deuterated desisopropyl atrazine as a performance reference compound, which enabled the calculation of a sampling rate of 0.015 L/day to find 3,5,6-trichloro-2-pyridinol concentrations in a range of 0.020-0.436 µg/L. Additionally, significant presence of Chlorpyrifos (0.17-1.93 µg/kg) and 3,5,6-trichloro-2-pyridinol (966.8-3949.2 µg/kg) was found in the sediments. A water quality modeling approach was performed using the United States Environmental Protection Agency Water Quality Analysis Simulation Program 8.4 model, which proved useful for conducting a probability assessment. The model indicates that Chlorpyrifos and 3,5,6-trichloro-2-pyridinol enter the reservoir through the sediments, although more data is needed to establish definitive conclusions. Finally, an assessment of environmental risk from acute and chronic exposure was conducted, both for human health and water and sediment. It was found that the Palmas Espíritu Santo tributary presents the highest risk from acute exposure in the water column, while 3,5,6-trichloro-2-pyridinol concentrations are significantly low, indicating low risk. However, both compounds in the sediments, although not exceeding the $\sum TU>1$ value, show values that indicate the need to address and control Chlorpyrifos concentrations in the tributary basins of the reservoir. Similarly, the assessment of environmental risk from chronic exposure to Chlorpyrifos in the tributaries indicates a high level of risk. Meanwhile, 3,5,6-trichloro-2-pyridinol concentrations represent low levels of risk. However, in the sediments, Chlorpyrifos indicates a high risk, especially in the tributaries, while 3,5,6-trichloro-2-pyridinol shows a high level and, therefore, concern in the reservoir mixing zone with Pantanillo pumping.

Keywords: *Passive Sampling, Water Quality, Risk Assessment, Pesticide, Degradation Product.*

Resumen

Esta tesis doctoral presenta un estudio sobre la dinámica del Clorpirifos (un pesticida organofosforado) y su producto de degradación 3,5,6-tricloro-2-piridinol en el embalse La Fe, un embalse artificial de montaña tropical. El objetivo de este trabajo es contribuir a una comprensión científica más profunda de las vías de degradación, destino y riesgo asociado al plaguicida Clorpirifos y su producto de degradación 3,5,6-tricloro-2-piridinol en cuerpos de agua dulce someros en latitudes tropicales, a través de la aplicación de muestreo pasivo. El muestreo pasivo con dispositivos de membrana semipermeable permitió estimar concentraciones de Clorpirifos en un rango de 0.002-0.31 µg/L en el embalse, y para estimar las concentraciones de 3,5,6-tricloro-2-piridinol se llevó a cabo una calibración *in-situ* utilizando atrazina desisopropil deuterada como compuesto de referencia para el rendimiento, lo que permitió calcular una tasa de muestreo de 0.015 L/día para encontrar concentraciones de 3,5,6-tricloro-2-piridinol en un rango de 0.020-0.436 µg/L. Además, se encontró la presencia significativa de Clorpirifos (0.17-1.93 µg/kg) y 3,5,6-tricloro-2-piridinol (966.8-3949.2 µg/kg) en los sedimentos. Se realizó una modelización de la calidad del agua utilizando el modelo de Water Quality Analysis Simulation Program 8.4 de la United States Environmental Protection Agency, el cual resultó útil para realizar una evaluación probabilística. El modelo sugiere que la entrada de Clorpirifos y 3,5,6-tricloro-2-piridinol al embalse ocurre a través de los sedimentos, aunque se requiere obtener más datos para establecer conclusiones definitivas. Finalmente, se llevó a cabo una evaluación del riesgo ambiental por exposición aguda y crónica, tanto para la salud humana como para el agua y los sedimentos. Se encontró que el Tributario Palmas Espíritu Santo presenta el mayor riesgo por exposición aguda en la columna de agua, mientras que las concentraciones de 3,5,6-tricloro-2-piridinol son significativamente bajas, indicando un bajo riesgo. Sin embargo, ambos compuestos en los sedimentos, aunque no superan el valor $\sum TU>1$, presentan valores que indican la necesidad de abordar y controlar las concentraciones de Clorpirifos en las cuencas de los afluentes del embalse. Del mismo modo, la evaluación del riesgo ambiental por exposición crónica al Clorpirifos en los afluentes indica un nivel de riesgo alto. Mientras tanto, las concentraciones de 3,5,6-tricloro-2-piridinol representan niveles bajos de riesgo. No obstante, en los sedimentos, el Clorpirifos indica un riesgo alto, especialmente en los afluentes, mientras que el TCP muestra un nivel alto y, por lo tanto, preocupante en la zona de mezcla del embalse con el bombeo Pantanillo. **Palabras clave:** *Muestreo Pasivo, Calidad Del Agua, Evaluación Del Riesgo, Plaguicida, Producto De Degradación.*

Chapter 1. Introduction

Chlorpyrifos (CPF) is one of the most widely used pesticides in Colombia, according to the Bulletin of Statistics on the Marketing of Pesticide Substances (ICA, 2019). It is a broad-spectrum organophosphate pesticide with insecticidal action, sold under various brands such as RÁFAGA® 4 EC, Látigo®, ARRIERO® 2.5, TRAPPER® EC, and NUFOS 4®. In 2019, 1,871 tons and 1,600 m3 of Chlorpyrifos in powder and liquid presentations, respectively, were marketed in the country due to its ratio cost-effectiveness. However, its indiscriminate use, technical and technological shortcomings for its correct application generate that this substance is transported outside the limits of the areas where it is intentionally applied and reaches other ecosystems. Chapter 2 covers in-depth the physical and chemical characteristics of CPF and its degradation product, 3,5,6-trichloro-2-pyridinol (TCP).

Due to their physical and chemical characteristics and interaction with other elements, these types of compounds are transformed into substances that are usually found at trace levels of μg/L or ng/L. Monitoring these compounds in aquatic ecosystems using conventional sampling techniques can be an expensive and impractical alternative since concentrations of pollutants vary over time, and episodic pollution events can be overlooked. Therefore, it is necessary to increase volumes, the frequency of sampling, and even automation of sampling (Vrana et al., 2005). Passive sampling represents a powerful approach to overcoming these problems. Since their emergence in 1970 when these devices were widely employed in industry to assess harmful chemicals in workplace air, later, the principles of passive sampling were used to study water environments (Vrana et al., 2005). These types of sampling tools have been recognized as effective instruments in environmental studies (Macías et al., 2023; MacKeown et al., 2022). Passive sampling is based on the free flow of analyte molecules from the sample matrix (water, air) to the reception phase (sorbent) (Zabiegała et al., 2010). The devices can provide additional information on organic compounds in freely dissolved aquatic ecosystems and provide time-weighted average concentrations (TWA) or equilibrium (Taylor et al., 2021). In this research, *Polar Organic Chemical Integrative Samplers* (POCIS) and *Semipermeable Pasive Sampler Devices* (SPMD) were used, chapter two explains functionality, theory and modeling of the kinetics of passive sampling. Highlighting the utility of passive samplers in monitoring substances such as organophosphate pesticides, which are of great interest to researchers, we propose in this study to pull the results obtained from passive sampling campaigns for water quality modeling. This approach aided to elucidate the dynamics of these substances in the aquatic ecosystem.

Water quality models are useful tools for assessment of the efficacy of management plans on water quality and predicting pollution scenarios These models simulate and predict the spatiotemporal dynamics and variability of water quality, stablishing them as key components in mitigation and pollution control measures (Ejigu, 2021; Milišić et al., 2019). There are several sorts of models available, both commercially and as freeware, for use in various aquatic environments (Rink et al., 2015). Globally, mathematical models and software have been developed to simulate, describe, and predict the ecological risks associated with pesticide use (Villamizar and Brown, 2016). Such as Soil and water assessment tool (SWAT) which model allows the simulation of water and sediment production in hydrographic basins, as well as the effect that agronomic practices have on water quality due to the use of pesticides and fertilizers (Neitsch et al., 2011); Perpest Model (Van Den Brink et al., 2006a) it is a model that predicts the ecological risks of pesticides in freshwater ecosystems, this system predicts the effects of a particular pesticide concentration on various endpoints of the aquatic community; CASCADE-TOXSWA model uses to predict the ecological risks of plant protection products in small watercourses, based on the good agricultural practices of these products. The scale of the area of interest is typically on the order of 10 km^2 (Adriaanse et al., 2014). And WASP model popular for its use interpreting and predicting water quality responses to natural phenomena and artificial pollution. It is a dynamic compartmental modeling program for aquatic systems, including both the water column and the underlying benthos (C. D. Knightes et al., 2019).

Hence, the selected model for studying the dynamics of chlorpyrifos and TCP in the reservoir was the Water Quality Analysis Simulation Program (WASP), developed by the United States Environmental Protection Agency. This model assists the user in interpreting and predicting water quality responses to natural phenomena and pollution caused by humans, in order to establish criteria for pollution management decision-making. It is a compartmental model that includes the water column and benthic bottom, allowing for simulation in one, two, and three dimensions for a wide variety of contaminants. The primary criteria for selecting the program for the proposed simulations in this study were its flexibility, the phenomenological processes it allows to be modeled, the ease of use of the interface, its open license, and its robustness in modeling different aquatic ecosystems (Ramos Ramirez et al., 2019).

Environmental Risk Assessment is the process of assigning magnitudes and probabilities to the potential adverse effects associated from exposure to physical, biological or chemical stressors. (Shea and Thorsen, 2012a). These stressors, are the focus of the assessment, which aims to determine the potential harm caused by human activities to living organisms within ecosystems (Rodier and Zeeman, 2019). A range of environmental risk assessment methodologies have been developed to address the complex interactions, these include integrated modelling approaches such as systems dynamics, Bayesian networks, coupled component models, agent-based models, and knowledge-based models (Kelly et al., 2013), and alternatives to complement the risk assessment such as Life Cycle Assessment, Technology-Based rules, precautory principle, health risk assessment and environmental impact assessment (Suter II, 2007a). As Chlorpyrifos pose a risk to aquatic ecosystems, impacting factors such as habitat conditions, behavioral patterns, growth rates, and reproductive capabilities of aquatic organisms (Carazo-Rojas et al., 2018; El-bouhy et al., 2023; Giddings et al., 2014; Kuzmanović et al., 2015; Mackay et al., 2014a). Despite the growing prevalence of Environmental Risk Assessments worldwide, there remains a scarcity of research on organophosphate pesticides in equatorial regions like Colombia (Gomez Arguello et al., 2020).

Therefore, this doctoral thesis proposes that based on the results obtained from monitoring, simulations, and an acute toxicity test, this thesis development an ecological risk assessment for the presence of Chlorpyrifos and its degradation product, TCP. This research was funded by the Administrative Department of Science, Technology, and Innovation for Colombia (Colciencias), now the Ministry of Science, Technology, and Innovation (Minciencias), under the framework of the 2015 National Doctoral Grants Call, Number 727.

1.1 Problem statement

La Fe reservoir is the main source of water supply for the La Ayurá and San Nicolás Valley water treatment plants, which provide 45% of the drinking water for the aqueduct system serving the population of the Aburrá Valley and San Nicolas Valley, Antioquia (Superintendecia de Servicios Públicos Domiciliarios, 2016) (Salazar, 2017).

However, its tributaries, especially the Pantanillo River, are heavily impacted by human activity, as the area is home to livestock farms, fruit, flower, and vegetable crops, as well as forest harvesting, posing a risk of pesticides discharge into the tributaries and thus the transportation of

Chlorpyrifos to the reservoir (Narvaez Valderrama, 2015). Although the estimated concentrations by (Narvaez Valderrama et al., 2013) do not exceed the maximum permissible concentration (1 μgL^{-1} CPF) established in Colombian Resolution 2115 of 2007, the associated risk of chronic exposure to low levels of Chlorpyrifos and its degradation product, TCP, remains unknown for this aquatic system. TCP, identified as the principal metabolite of Chlorpyrifos, has been detected in the urine samples of exposed individuals. Notably, exposure has been associated with an elevated risk of developing endometriosis (Li et al., 2020). However, the scope of studies examining its potential effects remains limited (Mora et al., 2022).

Given the significance of the La Fe reservoir, an assessment of Chlorpyrifos and TCP dynamics within the water column is imperative. This assessment will utilize sampling and modeling techniques to simulate various conditions and provide data for risk assessment regarding the target substances. Moreover, it will contribute to ecological risk assessment due to the threat posed by these compounds to the ecosystem. This study propose to evaluate whether tools such as passive sampling, water quality modeling, and scenario simulation offer a sufficient basis for assessing exposure risks to Chlorpyrifos and TCP in bodies of water used for potable water supply, such as the La Fe reservoir in Colombia.

As the project intends to develop risk management strategies for Chlorpyrifos and TCP pollution in the La Fe reservoir, the study's scope is limited by the watershed's size. Therefore, our focus will be on the reservoir itself and its tributaries, namely the Palmas-Espíritu Santo, San-Luis Boquerón, and Pantanillo River.

1.2 Background

Application of passive sampling for monitoring lipophilic organic compounds has been documented in various studies using SPMD, for instance, the monitoring of biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), in urban river water in Korea (Kim et al., 2014); to measure the concentrations of freely dissolved Polycyclic Aromatic Hydrocarbons (PAHs) in surrounding the Costa Concordia shipwreck in Isola del Giglio, Italy (Schintu et al., 2018); and rivers and dams in Johannesburg City, South Africa (Amdany et al., 2014). SPMDs are effective in capturing organic contaminants in the dissolved phase highlighting their ability to detect low concentration of these compounds, difficult to monitor by conventional volatility.

As well SPMD are used for lipophilic organic compounds, POCIS has gain recognition as and effective tool to monitoring polar compounds such as pharmaceutical compounds (Morin et al., 2012a), polar pesticides and their metabolites (Charlestra et al., 2012) and alkylphenols (Silvani et al., 2017). These devices have proven to be valuable tools for tracking the dynamics and distribution of organophosphate pesticides in the environment, facilitating risk assessment and the formulation of environmental management strategies.

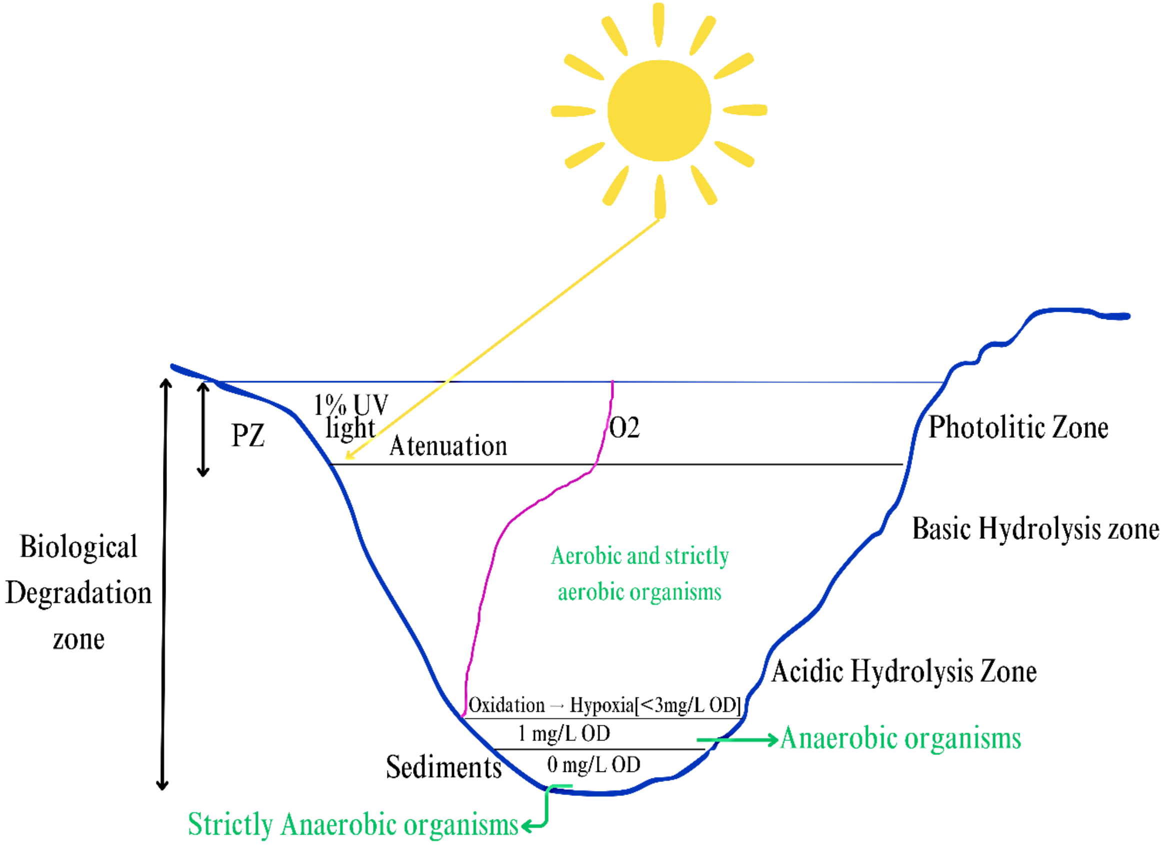
In aquatic environments, passive sampling has the potential to provide information on the fate and behavior of polar and non-polar industrial pollutants, and in the assessment of bioavailability, there is potential for substituting biota with other entities, offering benefits such as reduced expenses and variability, as well as enhanced repeatability and ethical acceptance (R. Greenwood et al., 2009).

In the research conducted by (Narvaez Valderrama, 2015), passive sampling techniques using SPMD and POCIS membranes were used to detect the presence of Chlorpyrifos and other pesticides in low concentrations. Chlorpyrifos was found in the Palmas-Espiritu Santo, San Luis – Boquerón streams and Pantanillo river, the reservoir, and at the entrance of the drinking water treatment plant (DWTP) in concentrations ranging from 1-25.8 ng/L, 1.7-9.4 ng/L, and 0.5-1.1 ng/L, respectively. The results showed higher levels of Chlorpyrifos in the inflows, especially the Palmas-Espiritu Santo stream, possibly due to direct entry into the bodies of water through runoff, while low levels were found in the reservoir and at the entrance of the DWTP, which could be associated with dilution and degradation of Chlorpyrifos.

Although preliminary risk assessment of exposure to Chlorpyrifos carried out by Narvaez resulted in an HQ of 0.00023, indicating a presumption of no danger to the human population, the effects that may be triggered through chronic exposure to low levels of Chlorpyrifos and some of its degradation products, such as TCP, are still unknown. TCP's solubility and persistence in the environment have been shown to be greater than Chlorpyrifos, making it an even more toxic substance than its parent compound (Khalid et al., 2016).

This prior investigation successfully identified degradation and hydrolysis as the dominant degradation mechanisms in the aquatic environment under consideration. These processes are significantly impacted by fluctuations in pH levels within the water column, as well as the involvement of photolytic degradation. Figure 1 shows the main degradation processes that occur in the water column of the reservoir.

Figure 1
Chlorpyrifos degradation processes in La Fe reservoir.



Note: Taken from (Narvaez Valderrama, 2015)

The conceptual model of chlorpyrifos degradation processes in La Fe reservoir is depicted in Figure 1. Indicates how solar radiation influences photolytic phenomena, to which chlorpyrifos is sensitive (Žabar et al., 2016), primarily occurs within the reservoir's photic zone. This zone is abundant aerobic organisms, enabling the potential biodegradation of chlorpyrifos by aerobic microorganisms (Chishti et al., 2013). Additionally, hydrolysis plays a significant role in the degradation of chlorpyrifos in natural aquatic environments (Adams et al., 2016). This study found that basic hydrolysis was the primary degradation process for chlorpyrifos in the reservoir, with transformation rates decreasing with increasing water depth.

1.3 Objectives

1.3.1 General Objective

Study the dynamics of the organophosphate pesticide Chlorpyrifos and its main degradation product TCP, from field evaluation, modeling and simulation of different scenarios and to evaluate the ecological risk and human health in the La Fe reservoir, Antioquia, Colombia.

1.3.2 Specific objectives

Update the evaluation previously carried out in the La Fe reservoir using the passive sampling technique using POCIS and SPMD devices.

Adjust the WASP modeling tool to the characteristic conditions of the region, for its application in the evaluation of the dynamics of Chlorpyrifos and its degradation product TCP in the La Fe reservoir.

Evaluate the ecological risk associated with exposure to Chlorpyrifos and its degradation product TCP in the La Fe reservoir, with the methodological guidelines for risk assessment proposed by US EPA (1998), ATSDR (2009) and RBCA E-2081-00 of 2015 of ASTM.

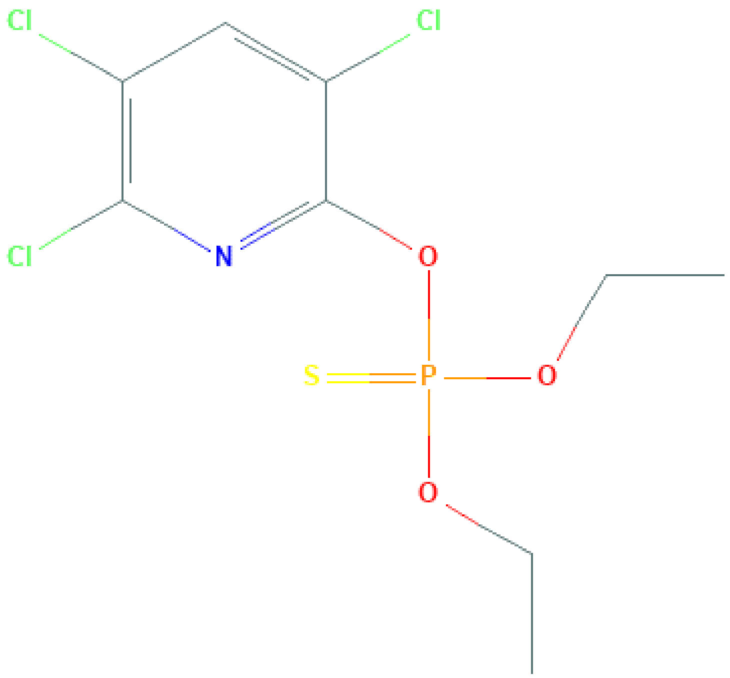
Chapter 2. Theoretical Framework

2.1 Chlorpyrifos

Chlorpyrifos (CPF) is an organophosphate insecticide with the chemical name O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate, (National Center for Biotechnology Information, 2020), as shown in Figure 2. Produced worldwide since 1965 (John and Shaike, 2015), CPF is a compound with a broad spectrum of action as an insecticide, acaricide, and nematicide. Its use extends to agricultural practices for pest control in crops, as well as in forestry, industrial, and residential applications to combat cockroaches, termites, fleas, ticks, and other (Giesy, Solomon, Cutler, Giddings, Mackay, Moore, Purdy, Williams, et al., 2014). The formulations for CPF include: emulsifiable concentrate, powder, microcapsules, granules, and aerosols. In this regard, when CPF is indiscriminately used through activities such as crop management, spray drift, accidental spills, container rinsing, etc., it results in excessive contamination of aquatic and soil components (Yang et al., 2005; Y. L. Yu et al., 2006).

Figure 2

Chemical Structure of Chlorpyrifos



Note. Taken from (National Center for Biotechnology Information, 2020)

2.1.1 Physicochemical properties of Chlorpyrifos.

The physical and chemical characteristics of Chlorpyrifos determine its degradation and persistence in the environment (Solomon et al., 2014a). Table 1 summarizes the physical and chemical properties of Chlorpyrifos that are crucial to its environmental fate. The half-life of Chlorpyrifos can range from a few days to over four years, depending on the amount of substance, ecosystem type, and environmental factors specific to the application zones (Gebremariam et al., 2012b).

Table 1

Summary of the physical and chemical properties of Chlorpyrifos.

	CHLORPYRIFOS
Chemical Name	O,O-diethyl-O-(3,5,6-trichloro- 2-pyridyl)phosphorothioate
Molecular weight (g/mol)	350,6
Empirical and structural formula	$C_9H_{11}Cl_3NO_3PS$
CAS Registry Number	2921-88-2
Melting Point (°C)	41,5 – 42,5
Vapor Pressure (mmHg)	$2{,}03e^{-05}$ at 25°C
$2{,}93e^{-06}$ atm-m3/mol	$1{,}03e^{-05}$
Density (g/mL)	1,51 at 21°C
Solubility in water(mg/L) at 25°C	2
Partition coefficient (n-Octanol and Water)	log K_{ow}= 4,82 - 5,11

Note. Adapted from (Cheng et al., 2007; National Center for Biotechnology Information, 2019; US EPA, 2018a)

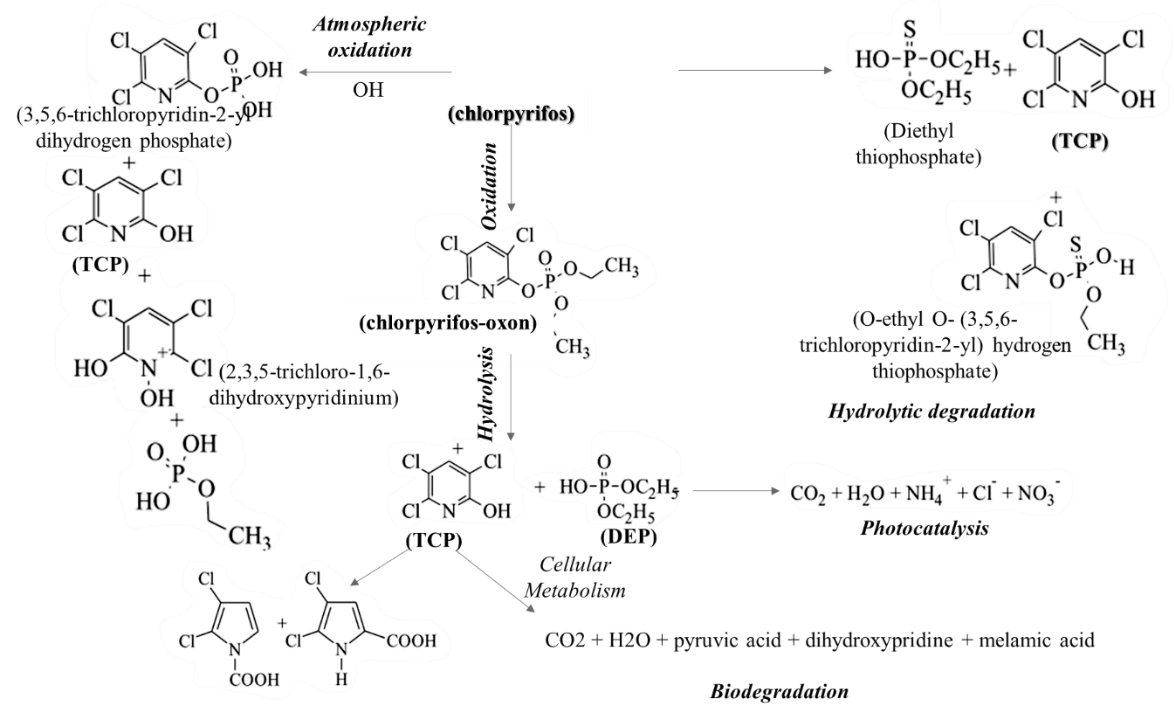
It is important to mention the property of the octanol-water partition coefficient, log Kow, as it relates to the lipid affinity of pesticides. A high value of log Kow, such as that of Chlorpyrifos, indicates a high affinity for the lipid fraction. This implies that the compound can easily pass through biological tissues, resulting in a high potential for bioaccumulation in the trophic chain (Narvaez Valderrama et al., 2012). Chlorpyrifos is harmful to several forms of life, even at low concentrations, and can be lethal to aquatic animals. The toxic effects of Chlorpyrifos have been confirmed through studies and trials conducted on various animal species (Sud et al., 2020).

Considering the low vapor pressure of Chlorpyrifos, volatilization is the dominant dissipation process within the first twelve hours after application. However, once the substance is absorbed by the foliage or reaches the soil, the rate of volatilization decreases (Giesy, Solomon, Cutler, Giddings, Mackay, Moore, Purdy, Williams, et al., 2014). Chlorpyrifos can be transported to bodies of water through processes such as volatilization and precipitation, runoff, leaching, and percolation (Köck S, 2014). Although Chlorpyrifos has a short to moderate persistence in the environment as a result of several dissipation pathways that can occur simultaneously, in aquatic ecosystems, Chlorpyrifos is removed from the water column through transformation and degradation processes such as hydrolysis, photodegradation, and biodegradation (Giesy et al., 1999).

Figure 3 shows the different degradation pathways of Chlorpyrifos in the environment and the structure of the resulting degradation products.

Figure 3

General degradation route of Chlorpyrifos



Note. Adapted from (Sud et al., 2020).

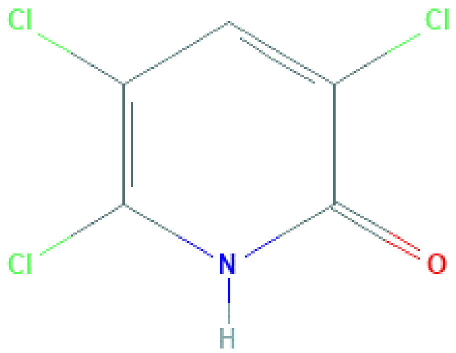
Chlorpyrifos is moderately soluble in water and contaminates aquatic ecosystems through runoff. When Chlorpyrifos is adsorbed, this phenomenon reduces the mobility of the substance into other environmental matrices. However, if adsorption occurs on erodible particles, dissolved organic matter, or mobile inorganic colloids, Chlorpyrifos increases its mobility (Mackay et al., 2014b; J. Zhao and Chen, 2016). In water, the half-life of Chlorpyrifos is highly dependent on the pH, since the half-lives for hydrolysis in water vary inversely with pH, they range from 16 to 73 days (Solomon et al., 2014b); besides, tropical conditions have higher breakdown rates compared to cold conditions due to higher photodegradation in tropical areas (Bose et al., 2021). In sediments, Chlorpyrifos has shown a great affinity for fine particulate matter, causing this contaminant to be adsorbed onto the sediment and remain there due to its low solubility in water and high K_{oc} (8500 mL/g). Therefore, there is a close relationship between these pesticides and the levels of organic matter present in sediments (Köck S, 2014).

2.2 3,5,6-trichloro-2-pyridinol (TCP)

The main degradation product of Chlorpyrifos is 3,5,6-trichloro-2-pyridinol (TCP), as shown in Figure 4, which is formed due to degradation and transformation processes in the environment, mainly adsorption, hydrolysis, oxidation, or photolysis (Giesy, Solomon, Cutler, Giddings, Mackay, Moore, Purdy, Williams, et al., 2014; Hui et al., 2010). TCP has higher water solubility than Chlorpyrifos, which favors widespread contamination in soils and aquatic environments (Echeverri-Jaramillo et al., 2020a).

Figure 4

Chemical structure of TCP



Note. Taken from (National Center for Biotechnology Information, 2018).

2.2.1 Physicochemical Properties of TCP

TCP is a polar molecule mobile in soil as well as leachable in both groundwater and surface water (Yadav and Khare, 2023). As soils have a low capacity for TCP absorption due to its high solubility in water and lower octanol-water partition coefficient (logKow), as observed in Table 2. As a result, TCP has the potential to widely contaminate aquatic and soil environments (Yang et al., 2005; Y. Zhao et al., 2017). It has been demonstrated that Chlorpyrifos and TCP accumulate in non-target organisms through biomagnification and have a strong toxic effect, including on humans (Y. Huang et al., 2021).

Table 2

Summary physical and chemical properties of TCP

	TCP
Chemical Name	3,5,6-trichloro-2-pyridinol
Molecular weight (g/mol)	198.44
Empirical and structural formula	$C_5H_2Cl_3NO$
CAS Registry Number	6515-38-4
Melting Point (°C)	208 - 209
Vapor Pressure (mmHg)	$1.03e^{-05}$ at 25°C
Density (g/mL)	1.67 at 26 °C
Solubility in water(mg/L) at 25°C	89
Partition coefficient (n-Octanol and water)	$\log K_{ow} = 3.21$

Note. Adapted from (Cheng et al., 2007; National Center for Biotechnology Information, 2018; US EPA, 2018a).

TCP is classified as a persistent and mobile contaminant by the United States Environmental Protection Agency (US EPA) (Lu et al., 2013), with a half-life ranging from 65 to 360 days in soil. Studies have reported that TCP is relatively more toxic than Chlorpyrifos (Suvarchala and Philip, 2016; Wang et al., 2014) and that the combination of both compounds could produce additive toxic effects in natural ecosystems (Echeverri-Jaramillo et al., 2020a; Y. Zhao et al., 2017). Recent studies have shown that TCP inhibits the secretion of sex hormones. Like CPF, TCP can bind to sex steroid hormone receptors and decrease the secretion of sex hormones (H. Gao et al., 2021).

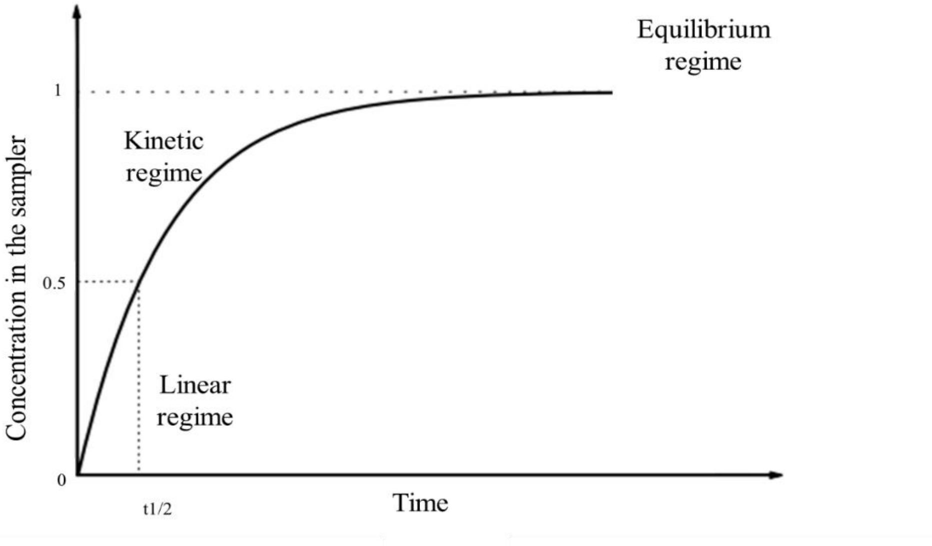
2.3 Passive Sampling

According to (Huckins et al., 2006a)) passive sampling is the process of concentrating pollutants through the diffusion of compounds from a high chemical potential or fugacity matrix into a low potential or fugacity matrix (receptor or sorbent phase). The passive sampling technique is used to sample a wide variety of substances, including polar organic compounds, non-polar organic compounds, and inorganic compounds, including metals (ISO, 2011). Passive sampling techniques were developed to address some of the limitations of traditional sampling methods, including the need for infrastructure and energy for monitoring, losses due to degradation or volatilization of compounds during transportation, as well as loss of target compounds during sample extraction and treatment processes. Additionally, traditional sampling methods often have higher detection limits for various compounds, making it expensive to detect trace and sub-trace levels of substances (Carpinteiro et al., 2016; Nguyen et al., 2020).

Passive accumulation of pollutants in a receiving phase offers several advantages, such as reducing the time and material-consuming procedures, achieving lower quantification limits through preconcentration, and continuous exposure to water pollutants for 15 to 30 days, allowing the assessment of the overall pollution level without identifying short-term pollution events (Lissalde et al., 2014). Thus, the use of passive sampling technologies for monitoring persistent organic pollutants and emerging organic pollutants has become a globally accepted robust technique (Alvarez, 2010; X. Gao et al., 2019; O’Brien et al., 2012).

To understand the passive sampling process, Huckins et al., 1999 and (Booij et al., 2007; Huckins et al., 1999) presented a model that describes the accumulation of contaminants in passive sampling devices in terms of mass transfer coefficients: k_0 as the overall mass transfer coefficient and K_{SW} as the sampler-water partition coefficient, considering the volume of the sampler (V_s) and the interfacial exchange area (A) (Alvarez et al., 2004) defines that the accumulation of chemical substances in passive samplers usually follows a first-order kinetics, which is characterized by an initial linear phase, followed by curvilinear and equilibrium partitioning phases, see Figure 5.

Figure 5
Chemical accumulation of contaminants in passive sampling devices



Note. The figure displays three phases of contaminant accumulation in a passive sampler. Taken from (Huckins et al., 2006b)

At the beginning of the deployment of passive samplers, the uptake rate (k_u) in the sampler is high while its elimination rate is very small (k_e), and therefore negligible. It is observed that the sampler is operating in the linear uptake phase (equation 1).

$$C_s = C_w k_u t \qquad \text{(Eq. 1)}$$

Where Cs [µg/L] is the concentration of the analyte in the sampler, Cw [µg/L], the concentration of the compound in the media, and *t* [days], the time of deployment. In this rate of sampling, it is assumed that the mass transfer rate or sampling rate remains constant throughout the duration of sampling, and that the relationship between the concentration of target analytes in the sample matrix and the amount of analytes extracted is linear (Zabiegała et al., 2010).

During the linear uptake phase, the calculation of time-weighted average (TWA) concentration of contaminants in water can be simplified (equation 2) by relating the mass of analyte accumulated in the passive sampler (M_s) [ng], to the sampling rate (R_s) [L/day] and the deployment time (*t*), where:

$$C_w = \frac{M_s}{R_s t} \qquad \text{(E q.2)}$$

Sampling rate (Rs) estimates target analyte concentrations based on passive sampler contaminant absorption, estimating concentrations in the medium. It is intrinsically linked to the specific LogK_{ow} of the target analytes, as well as the physicochemical properties of the compounds under study, the water flow rate, the temperatures at the exposure site, and the amount of biofouling present on the sampler Surface (Booij and Smedes, 2010).

Sampling rates can be estimated from the dissipation rate of Performance Reference Compounds (PRCs). PRCs are compounds with certain characteristics: they should not occur naturally in the environment, they should not interfere with the sampling or analytical determination process, and their structure should be similar to that of the compounds of interest. PRCs are added to the sampler before deployment, and subsequent determination of in situ PRC losses allows the absorption kinetics of the analyte to be determined, provided that both show isotropic exchange behavior (Booij and Smedes, 2010; K. Smith, 2020). Therefore, a good PRC should allow for accurate measurement of its loss and follow the same exchange kinetics as the target analyte. It is recommended to use a selection of PRCs that share a range of properties and exchange kinetics with the compounds of interest, which are subsequently determined by interpolation (Vrana et al., 2021).

Dissipation of the PRC is governed by:

$$N = N_0 e^{-k_e t} \qquad \text{(Eq. 3)}$$

According to Alvarez (2010), to estimate the specific Rs of a chemical product at the sampling site and its concentration in water (C_w) based on the log K_{ow} of the chemical product, the release rate constant of the PRC (k_e), and the SPMD-water partition coefficient (K_{SW}). The elimination rate of a PRC is determined from the amount of PRC initially added to the SPMD (N_0) and the remaining amount at the end of the sampling period (N), as shown in Equation 4.

Given the initial amount of PRC (N0) at time t=0, the release rate constant can be estimated by measuring N and N0 using the formula:

$$k_e = -\frac{\ln\frac{N}{N_0}}{t} \qquad \text{(Eq. 4)}$$

When the PRC's k_e and K_{sw} are known, its Rs can be calculated as follows

$$\mathrm{R_s} = \mathrm{V_s K_{Sw}} k_e \qquad \text{(Eq. 5)}$$

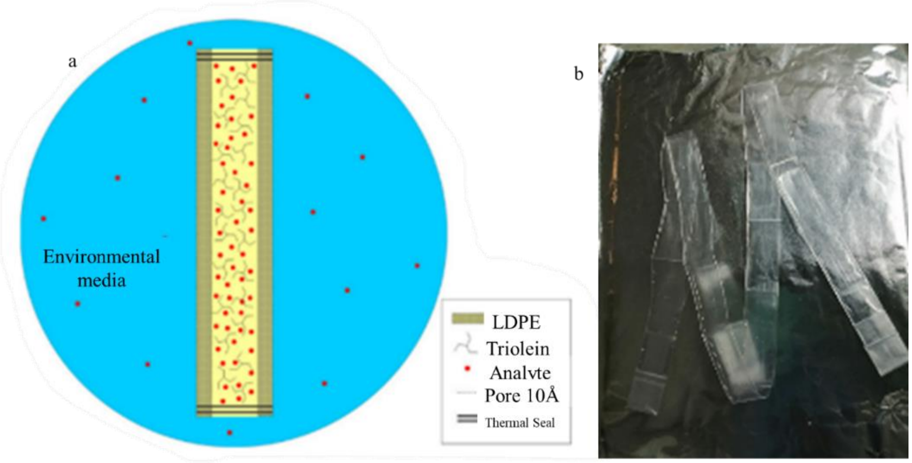
In the last two decades, numerous variations of passive samplers have emerged for monitoring various types of pollutants, including nonpolar organic compounds, polar organic compounds, organo-metals, and metals found in aquatic environments (Schintu et al., 2014). For polar compounds devices like Chemcatcher® which Consists of a disk as a receiving phase with a diffusion membrane sealed in a housing, it can sample various contaminants by using different combinations of receiving phases and membranes; Diffusive Gradients in Thin Film Technology (DGT) initially designed for accumulating metals but modified for polar organic compounds. It is suitable for monitoring polar organic pollutants with adjustments in binding gels and POCIS passive sampler that accumulates organic pollutants in water over time (Gong et al., 2018) As well passive samplers for non-polar compounds include Semi-Permeable Membrane Devices (SPMDs), also silicone rubber and low-density polyethylene (LDPE), have been found to be effective for the target and nontarget analysis of moderately polar and nonpolar substances in water (Allan et al., 2013). This research applied SPMDs for monitoring Chlorpyrifos due to its hydrophobic properties, and POCIS for TCP due to its hydrophilic properties.

2.3.1 Semipermeable Membrane Devices (SPMD).

SPMD membranes consist of a flat tube made of low-density polyethylene (LDPE) with standard dimensions of 2.54 cm in width and 92 cm in length, which contains triolein (1,2,3-tri-(cis-9-octadecenoyl) glycerol) as a receiving medium. Triolein is a fatty acid present in most aquatic organisms and mammals (Quinn et al., 2014). Polyethylene, often referred to as impermeable, actually consists of transport channels with pore size of less than 10 Å in diameter (R. Smith, 2019). The device weighs around 4.5g, with 20% of its weight being triolein. The ratio between the surface area and volume of triolein is approximately 460 cm^2/mL. SPMD devices can concentrate a wide range of hydrophobic organic compounds, with Log Kow ≥ 3, such as polycyclic aromatic hydrocarbons, organochlorine pesticides, and emerging contaminants such as triclosan (Huckins et al., 2006c).

Figure 6

Standtar Configuration of SPMD



Note. a) Functioning model of SPMD membrane adapted from (Esteve-Turrillas et al., 2008, p. 445). b) SPMD membrane preparing for deployment in the field.

Triolein is a neutral triglyceride and the major nonpolar lipid found in aquatic organisms. There is a close relationship between the triolein-water coefficient (K_{TW}) and the octanol-water coefficient (K_{ow}), which is a physical parameter easily available in the literature for a multitude of compounds (Esteve-Turrillas, 2007) Triolein was chosen as the standard for the use of SPMDs for the following reasons (Huckins et al., 2006c):

- It is an important storage lipid found in most organisms.
- Its high molecular weight of 885.5 Daltons results in extremely low permeability in the LDPE membrane, even during the recovery of analytes by dialysis.
- High-purity synthetic triolein is commercially available.
- The triolein-water partition coefficient and the octanol-water partition coefficient (Kow) are similar in magnitude and correlated.
- It remains in a liquid state down to −4°C and provides a good reservoir for PRC compounds.

- SPMDs simulate the absorption of compounds through cellular membranes and can be used to evaluate the bioaccumulation factor in aquatic animals (Esteve-Turrillas et al., 2008).

2.3.2.1 Analyte Uptake Dynamics in SPMDs Using PRCs

Following the kinetic and equilibrium sampling model proposed (Huckins et al., 2006c), the analyte concentration within SPMDs (Cs) increases gradually over time until it achieves equilibrium, as described in Equation 6:

$$C_s = K_{SW} C_w [1 - e^{-k_e t}] \qquad \text{(Eq. 6)}$$

Where:
Cs= analyte concentration in sampler
K_{SW}= is the de sampler water partition coefficient
C_w= Analyte aqueous concentration
ke = the rate constant for the release process
t = the deployment time

The equilibrium value is reached when the elimination rate during deployment time $k_e t$ >>1, causing the concentration in the sampler to attain its equilibrium state, the type of exposure in this situation is known as equilibrium sampling:

$$C_s = K_{sw} C_w \qquad \text{(Eq. 7)}$$

If $k_e t$ << 1, indicating short exposure times and/or highly hydrophobic compounds, the exponential decay function, term within the square brackets in Equation 6, can be approximated to $k_e t$, and the concentration in SPMDs (Cs) can be calculated as follows:

$$C_s = K_{sw} C_w k_e t \qquad \text{(Eq. 8)}$$

The phase of an exposure in which Cs increases linearly with time is known as the "kinetic sampling" or "linear uptake mode", and sampling in this phase is time-integrative. The amount (N) absorbed by SPMDs throughout kinetic sampling is represented as:

$$N = R_s C_w t \tag{Eq. 9}$$

Equation 5, offers a characterization of the water sampling rate (Rs) in terms of kinetic sampling, as a function of the sampler volume (V_s), its sampler-water partition coefficient (K_{sw}), and the elimination rate (k_e), Assuming that the *in-situ* sampling rates of target compounds sharing similar physicochemical characteristics with the PRC can be accurately represented by the PRC R_s, the interest analyte can be calculated from Eq. 8

The conceptual link between classical batch extraction techniques and passive sampling with SPMD is established through sampling rates. The error involved depends on the degree of equilibrium achieved, but neither approximation is necessary. By integrating the definition of Rs (Eq. 5) into the full model (Eq. 6), the links between calibration data (R_s and K_{sw}), absorbed amounts, and aqueous concentration are established:

$$N = V_s K_{sw} C_w \left(1 - \left(e^{-\frac{R_s t}{V_s K_{sw}}}\right)\right) \tag{Eq. 10}$$

Consequently, the aqueous concentration can be estimated from the absorbed amount by using this equation:

$$C_w = \frac{N}{\left(\left(V_s K_{SW}\ (1 - \exp\left(\frac{-R_S t}{V_S K_{SW}}\right)\right)\right)} \tag{Eq. 11}$$

The benefit of using Equation 11 is that there is no need to establish arbitrary boundaries for the linear or kinetic sampling modes.

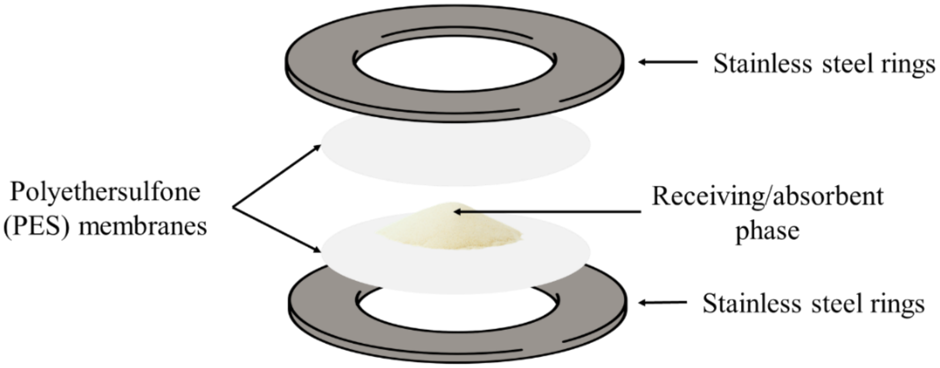
2.3.2 Polar Organic Chemical Integrative Samplers (POCIS)

Designed by (Alvarez et al., 2004) POCIS-type membranes were designed to sample a wide range of hydrophilic organic compounds such as polar pesticides, pharmaceuticals, hormones, or organic compounds with $\log K_{ow}$ <4.0. POCIS devices were designed to replicate the respiratory exposure of aquatic organisms to dissolved chemicals. POCIS sampling aids to address the issues stemming from dietary assimilation of chemicals, metabolism, chemical elimination, evasion of contaminated areas, and mortality of test organisms *in-situ.*

The POCIS device consists of a receiving phase made of solid sorbent sandwiched between two microporous polyethersulfone diffusion-limiting membranes with a pore size of 100 nm, maximizing the surface area for chemical uptake (shown in Figure 7). The sampler device is typically compressed together using two stainless steel rings with an inner diameter usually ranging from 51 to 54 mm, exposing a surface area of 41 to 46 cm2. Currently, two sorbent configurations are commercially available, one being the configuration for pesticides, which was initially used for monitoring polar pesticides, and is a triphasic mixture of polymeric resins and a small amount of activated carbon, and the other being the configuration for pharmaceutical and personal care product, which is a mixture of HLB polymeric blend, a type of sorbent used in solid-phase extractions (SPE) that is characterized by its balance between the attraction for hydrophilic and lipophilic substances (Dias and Poole, 2002). The choice of sorbent depends on the class of target analytes, but it is not necessary to limit oneself to the two types mentioned above, it depends mostly with the affinity of the sorbent with the target compound (Bailly et al., 2013; Harman, Allan, and Thomas, 2012; Huckins et al., 2006c; Morin et al., 2012b).

Figure 7

Configuration of a POCIS device.



Note. View of the configuration of a POCIS device. Adapted from (Morin et al., 2012b, p. 146)

The POCIS device should be immersed in water for several days or weeks. It is then retrieved and transported to the laboratory for dismantling to collect the receiving phase. The analytes are extracted from the solid sorbent using solid-phase extraction (SPE), sonication, or pressurized solvent extraction (PSE). Subsequently, the eluate is typically analyzed using liquid chromatography coupled with mass spectrometry (LC/MS) or gas chromatography coupled with mass spectrometry (Morin et al., 2012b). The estimation of the contaminant in water for integrative passive sampling devices such as POCIS (Huckins et al., 2002) cited by Alvarez et al. (2007) can be carried out by the equation 12.

$$C_w = \frac{C_S M_S}{R_s t} \qquad \text{(Eq. 12)}$$

Where Cw is the concentration of the analyte in water, Cs is the composite concentration in the sorbent material, Ms is the mass of recovered sorbent, Rs is the sampling rate, and t is the exposure time. To estimate the sampling rate using performance reference compounds (PRCs), (Mazzella et al., 2010) suggested that under isotropic exchange conditions, the constant elimination rate, k_e of a PRC of the passive sampling sorbent can be determined using the following first-order relationship, equation 13:

$$ln \frac{C_0}{C_t} = k_e t \qquad \text{(Eq. 13)}$$

Where C_t is the residual concentration (µg/g) of PRC in the receiving phase after an exposure time (*t*) and C_0 is the PRC concentration in the receiving phase before exposure. When the elimination rate constant of the same PRC is determined under both calibration (k_{ecal}) and field ($k_{ein\ situ}$) conditions, then the actual field sampling rate ($Rs_{\text{in-situ}}$) can be approximated with a corrected value of the calibrated sampling rate (Rs_{cal}) as follows (Equation 14):

$$R_{s(corr)} = \frac{k_{e\,(in\ situ)}}{k_{e\,(lab)}} R_{s\,(lab)} \qquad \text{(Eq.14)}$$

In this study, we calculated the in situ Rs_{PRC} from the lab Rs_{PRC} obtained in previous studies in order to obtain an approximate estimation of the concentration of TCP in the water.

2.4 Water Quality Modeling

According to (Nirmalakhandan, 2002), modeling is the systematic use of acquired knowledge to simulate or describe the functioning of a system in the real world. Models can function as economical and effective instruments in situations where it is impractical to work directly with real, frequently intricate systems. Various environmental models, including hydrologic models, water quality models, and ecohydrological models, have been created to enhance the comprehension of environmental phenomena. Water quality modeling plays a crucial role in scientific research as it offers a systematic approach for integrating data and facilitates effective resource management through the use of dependable predictive frameworks (Effler et al., 1996). These computational models facilitate the conduct of computational experiments, which enable the investigation of the impacts of modifications made to the system. Such modifications may be prohibitively costly or unfeasible to carry out in actuality (Mai, 2023).

A wide range of models exists for the analysis and characterization of phenomena occurring in aquatic systems. These models provide detailed descriptions of the various processes and dynamics taking place within such systems. According to (Rauschenbach et al., 2016), the utilization of intricate models is crucial in effectively tackling the challenges within scientific domains, and these models have made significant advancements in terms of their sophistication and refinement. Water quality models utilize hydraulic models and various inputs to forecast the spatial and temporal dispersion of substances within a distribution system. The constituents encompass various factors such as the proportion of water originating from a specific source, water age, the concentration of an inert constituent, the quantification of a chemically active substance, and the quantification of by-products generated through disinfection (Clark, 2012). In order to comprehend biogeochemical processes related to surface water and evaluate water quality and pollution, several models have been developed (Bai et al., 2022). The utilization of models allows the incorporation of various temporal and spatial variables in the prediction of water quality. The popularity of simpler models that focus on the most significant processes has increased due to the complexity of parameter modeling, rendering a general model impractical (Palmer, 2001).

There has been a growing global interest among scientific, industrial, and government sectors regarding the presence of xenobiotics in food and multiple environments. This concern has prompted an upsurge in scientific research aimed at elucidating and comprehending the dynamics of pesticides in diverse environmental matrices. The ultimate goal of these efforts is to facilitate improved resource management strategies (Giesy et al., 2014). Table 3 displays a comparative analysis of various models employed in the evaluation of pesticide dynamics within aquatic environments.

Table 3

Pesticide dynamics models commonly utilized worldwide

Model´s Name	Objetive	Source
Perpest	This is a model that predicts the ecological risks of pesticides in freshwater ecosystems. This system predicts the effects of a particular concentration of a pesticide on various community endpoints, based on empirical data extracted from the literature.	(Van Den Brink et al., 2006b)
CASCADE-TOXSWA	To evaluate the exposure concentrations of pesticides in small watercourses systems, based on good agricultural practices of these products. The scale of the area of interest is typically on the order of 10 km².	(van den Berg et al., 2011)
Water Quality Analysis Simulation Program (WASP)	This model aids in interpreting and predicting water quality responses to natural phenomena and artificial pollution. It is a compartmental program for dynamic modeling of aquatic systems, including the water column and underlying sediment.	(Ambrose and Wool, 2017)
Surface Water Scenario Help (SWASH)	Calculate pesticide exposure concentrations in surface water scenarios using five different tools and models: -FOCUS Derivatives Calculator, which calculates pesticide inputs through deposition from spray drift. -PRZM-3, which calculates pesticide inputs through runoff. -MACRO, which calculates pesticide inputs through drainage. -TOXSWA, which calculates the behavior of pesticides in small surface waters. -SPIN, which is a central database for storing and editing pesticide properties.	(Roller et al., 2015)
Soil and Water Assessment tool SWAT	A soil and water assessment tool is a small watershed-scale model used to simulate the quality and quantity of surface and groundwater and predict the environmental impact of land use, land management practices, and climate change.	(Arnold et al., 2002)

Note: A comparative review of commonly used models for pesticides and water quality.

The selection of the WASP model for simulating the pesticide chlorpyrifos an its main degradation product TCP can be attributed to several factors. Firstly, it presents an economically viable solution by offering both commercial and free licensing options. Secondly, its adaptability facilitates the modeling of a wide range of aquatic systems, rendering it appropriate for an array of applications. Thirdly, the model accommodates the simulation of numerous variables, thereby enabling a thorough examination of the pesticide's influence. Lastly, the model is characterized by straightforward installation and an intuitive interface, expediting user accessibility and promoting extensive utilization.

2.4.1 Water Quality Analysis Simulation Program (WASP) Model

The WASP model is a water quality model that operates on a process-based framework, with the potential to be either mechanistic or deterministic in nature. The objective of this study is to anticipate the reactions of aquatic systems to outside influences (Ambrose and Wool, 2017). The Water Quality Analysis Simulation Program was developed as a tool for simulating the behavior and movement of pollutants in surface waters. This software offers a high degree of adaptability, allowing modelers to incorporate various kinetic processes, their corresponding inputs, transport mechanisms, and the physical characteristics of the surrounding environment. The principle of conservation law is a fundamental characteristic of WASP framework, as described by (Moses et al., 2015). The compartment modeling approach allows for the application of the model in various dimensions, including one, two, or three dimensions. This approach involves the consideration of advective and dispersive transport between discrete compartments or segments. The Water Quality Analysis Simulation Program (WASP) offers a range of modules that enable the simulation of various water quality parameters. In its latest version, 8.4, WASP introduces the Advanced Toxicant module, which has been enhanced to incorporate a greater number of state variables. In the general framework of WASP modeling, the user typically engages with the interface to generate the WASP input file (WIF), which is subsequently read by the software to carry out the simulation (C. Knightes et al., 2019). This process is illustrated in

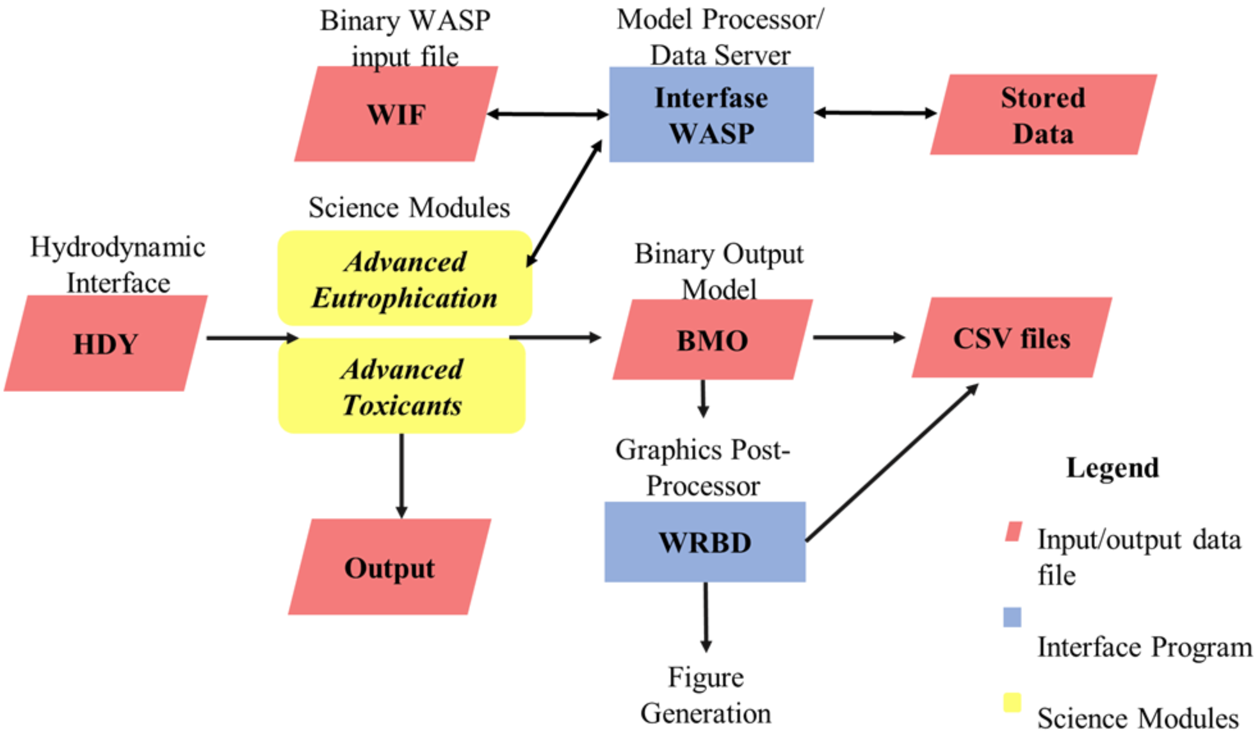
Figure **8**.

The efficacy of the WASP system is also reliant on the precision in collecting data regarding boundary and inflow conditions, along with environmental constants (Moses et al., 2015). The WASP8 Advanced Toxicant Module has been designed with a flexible structure that allows for the construction of processes that govern the contaminants of interest. The user makes a selection regarding the nature of the state variables and specifies the quantity for each. A diverse category of contaminants that can be simulated using WASP8, ranging from simple to complex forms, are enumerated as follows (Ambrose et al., 2017):

- Metals: Copper, Lead, Zinc, Cadmium, Arsenic, Tin, Selenium, Chromium.
- Mercury: Elemental, Divalent, Methyl (Explicit mercury model that will be released).
- Organics: MTBE, PCB, Petroleum, BTEX, HAP, Chlorinated solvents, VOCs, Pesticides, Organic acids.
- Nanomaterials: Carbon nanotubes, Graphene oxide, Titanium dioxide, Silver sulfide.

***Figure* 8**

WASP 8 Model Framework



Note. Taken from (C. Knightes et al., 2019)

A balance equation for dissolved constituents in a water body must encompass all material inflows and outflows through direct and diffusive loading, as well as advective and dispersive transport, and physical, chemical, and biological transformations. In this regard, it is essential to consider the coordinated system represented by Equation 15, where the *x* and *y* coordinates are situated in the horizontal plane, and the z-coordinate is situated in the vertical plane.

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(U_x C) - \frac{\partial}{\partial y}(U_y C) - \frac{\partial}{\partial z}(U_z C) + \frac{\partial}{\partial x}\left(E_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial Z}\left(E_z \frac{\partial C}{\partial z}\right) + S_L + S_B + S_K$$
(Eq. 15)

Where:
C = concentration of the water quality constituent, mg/L or g/m^3
t =time, days
U_x, U_y, U_z = advection mechanisms, longitudinal, lateral and vertical advective velocities, m/day
E_x, E_y, E_z = diffusion mechanisms, longitudinal, lateral and vertical diffusion coefficients, m^2/day
S_L = direct or diffused loading rate, g/m^3-day
S_B = boundary loading rate (including upstream, downstream, benthic and atmospheric), g/m^3-day
S_k = the kinetic transformations; positive is source, negative is sink, g/m^3-day

The WASP model has been previously implemented in various aquatic systems and has been applied to a wide range of contaminants, such as dissolved nitrogen concentrations in the Altamaha River Estuary, Georgia(Kaufman, 2011) water quality for eutrophication control for a reservoir in the Peruvian Andes (Mamani Larico and Zúñiga Medina, 2019), Simulation of nutrients, dissolved oxygen (DO), and chlorophyll-*a* dynamics in the Shenandoah River basin (Mbuh et al., 2019), Simulation of Cr-III dispersion in the High Bogotá River Basin (Ramos Ramirez et al., 2019), Transport and Fate of Copper and Nickel across the South Saskatchewan River Using (Prajapat et al., 2023)

Despite the widespread use of WASP in numerous studies, a comprehensive literature reviews up to December 2022 revealed a significant gap in its application. No published papers were found that utilized the WASP model to investigate the pesticide as chlorpyrifos or its degradation products. This absence suggested a prospective area for future research and the evolution of WASP's application to environmental studies.

2.5 Risk Assessment

The risk assessment has become a commonly used approach in examining environmental issues (Fairman et al., 2020). Risk assessment is the process of estimating the probability of unwanted effects occurring or already occurring as a result of exposure to one or more stressors (US EPA, 2000). These assessments are based on collecting data on the impact of the presence of compounds in certain environments and their interaction with the environment (US EPA, 1998). The environmental risk assessment was adapted from the framework of human health risk assessments in the presence of a stressor (Suter II, 2007).

2.5.1 Environmental Risk Assessment (ERA)

The concept of environmental risk assessment refers to the probability of an unwanted ecological event taking place due to various stressors, which include physical, geological, hydrological, or biological factors. Examples of such stressors may involve the degradation of natural habitats, soil erosion, droughts, floods, or the release of pollutants into the environment (Suter and Norton, 2019).

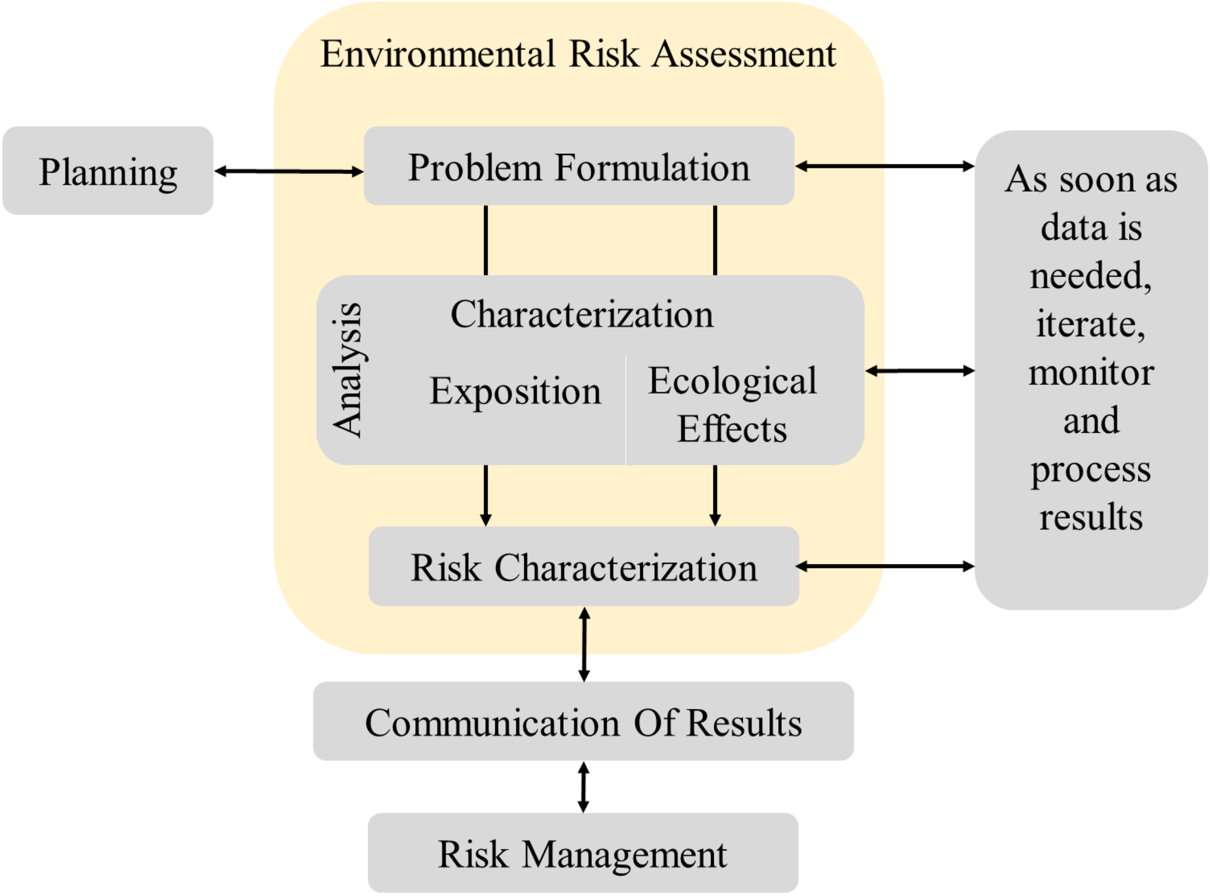
The most commonly used framework for environmental risk assessment is proposed by the (US EPA, 1998a). The ecological risk assessment process is based on two main elements: effects characterization and exposure characterization. These provide the approach to carry out the three phases of risk assessment: problem formulation, analysis, and risk characterization, as outlined in Figure 9. However, the risk assessment approach is generally driven by the type of management decisions that need to be made. Monitoring and acquisition of other data are often necessary during any phase of the risk assessment process, and the entire process is usually iterative rather than linear. The assessment of new data or information may require revising a part of the process or conducting a new assessment (Shea and Thorsen, 2012b).

(Suter II, 2007b) outlines the phases of risk assessment as follows:

2.5.1.1 Problem Formulation Phase. In this initial phase, the first hypotheses are proposed about the potential ecological effects resulting from the presence of stressors such as Chlorpyrifos and TCP. Objectives for the risk assessment are established, along with its scope, relevant evaluation criteria from an ecological perspective, and an analysis plan that outlines the assessment's design, data needs, and methods required to carry out the analysis phase of the risk assessment.

Figure 9

Ecological Risk Assessment Processes



Note. The first three phases of risk assessment are typically carried out by a risk assessor, while the phases of results communication and risk management (outside of the box) are activities that fall under the responsibility of the risk manager. Adapted from (US EPA, 1998b) and (Suter and Norton, 2019).

2.5.1.2 Analysis Phase. This is the phase where a technical assessment of data related to exposure and effects is carried out. The main objective is to characterize the potential risks associated with the presence of Chlopyrifos and the TCP, in the environment, considering their exposure pathways and the effects they may produce on the biotic and abiotic components of the ecosystem. To achieve this, a detailed analysis of the available data is conducted, including the identification of data gaps and uncertainties, and the selection of appropriate models and methods to estimate exposure levels and predict ecological effects. Ultimately, the goal of this phase is to provide a comprehensive understanding of the potential risks associated with a given stressor, and to identify any additional data or analyses that may be necessary to improve the accuracy of the risk assessment.

2.5.1.2.1 The Risk Characterization component of the exposure analysis involves:

- Exposure measures: measurement results indicating the nature, distribution, and amount of the agent at potential points of contact with receptors.
- Exposure analysis: a process of estimating the spatial and temporal distribution of exposure to the agent.
- Exposure profile: a summary of the results of the exposure analysis.

2.5.1.2.2 Effects Characterization. The component consists of:

- Effect measures: results of measurements or observations that indicate the responses of the assessment endpoints to the variation in exposure.
- Ecological response analysis: a quantitative analysis of effect data.
- Stress-response profile: the component of the ecological response analysis that specifically deals with defining a relationship between the magnitude and duration of exposure and the ultimate effects.

2.5.1.3 Risk characterization. This is the phase where the results of the analysis phase are integrated to estimate and describe risks. It consists of:

- Risk estimation: the process of using the results of exposure analysis to parameterize and implement the exposure-response model, estimate risks, and analyze associated uncertainty.
- Risk description: the process of describing and interpreting the results of risk estimation for communication with the risk manager.

Risk management is the process of deciding about the need for regulation, remediation, or restoration, and determining the nature and scope of the action. Risk assessors can interact with the risk management process in two ways:

- At the end of the risk assessment, the results of the risk characterization may simply be communicated to the risk manager, who determines the course of action.

- Risk assessors may interact with other analysts contributing to the decision, such as cost-benefit analysts or decision analysts, to provide integrated decision support.

Environmental Risk Assessment has become a very useful tool for developing environmental protection and management programs, as the results of the analysis provide a basis to support decision-making for the management of environmental resources (Evans et al., 2003). Ecological risk assessments are conducted to transform scientific data into meaningful information about the risk of human activities to the environment. Their purpose is to enable risk managers to make informed environmental decisions (US EPA, 1998b).

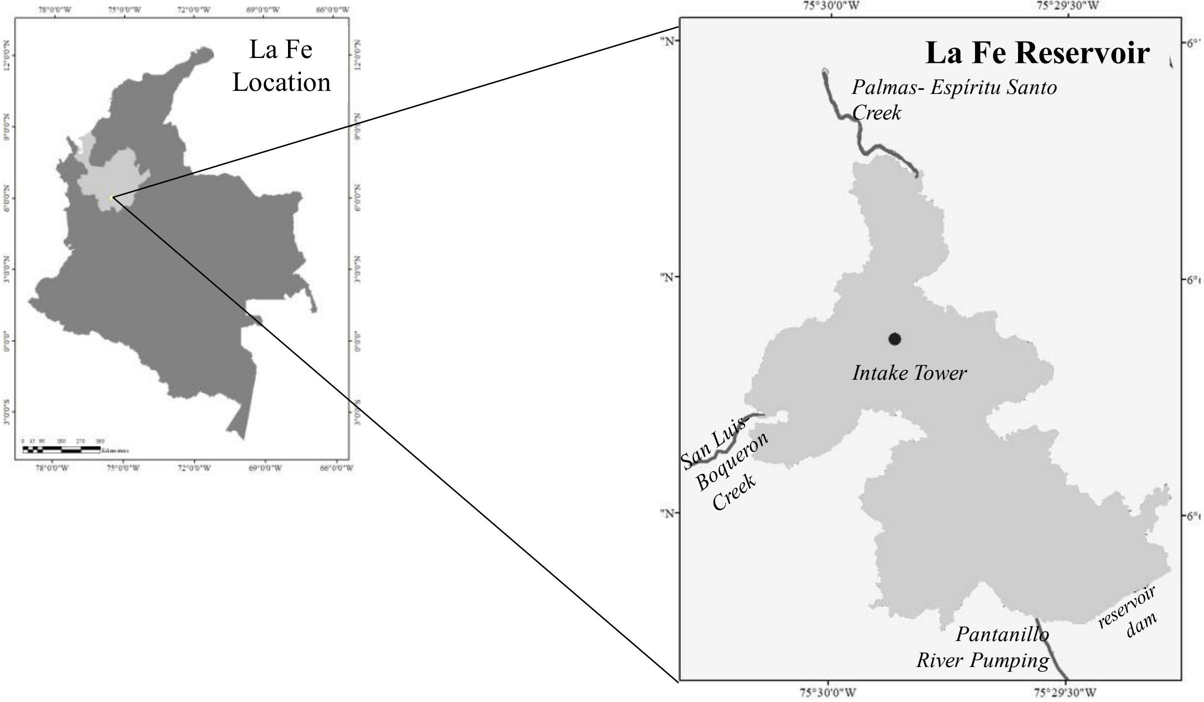
Chapter 3: Methodology

3.1 Study Area

La Fe reservoir is located in the municipality of El Retiro, in the eastern region of the department of Antioquia, Colombia, approximately 20 km from the city of Medellin. The reservoir is located at coordinates 75°28’ W and 06°12’90” N, at an altitude of 2175 meters above sea level (Figure 10). It has a surface area of 1.39 km^2 (Escobar et al., 2005) and a maximum water column depth of approximately 27 m (Florez-Molina et al., 2018).

Figure 10

Location of La Fe Reservoir



The La Fe reservoir is an artificial reservoir formed by two basins connected by a narrow and shallow channel corresponding to the old dam of the first phase of the project, called Los Salados, which was put into operation in 1967. The north basin, which was expanded in 1974, contains the intake tower (Román-Botero, Gómez-Giraldo, and Toro, 2013). With a storage capacity of 12 million m3, the reservoir is used for water supply to the La Ayurá and San Nicolás potable water treatment plants, electricity generation, and recreation. Additionally, it has a 18 MW mini hydroelectric power plant (Roman, 2011; Sierra and Ramirez, 2000). The La Ayurá plant has a water intake capacity of 9.2 m^3/s, which supplies water 3 million inhabitants in the metropolitan area of the Aburrá Valley (Salazar, 2017). While the San Nicolás plant has a water intake capacity of 0.20 m^3/s, which supplies some areas near of La Fe reservoir.

The area is characterized by the presence of agricultural, agroindustrial, industrial, mining, and commercial activities, as well as a strong urbanization process (Villabona-González et al., 2014). In 2016, the first stage of the water intake service for the San Nicolas water treatment plant was implemented. This facility supplies potable water to the rural areas of the municipalities of El Retiro, Rionegro, and Envigado. The basin is situated in a mountainous region characterized by enclosed topography. The altitude of the basins within this area varies between 2150 and 2900 meters above sea level. The precipitation pattern exhibits two distinct modes and has an average annual precipitation ranging from 2000 to 2200 mm (GAIA et al., 2016).

3.1.1 Influents

The average water residence time in the reservoir is 28 days (Román-Botero, Gómez-Giraldo, and Toro-Botero, 2013). The reservoir is supplied by natural gravity-fed tributaries and water imported from other basins via a pumping system (Florez-Molina, Parra-Sánchez, et al., 2017; Narvaez Valderrama, 2015). These water sources include:

3.1.1.1. Las Palmas Creek. It originates in the municipality of Envigado, between elevations of 2765 and 2670 meters above sea level. It receives contributions from the Espíritu Santo stream shortly before entering the reservoir. The water quality of the stream is related to the highwater demand, inadequate land use practices, and large earth movements that extract the organic layer. The tributaries have been reported as contaminated by the use of agrochemicals and wastewater.

3.1.1.2. Espíritu Santo Creek. This stream originates from the El Chagualo hill, located in the Municipality of Envigado, at an elevation of 2,700 meters above sea level. Its main tributary is the La Marta stream, which joins its waters just before the Espíritu Santo stream flows into Las Palmas. The Las Palmas and Espíritu Santo streams converge 1 km upstream from the north zone of the reservoir.

3.1.1.3. Potreritos Creek. The Potreros creek is the name given to the union of San Luis and Boquerón creeks, a watercourse that flows into the western area of the reservoir

3.1.1.4. Pantanillo River Pumping. The waters imported from the Buey and Piedras rivers are pumped at the Pantanillo River. During periods of drought, water is pumped from the Pantanillo River to feed the reservoir. The pumping is done through a submerged pipeline and a surface channel, both of which are located in the southwestern area of the reservoir.

3.1.2 Soil Characteristics and Land Use in La Fe Reservoir Basin

The soils in the study area are characterized by a pyroclastic material cover, with volcanic origin, and therefore are rich in minerals, total nitrogen, and organic matter, making them suitable for agricultural use. Several types of soils are found in the drainage basin, but all are covered by Andisols. The depth of soils is moderately deep in areas with volcanic ashes, and tends to be shallow in more rugged areas. Drainage is good on slopes and imperfect in depressions, resulting in erosion due to diffuse runoff, rills, gullies, and localized mass movements. Most of the land in the reservoir basin is located in mountain and hill landscapes, with soils suitable for agroforestry and silvopastoral systems. Land use includes flower cultivation and livestock farming. Oak forests are observed in the upper parts of the basin, while eucalyptus, cedar, and patula pine plantations are observed in the reservoir's influence zone. In the drainage basin of the Las Palmas and Espiritu Santo creeks, there are forest plantations, some fallows and secondary forests, as well as recreational farms, land parcels, human settlements, and some livestock farms. Meanwhile, in the upper part of the Pantanillo river basin, La Agudelo and Potreros creeks, large livestock farms, some forest plantations, secondary forests, and low fallows are present (Florez-Molina, Parra-Sánchez, et al., 2017; Gutiérrez-Cifuentes et al., 2017).

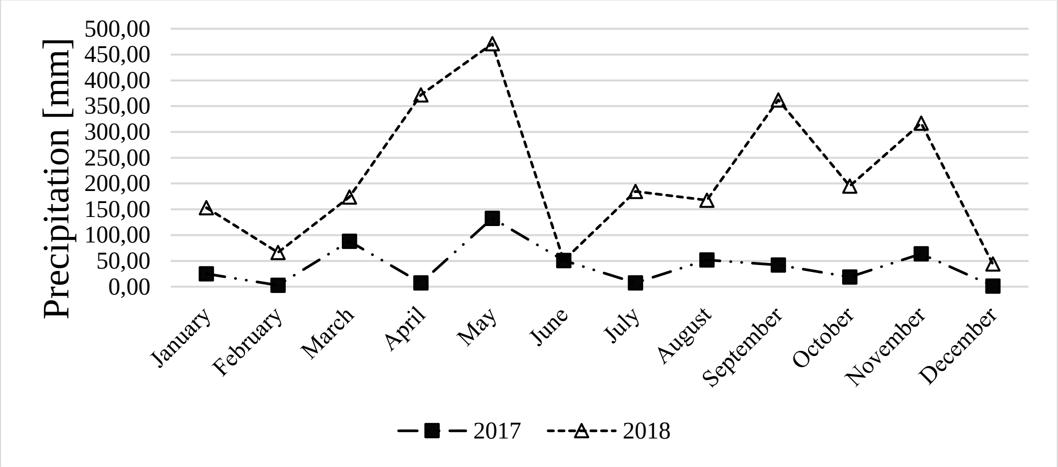
Agricultural activities in the inflows basins include the cultivation of potatoes, beans, blackberries, avocados, and various vegetables. Furthermore, flower cultivation is common in the upper reaches of the Pantanillo stream. The major land use pattern is sub-urban, which includes residential subdivisions, condominiums, and recreational farms. However, there are still large estates owned by a few individuals, complete with forest plantings and livestock. Pasture management accounts for more than half of land usage in these areas, with the most common crops being kikuyu grass (Pennisetum clandestinum), clover (Trifolium repens), and dandelion (Taraxacum officinale). Pastures are routinely fertilized to improve sustainability and cow productivity. However, the use of pesticides on grass is a substantial source of indirect contamination of water resources (Narvaez Valderrama, 2015).

3.1.3 Climatic Characteristics

Colombia's climate is primarily influenced by its equatorial location, which results in the absence of distinct seasonal variations. Consequently, the country's climate is primarily defined by the yearly patterns of rainfall distribution. The nation exhibits a monomodal regime in both the southern and northern zones, while adopting a bimodal regime in the Andean region. Furthermore, the climate of the country is subject to the influence of the Pacific Ocean's temperature, which exerts its impact through the El Niño-Southern Oscillation (ENSO) phenomenon (Duque Escobar, 2008). The data presented in Figure 11 illustrates the monthly precipitation measurements for the years 2017 and 2018, which were obtained from the meteorological station situated at the reservoir. The reservoir's location in the Andean region is characterized by a bimodal rainfall pattern, wherein the highest precipitation occurs during the second and fourth quarters of the year. However, during the year 2017, a significant disparity in precipitation levels was observed due to a decrease in rainfall attributed to the occurrence of the El Niño phenomenon during that particular year.

Figure 11

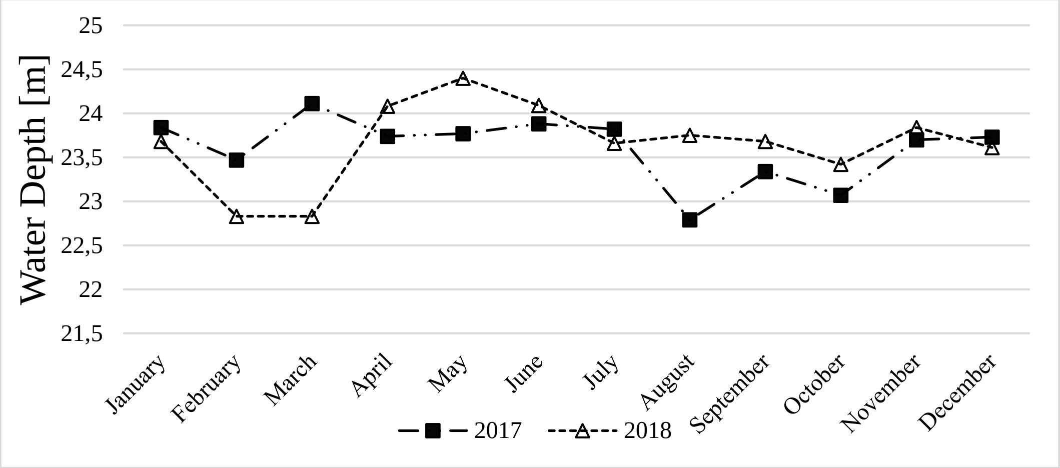
Precipitation in the La Fe reservoir



Note. Climatological data from a station located within the reservoir.

As a water reservoir, the levels of the La Fe reservoir are directly affected by the rainfall regime in the area, as well as by the minimum volume control through the pumping of water from the Pantanillo River. Figure 12 shows the depth levels of the reservoir during the period 2017-2018.

Figure 12
Water Depth in the Reservoir



Note. Climatological data from a station located within the reservoir.

3.2 Sampling Campaigns

The selection of the sampling devices was based on the physicochemical properties of the targeted compounds and the environmental conditions of the study area. Moreover, the collection of sediment samples complements the study by providing information on the distribution and persistence of the target compounds in the environment, as sediments serve as sinks for many pollutants. Given the physical and chemical characteristics of the compounds under study, two types of passive samplers were used: SPMD devices for Chlorpyrifos and POCIS devices for TCP. In addition, surface sediment samples were collected to evaluate the presence of these substances in this matrix.

3.2.1 Preparation of Passive Sampling Devices

Due to the hydrophobic characteristics of Chlorpyrifos, semi-permeable membrane devices (SPMDs) were chosen for sampling. These devices were obtained from Environmental Sampling Technologies (EST-Lab), USA. The configuration used consisted of standard membranes that were 92 cm long and 2.5 cm wide, containing 1 ml of high purity triolein doped with 100 ng of PCB-14, which served as a performance reference compound. SPMD membranes were stored in original packaging, containing pressure-sealed lid and argon, and maintained at -20°C until field deployment.

To assemble the POCIS devices, 200 mg of Oasis® HLB sorbent from EST-Lab, USA, was weighed and packed between two polysulfone membranes compressed between two stainless steel rings (Figure 13). The POCIS devices were assembled in the laboratory with the following configuration: an internal diameter of 5.1 cm and an external diameter of 8.9 cm, providing a surface area of 41cm^2 for exchange. They were stored in sealed containers, protected from light, and refrigerated at 4°C until deployment in the field. To calibrate the sampling rates using the PRC method, the methodology proposed by (Mazzella et al., 2010) was followed for the preparation of the spiked sorbent medium with deisopropylatrazine-d5 (DIA-d5), a deuterated compound. 2.5 g of Oasis® HLB were mixed with 12.5 mL of methanol, to which 10 µg of DIA-d5 were added, and the solution was sonicated for 5 minutes. The sorbent was then dried under a gentle flow of nitrogen.

Figure 13

Preparation of POCIS in the laboratory

The POCIS and SPMD devices were assembled and placed on the supports inside the stainless steel basket (see Figure 14) which were also acquired from EST-Lab. This configuration protects the devices from damage or loss, and also allows for a constant flow of water, preventing the sampling devices from being affected by flash floods that carry large solid materials or animals.

Figure 14
Arrangement of passive sampling devices in the field

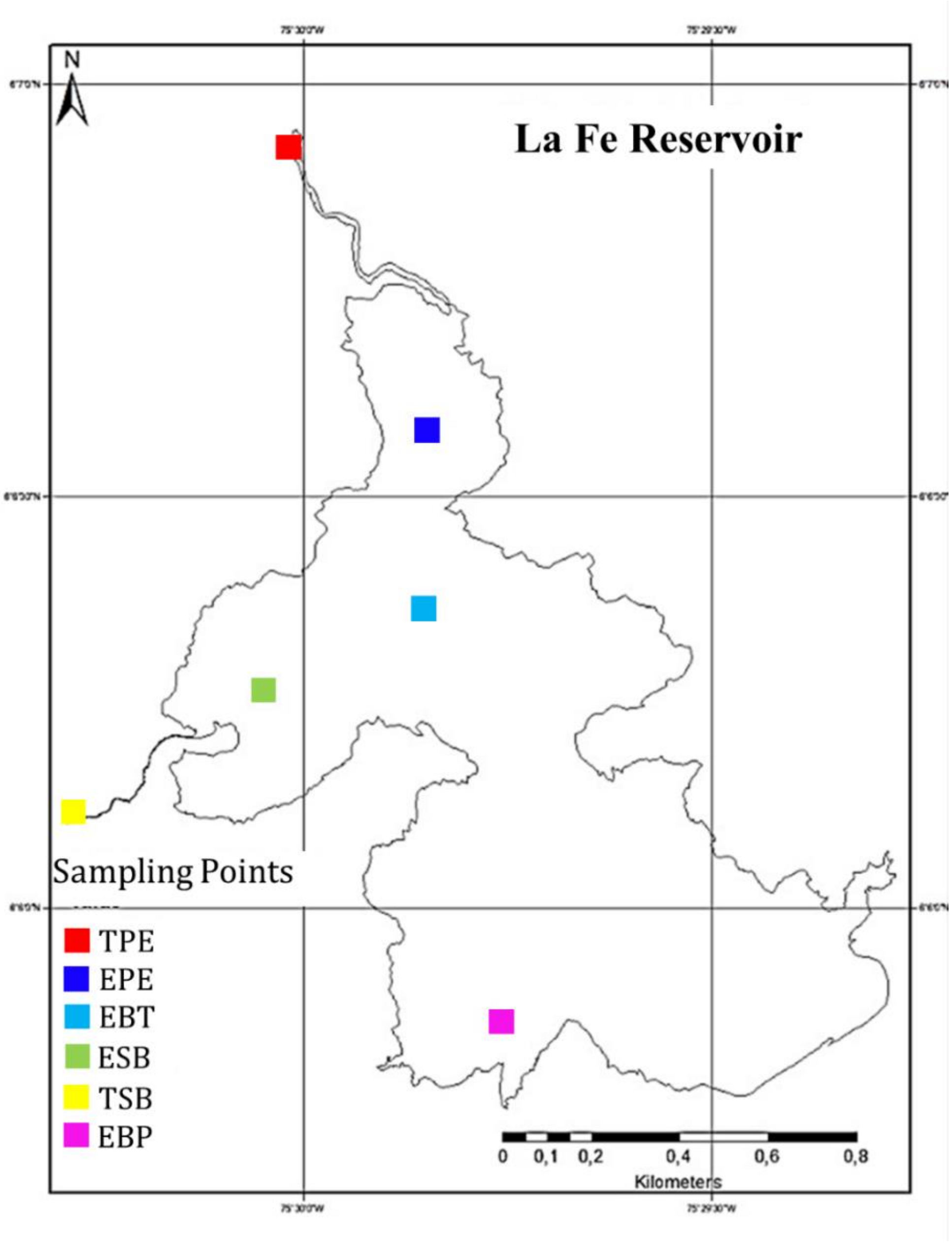
3.2.2 Field Deployment

To conduct this study, a convenience sampling approach was employed for sample collection, as an aleatory sampling method would not have been feasible due to limitations in accessibility and safety conditions at the sampling points. In order to mitigate the risk of theft or loss of the sampling equipment, sampling locations were selected where existing infrastructure provided protection, thereby minimizing the likelihood of equipment loss or damage. Six monitoring points were located in the reservoir, considering the discharge of the tributaries and the mixing zones of the reservoir with its tributaries, as shown in Figure 15. The infrastructure present in the reservoir was used, such as cages specifically designed to place the devices using infrastructure present in the tributaries (Palmas-Espíritu Santo and San Luis-Boquerón streams), as well as flotation buoys for delimitation of ultrasound equipment for the control of cyanobacteria blooms for the installation of the baskets and anchors present in the water intake tower. In this way, it was ensured that the sampling devices remained submerged in the water and protected from the drag or damage caused by the presence of fauna in the ecosystem and the suspended solid material carried during flood season. Additionally, a flotation device was used in the Reservoir-Pumping

Pantanillo (EBP) mixing zone (Appendix 6) where there is no existing infrastructure within the water body that could serve as a base for the installation of the sampling devices.

Figure 15

Sampling points Reservoir La Fe



The monitoring points were located in areas that had been previously prepared to accommodate the baskets containing the sampling devices, as shown in Table 4 which provides the georeferenced locations of the monitoring stations established for this study.

Table 4
Sampling Points

Sampling Site	Name	Coordinates	
San Luis Boquerón Tributary	TBS	6° 6' 6.37"N	75°30'16.92"O
Palmas Espiritu Santo Tributary	TPE	6° 6'55.72"N	75°30'0.50"O
Reservoir – Tributary Palmas Espíritu Santo	EPE	6° 6'34.44"N	75°29'51.11"O
Reservoir intake tower	EBT	6° 6'22.18"N	75°29'51.50"O
San Luis Boquerón Tributary-Reservoir	ESB	6° 6'15.18"N	75°30'2.53"O
Reservoir- Pumping Pantanillo River	EBP	6° 5'51.70"N	75°29'45.79"O

3.2.2.1 Monitoring and Collection Campaigns. During the development of this doctoral thesis, three passive monitoring campaigns were carried out in 2017, 2018, and 2019 (Appendix 2, Appendix 3 and Appendix 4) around the months of September, October, and November, during the second phase of the rainy season. The campaigns were carried out during the second rainy season of the year to ensure a permanent water volume in the reservoir and its tributaries, given that in the first deployment, there was a loss of membranes due to a decrease in water flow caused by the variability of water levels in the Pantanillo River pumping. In view of this situation, this sampling point was discarded for the monitoring campaigns in the context of this research.

The monitoring schedule for SPMD devices consisted of three field campaigns comprising six deployments, and for POCIS devices, two campaigns comprising five field deployments, in addition to a campaign for the calibration of POCIS devices to calculate the sampling rate. Additionally, during this period, surface sediments were collected at the monitoring points during the three campaigns.

3.2.2.1.1 Sediment sample collection. Surface sediment samples were collected using an Eckman-type dredge at each designated sampling point, coinciding with the location of the canisters that contained the passive samplers as referenced in (Table 4). Sediment retrieval occurred once during each deployment, with an annual frequency, resulting in a total of three sediment samplings. After collection, the sediments were placed in sealed containers and refrigerated until they could be transported to the laboratory. There, they were air-dried for 48 hours at room temperature (20°C) in an extraction hood under dark conditions.

3.2.2.1.2 POCIS Calibration for Rs Estimation. In order to estimate the sampling rate of POCIS, a sampling site was set up at the water intake tower (EBT), samplers were recovered by triplicate (n=3) with a weekly frequency for 21 days. The extraction, cleaning, and preparation of these samples are described in the following section.

The water intake tower was chosen as the sampling location due to its strategic position in capturing the water flow from the tributaries and the reservoir. The weekly frequency of POCIS sampling was selected to ensure that the samples accurately represented the concentration of contaminants in the water during the entire monitoring period. The use of multiple POCIS for each sampling period ensured the reproducibility and reliability of the results. The subsequent extraction, cleaning, and preparation of the samples followed standard protocols to avoid any potential contamination or bias in the analysis.

3.3 Extraction, Cleaning and Preparation of Samples for Quantification

Due to their ability to accumulate a wide variety of contaminants, the processing of the passive samplers for analyte extraction plays a crucial role in detecting and quantifying the target analytes, in this particular case, TCP and CPF. Therefore, the extraction and cleaning processes of the samples from the passive sampling devices used in this research, as well as the sediments collected during the deployment campaigns, are presented in this section.

3.3.1 Chemical Analysis of Samples

A Thermo Scientific Ultra TRACE GC- ISQ single-quadrupole Mass Selective Detector Gas Chromatograph and a 95% dimethylpolysiloxane-5% diphenyl chromatographic column, 30m x 0.25mm ID and a film thickness of 0.25µm, was used to identify and quantify CPF and TCP in semipermeable membranes devices, POCIS, sediments, and elutriates. The operating conditions presented in Table 5 were used.

Table 5

Operating conditions of chromatography equipment

Item	Condition
Carrier Gas	Helium
Flow per column	1,0mL /min
Pressure to head of column	15 PSI
Injector temperature	250° C
Interface temperature	270 °C
Source Temperature	200 °C
Oven programming	-Starts at 50ºC, stays for 2 minutes up to 190°C to 30°C/min -from 190°C for 5 minutes to up to 200°C to 2°C/min -from 200°C for 4 minutes to 250°C to 15°C/min
Injection mode	Splitless
Splitless time	1 minute
Injection volume	1 µL
Ionization Mode	Electronic impact
Electronic Power	70 eV

Note. Operating conditions adjusted to EPA 8141C and 8270D methods

For the identification of the target analytes CPF, TCP, PCB 14, DIA-d5, Atrazine, and Triphenylphosphate, the following identification ions were used (Table 6):

Table 6

Identification ions of analytes of interest

	CPF	**TCP**	**PCB-14**	**Atrazine**	**DIA-d5**	**Triphenyl-phosphate**
Peso Molecular	322.5	198.4	223.1	215	178.6	326.3
m/z 1	97	254	152	200	179	326
m/z 2	197	256	222	215	137	77
m/z 3	314	93	224	58	-	-

Note. Data obtained from (National Center for Biotechnology Information, 2019)

The experiments conducted to determine linearity, range, limits of detection and quantification for method verification were carried out as follows: for the calibration curve of Chlorpyrifos and PCB-14 used as a PRC for the calculation of the RS in SPMD, curves were constructed with six concentration levels in the range of 25 µg/L to 500 µg/L, showing an R^2 of

0.995 for CPF and 0.9998 for PCB-14, and an RSD of 3.5%. For TCP and DIA-d5, R^2 =0.9982 and 0.9943 respectively, with an RSD of 7.3% for Atrazine.

3.3.2 SPMD Processing

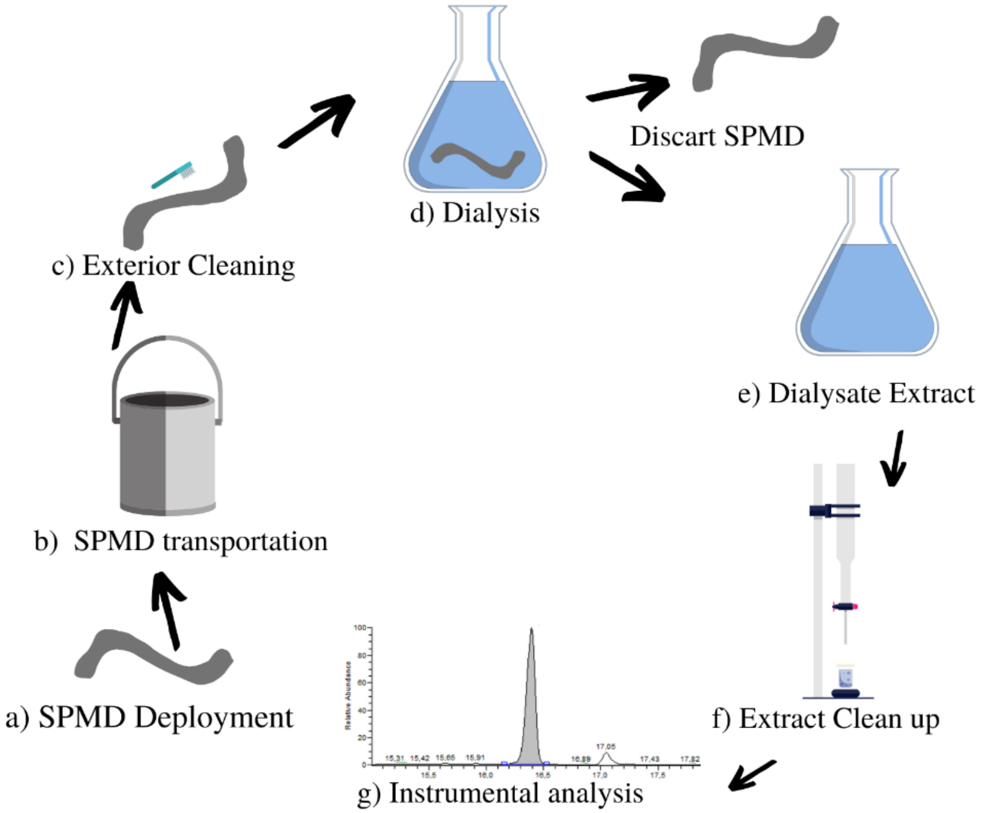
The processing steps for SPMD devices for sample extraction were presented by (Huckins et al., 2002), as cited in (Huckins et al., 2006c). Figure 16 provides a graphical summary of the processing procedure. Once the SPMD membranes were recovered after deployment, they were washed according to the procedure described by (Huckins et al., 2006a), after field retrieval and transportation to the laboratory, the SPMDs were cleaned using a soft-bristled brush under a gentle flow of tap water to remove the biofilm and periphyton that had accumulated on the membrane's surface. Each SPMD was then submerged in hexane for 30 seconds, followed by immersion in 1M HCl for another 30 seconds to remove any mineral salts adhering to the membrane. The acid was rinsed off with running water, and a rinse with high-purity acetone and isopropyl alcohol was performed to remove excess water from the membrane surface. Finally, the membranes were air-dried for 5 minutes on trays covered with previously solvent-rinsed aluminum foil.

After the cleaning process, the extraction of the target analyte was carried out using the dialysis technique. Three SPMDs corresponding to each sampling point were submerged in 250 mL of chromatographic-grade hexane with medium-speed agitation at 450 rpm for 24 hours. Following this, the first fraction was collected, and the dialysis process was repeated for another 24 hours. The collected sample was concentrated down to 2ml using a rotary evaporator.

As traces of triolein is also in the dialyzed fraction, a cleaning procedure for the extracts must had been performed. Following the method described by (Šetková et al., 2005), gel permeation chromatography, which involved the use of 1.5g of Bio-Beads® S-X3 in a chromatography column to separate triolein and other interferences from the analytes. Bio-Beads® S-X3 were prepared using 10mL dichloromethane as solvent to prepare column, the 2mL sample were eluted with 10 mL of a 50:50 % volume solution of cyclohexane: ethyl acetate, followed by 5 mL of ethyl acetate, was concentrated to near dryness under a gentle flow of nitrogen in a water bath at 35°C up to a volume of 1mL. It was reconstituted with chromatographic grade acetone up to 2 mL and 10µL of triphenyl phosphate that was added as an internal standard (ISTD). To proceed with gas chromatography coupled with mass spectrometry analysis as previously described in item 3.3.1, Chemical Analysis of Samples.

Figure 16

SPMD Processing

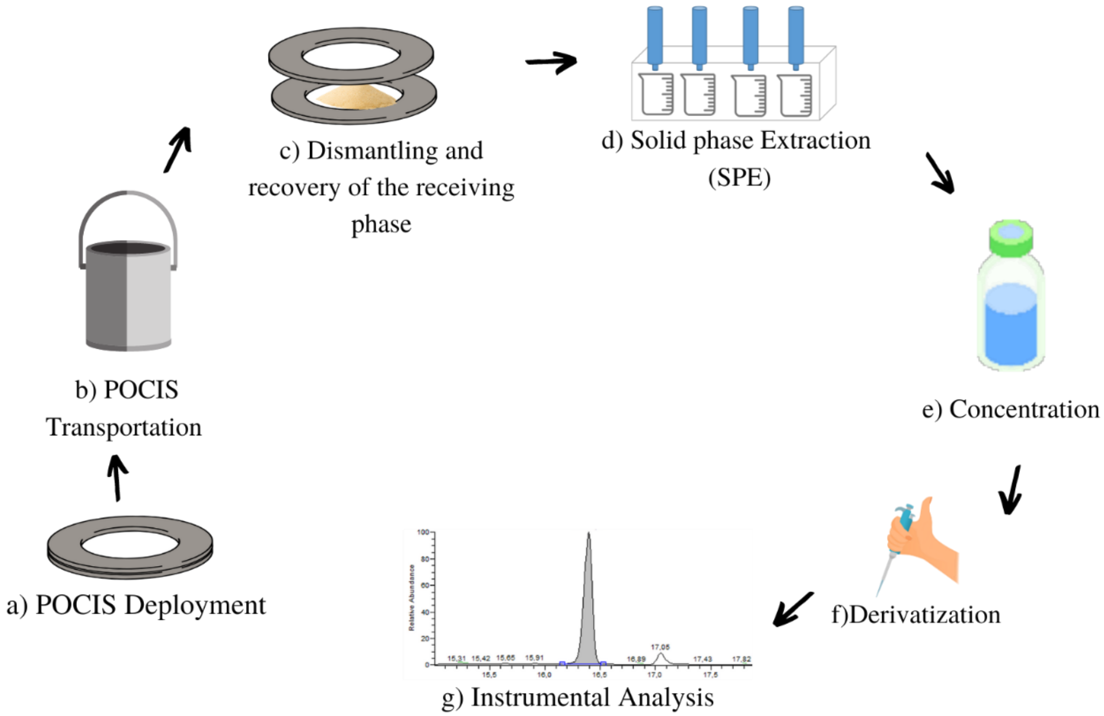


Note. Steps for the processing of SPMD devices from their recovery in the field (a) to their instrumental analysis (e), which in the case of this study was by gas chromatography coupled to mass spectrometry. Source: Adapted from (Huckins et al., 2006c).

3.3.3POCIS Processing

The methodology proposed by (Narvaez Valderrama, 2015; Yabuki et al., 2016) as well EPA Methods 3535 and 3500, were adapted to carry out this study, as shown graphical summary in Figure 17. Prior to disassembling the POCIS devices for sorbent recovery, the devices were gently washed with ultrapure water to remove any biological deposits or other debris from the PES membranes. The sorbent material was carefully recovered from the POCIS devices and transferred to a pre-weighed empty SPE tube. The sorbent was then completely dried under vacuum Visiprep™ SPE Vacuum Manifold. Once the sorbent was dried, the SPE tubes were weighed again. Subsequently, the dried sample was eluted from the SPE tubes with 20 ml of a mixture of Acetone-Methanol-Acetonitrile (15:10:5) until dryness was achieved under vacuum. The collected elutions were then completely dried under a gentle flow of nitrogen gas and spiked with 20µL of atrazine as reference standar. Next, the samples were reconstituted with 1ml of acetone. Due to the polar nature of TCP, a derivatization process was carried out by adding 20µL of N-(tert-Butyldimethylsilyl)-N-methyltrifluoroacetamide (MTFBSTA) to the sample and incubating the samples at a temperature of 70 °C for 60 minutes.

Figure 17
POCIS processing



3.3.4 Sediment Processing

Once the sediment was dried, it was sieved through an ASTM #200 mesh to obtain a particle size <75µm. For the extraction of analytes, the protocol established in EPA method 3546 for Microwave Extraction of Insoluble and Poorly Soluble Organic Compounds from Soils, Clays, Sediments, and Solid Waste was followed. 0.5g of sediment was weighed and a solvent solution of Hexane: Acetone (1:1, v/v) was used. The solution was placed in PTFE material cells in the microwave-assisted solvent extraction system.

The GAIA group in their laboratory has the MILESTONE ETHOS ONE equipment for CPF and TCP microwave-assisted extraction. The equipment was programmed under the following operating conditions: 10 minutes up to 120°C and then held constant at 120°C for 20 minutes.

Subsequently, the sample was cleaned using Florisil following the EPA-3620C method. 2.5g of Florisil were weighed and added to a glass chromatographic column, which was fitted with a glass stopper previously washed with acetone. Anhydrous sodium sulfate was added to form a layer of 1cm in height. The column was pre-eluted with 10mL of hexane, discarding this eluate. Just before exposure to air, 2mL of the sample extract was added, and the transfer was completed with 2 rinses of 2mL of hexane. Then, the column was washed with 10mL of an ethyl ether: hexane solution in a vol: vol proportion of 6:94, at a drip rate of 5mL per minute; the column was then eluted again with an ethyl ether: hexane solution in a vol: vol ratio of 15:85, and a third elution: ethyl ether: hexane solution in a vol: vol ratio of 50:50. All the eluate was collected in a 48mL vial previously washed with acetone. The collected elution was concentrated under a gentle flow of nitrogen in a water bath at 35°C, 10µL of triphenyl phosphate was added as an internal standard, and it was made up to 1mL with chromatographic grade acetone, from which a duplicate was taken for MTFBSTA derivatization to read the polar compound, TCP. Additionally, a total carbon (TC) characterization was performed by acid digestion and spectrophotometry, and a mineral characterization of the sediments was carried out using X-ray fluorescence (XRF) on a Thermo Scientific™ ARL™ OPTIM'X instrument (see Appendix 8 and Appendix 9)

3.3.5 Preparation of Elutriates for Acute Toxicity Test Tests

Elutriates of sediments were used for acute toxicity tests, following the methodology proposed by (Poveda-Saenz, 2012). A sediment: water volume (1:4) was prepared in a container with 100 ml of sediment and 400 ml of reconstituted water, which was stirred (280 rpm) for 48 hours in light-protected containers. The supernatant was then separated and passed through a 0.45µm fiberglass filter. The filtered supernatant was then used to perform acute toxicity tests, using a *Daphnia pulex* strain from the La Fe reservoir as the test species, for which the GAIA research group laboratory is accredited. To determine the concentrations of TCP and CPF in the elutriate samples, solid-phase extraction (SPE) was performed using EPA Methods 3500 and 3535A with 10ml of each prepared elutriate sample. The chemical analysis performed on the samples is specified in the following sections, and the results obtained from the ecotoxicity tests are detailed in Chapter 4.

3.4 Modeling and Simulation of the Dynamics of Chlorpyrifos and TCP in La Fe Reservoir

To achieve the second objective of this study, namely "to adjust the WASP modeling tool to the characteristic conditions of the region for its application in evaluating the dynamics of Chlorpyrifos and its degradation product TCP in the La Fe reservoir," we employed the Water Analysis Simulation Program (WASP 8.4). This tool enabled us to model the behavior of Chlorpyrifos and TCP within the La Fe reservoir while accounting for the region's specific environmental conditions. The model's parameterization and calibration were informed by data collected during several passive sampling campaigns. These campaigns allowed us to obtain real-world concentrations of CPF and TCP, which were then integrated into the WASP model for more accurate and realistic simulations. The detailed concentrations obtained from these sampling campaigns are documented in Appendix 10 and Appendix 11. This approach allowed us to investigate the dynamics of CPF and TCP in a comprehensive and rigorous manner.

Climatological data for the period 2017-2018 were obtained from the meteorological station located at the La Fe reservoir, which also monitors water temperature at different levels as presented in Figure 11. Physicochemical characteristics were measured using the HANNA 9829 multiparameter instrument (see Table 15). For hydraulic variables, data obtained in the field, as well as bathymetry and flow measurements provided from Empresas Publicas de Medellin (EPM) and previous studies conducted in the reservoir were used as reference (Amaringo Villa, 2022; Florez-Molina, Parra-Sánchez, et al., 2017; Narvaez Valderrama, 2015; Román-Botero, Gómez-Giraldo, and Toro, 2013). The steady-state model was used because the volume variations are not significant, and pumping from the Pantanillo river is activated precisely to prevent a decrease in reservoir levels. It is turned off during rainfall events to avoid exceeding the reservoir's capacity.

3.4.2 WASP Model Configuration and Parametrization

The modeling of aquatic systems is a valuable tool for evaluating the transport and fate of pollutants in aquatic environments. In this study, we employed the widely used Water Quality Analysis Simulation Program (WASP) version 8.3 (Ambrose and Wool, 2017) to simulate the movement of Chlorpyrifos and 3,5,6-trichloro-2-pyridinol (TCP) in a reservoir. The simulation was conducted on a computer with 8GB RAM, the Windows 10 operating system, and an Intel® Core i7-5500U processor.

The modeling approach was based on the flow-routing option, which employs a specific flow for each segment, volume, depth, and velocity for the segments within the reservoir. We employed the Euler method as the numerical solution method, which allows for the resolution of the segments based on specific initial and boundary conditions. To model the organic compounds, we used the Advance Toxicant module, a useful tool for predicting the fate and transport of organic pollutants in aquatic systems. The CPF and TCP concentrations, as well as the depth, width, and length characteristics of the segments showed in Table 7, were entered as input information for the simulation using the program's user interface. The data utilized in this study were procured through a combination of field measurements, reservoir management records, and open-source GIS data.

Table 7

Hydraulic characteristics of the La Fe reservoir

Sampling Site/ SegmentID	Length (m)	Width (m)	Area (m^2)	Average depth (m)	volume (m3)	Caudal (m^3/s)
TSB	382[a]	1.3[a]	-	0.6[a]	297.96	1.4*
TPE	685[a]	14.18[a]	-	1.5[a]	14385	1.4*
EPE	-	-	159133.33[b]	12[a]	1909599.96	-
EBT	-	-	334570.88[b]	18[a]	6022275.84	4.36*
ESB	-	-	172803.07[b]	6[a]	1036818.42	-
EBP	-	-	5881370.12[b]	20[a]	117627402	4.0*

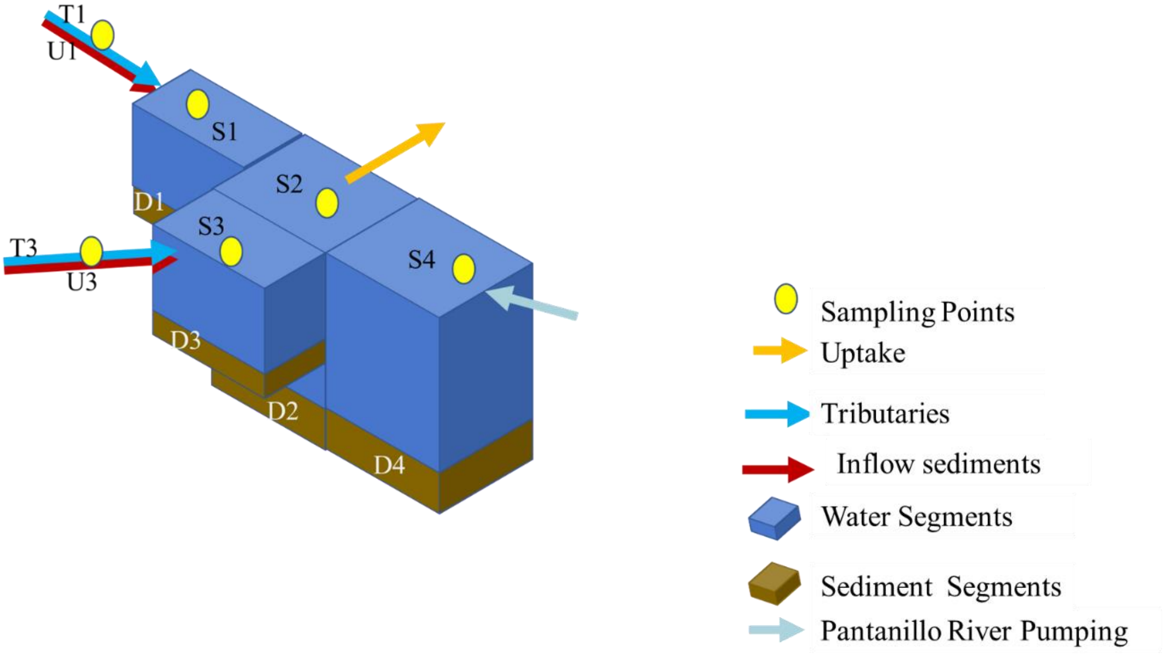
Note. * Data obtain from EPM. [a] Field-measured data. [b] Data obtained from measurements supported by Open GIS systems.

The segmentation of the reservoir as illustrated in Figure 18, was determined by the locations of the monitoring points, using a method called convenience sampling. Convenience sampling involved selecting locations that were easily accessible and safe while ensuring that the model accurately represents the entire reservoir.

Several factors were considered when choosing these points. Firstly, identifying optimal sampling locations was crucial for taking a comprehensive understanding of CPF and TCP dynamics within the reservoir. Safety was another important aspect to consider, it was essential to select sampling locations that minimized potential hazards as vandalism, associated with the sampling process. Lastly, the representativeness of the model was a primary concern. The sampling points were chosen to cover various areas and conditions in the reservoir, ensuring an accurate representation of pollutant dynamics across the entire reservoir.

Figure 18

Segmentation of La Fe reservoir for WASP simulation



Note. The water column segments were identified as T1=TPE, T3=TSB, S1=EPE, S2=EBT, S3=ESB, and S4=EBP. Sediment segments were identified as U1=TPE, U3=TSB, D1=EPE, D2=EBT, D3=ESB, and D4=EBP.

The "Flow Routing" transport mode was chosen for the simulations of Chlorpyrifos and its degradation product TCP in the La Fe reservoir as shown in Table 8 using WASP, due to its ability to accurately represent the primary physical processes influencing pollutant transport in the reservoir. This approach allows the model to use specified flow rates for each segment of the reservoir without adjusting the volume, depth, or velocity in response to changes in flow (Ambrose and Wool, 2017). This transport mode simplifies the model by treating flow, volume, depth, and velocity as independent parameters. This approach is particularly advantageous given the complex nature of the reservoir's hydrodynamics and the need to balance computational efficiency with model accuracy.

Table 8

Segment definition and transport mode

Segment Name	**Segment Type**	**Transporte Mode**	**Segment Below**
S1	Surface Water	Flow Routing	D1
S2	Surface Water	Flow Routing	D2
S3	Surface Water	Flow Routing	D3
S4	Surface Water	Flow Routing	D4
D1	Surface Benthic	Flow Routing	None
D2	Surface Benthic	Flow Routing	None
D3	Surface Benthic	Flow Routing	None
D4	Surface Benthic	Flow Routing	None

Table 9 presents the options for water column flow movement entered into the WASP model interface.

Table 9

Water Flow Path

T1		**T3**		**T4**	
From	**To**	**From**	**To**	**From**	**To**
Boundary	1: S1	Boundary	3: S3	Boundary	4: S4
1: S1	2: S2	3: S3	2: S2	4: S4	2: S2
2: S2	Boundary	2: S2	Boundary	2: S2	Boundary

Note. T1: TPE, T3: TSB, T4: EBP

Advective transport was determined by introducing the flow values at the initial state of each segment. This method facilitated the depiction of flows associated with water streams within the simulated system. The dispersive element was identified based on cross-sectional and longitudinal dimensions, as detailed in Table 10.

Table 10

Sediment-Water Column Exchange

From	To	Area [m2]	Distance [m]	Benthic-Water Diffusion coefficient [cm2/sec]
5: D1	1: S1	129479	0.05	4.41e-05*
6: D2	2: S2	51767	0.05	
7: D3	3: S3	176995	0.05	
8: D4	4: S4	411333	0.05	

Note. * taken from (Luo and Zhang, 2009)

The post-processing module of WASP enabled the exportation and examination of concentration fluctuations of both CPF and TCP across spatial and temporal scales. Stablishing the boundary conditions as shown in Table 11.

Table 11

Boundary Conditions for initial parametrization [mg/L]

	CPF	TCP
S1	0.000309	0.000193
S3	1.24e-05	0.000205
S4	2.93e-05	0.000763

Note. TWA concentrations estimated from passive sampling

Table 12

Parameters and parameter values used in WASP

Parameter	CPF	TCP
Molecular weight [g/mole]	358.59[a]	198.44[b]
Henrys Law Constant [atm/(mole/m3)]	1.85e-05[a]	4.2e-06[b]
Vapor Pressure [atm]	2.46e-09[a]	1.36e-06[b]
Solubility [g/m3]	1.4[a]	220[b]
Partition Coefficient of chemical to Solid(1)- [L/kg]	5509[c]	149[d]
Phototransformation rate constant- wavelength [(1/day)/(W/m2)]	0.0234[e]	-
First-order biodegradation rate constant [1/day]	0.916[f]	-

Note. [a] (National Center for Biotechnology Information, 2020), [b] (National Center for Biotechnology Information, 2018), [c](Sabzevari and Hofman, 2022), [d] (University of HertFordshire, 2018), [e] calculated from (Mackay et al., 2014b), [f] (Sud et al., 2020).

3.3.4 Model Calibration

To identify the critical parameters that influence the model response, the model calibration was conducted. For calibration purposes, parameter values were selected to adjust the model to the real conditions of the reservoir, using three sets of different contaminant concentrations.

During the calibration process, simulated concentrations by the model will be compared to the concentrations observed in the reservoir. To evaluate the model accuracy, statistical techniques such as the coefficient of determination, R^2 and the mean absolute error (MAE), equation 15; were employed. A high R^2 value and a low MAE value indicates that the model is properly calibrated and capable of accurately reproducing contaminant concentrations in the reservoir.

$$MAE = \left(\frac{1}{n}\right) * \Sigma|i = 1, n||y_i - \hat{y}_i| \qquad \text{(Eq. 15)}$$

Where:

n = total number of observations
y_i = observed value of the i-th observation
$\hat{y}_i$ = predicted value by the model for the i-th observation

3.3.5 Model Verification

The Index of Agreement (IOA) was used to check how well the model was doing, where a score above 0.6 indicates good performance (Willmott et al., 2012). Equation 16 help us calculate how much the model's predictions differ from actual measurements, which is important for making sure the model is reliable. The data used to test the model includes real measurements and the model’s own predictions of the amounts of a chemical called TCP.

$$IOA = 1 - \frac{\sum_{i=1}^{n}(O_i - P_i)^2}{\sum_{i=1}^{n}(|P_i - \bar{\mathrm{O}}| + O_i - \bar{\mathrm{O}})^2} \qquad \text{(Eq. 16)}$$

3.3.6 Scenario Simulations

For the purpose of this investigation, we will consider simulating two scenarios: changes in climate conditions and changes in land and water management practices upstream of the reservoir. These scenarios were chosen because they can have a significant impact on water quality and the dynamics of chlorpyrifos and its degradation products in the reservoir:

Changes in Climatic Conditions: In addition to precipitation variability, other changes in climatic conditions such as temperature and humidity can influence the dynamics of chlorpyrifos and its degradation in the reservoir.

Changes in Land and Upstream Water Management Practices: If there have been changes in land and upstream water management practices, such as the adoption of sustainable agricultural practices or the construction of new infrastructure, these changes can have an impact on water quality and could be considered as a scenario to be simulated.

3.3.7 Methodologic considerations

An important limitation of this study lies in the limited availability of sampling data for the degradation product TCP contaminant. While sampling data were available for Chlorpyrifos in the years 2017, 2018, and 2019, data for TCP were only available in 2018 and 2019. This implies that specific TCP information from 2017 is not available for inclusion in the analysis. However, the CPF information and TCP sampling data from 2018 and 2019 were taken into consideration to calibrate the model parameters and estimate the TCP dynamics based on the relationship with its parental product. Despite this limitation, measures were taken to ensure that the obtained results are as accurate and representative as possible.

3.5 Risk Assessment

To conduct the proposed risk assessment for this research, the Guidelines for Ecological Risk Assessment by the US Environmental Protection Agency (US EPA, 1998a) and an analysis based on the Standard Guide for Risk-Based Corrective Action (ASTM, 2015) were implemented. The data collection and evaluation processes were conducted in a stepwise manner to ensure a rigorous and systematic approach. The analysis involved assessing data obtained from a literature review, field measurements, and an acute toxicity bioassay with *Daphnia pulex*, a reliable bioindicator of water quality.

In the absence of significant data obtained from ecotoxicity tests with *Daphnia pulex* conducted in this research, as shown in Chapter 5, deterministic methods have been used to estimate the risk of chronic and acute exposure to Chlorpyrifos and TCP. Specifically, risk assessment models proposed by the United States Environmental Protection Agency (US EPA) have been applied, including the US EPA's Exposure Assessment model and US EPA's Risk Assessment model. For chronic risk assessment, Chlorpyrifos and TCP concentrations in water and sediments of the reservoir, as well as the frequency and duration of exposure, were considered. Meanwhile, acute risk assessment took into account the maximum concentrations of both chemical compounds and the duration of exposure.

3.5.1 Formulation of the problem

First, a review of existing literature was conducted to identify potential hazards and exposure pathways for the chemicals of concern. This information was used to develop a conceptual model to guide the risk assessment. Second, field measurements were collected to characterize the physical and chemical properties of the study site, as well as to quantify the concentrations of the chemicals of concern.

3.5.2 Analysis Phase

In this phase, the data to be used was defined based on their usefulness in evaluating risk hypotheses. Exposure was analyzed by examining sources of stressors, the distribution of stressors in the environment, and the degree of occurrence or contact. Effects were analyzed by examining stressor-response relationships, evidence of causality, and the relationship between effect measures and endpoints of evaluation.

3.5.2.1 Characterization of the Exposition. To estimate the potential or actual contact or coexistence of stressors with receptors, based on exposure measurements and ecosystem and receptor characteristics that are used to analyze sources of stress, passive sampling results and analyte concentrations in sediments were used. In particular, SPMD samplers were used for Chlorpyrifos, and POCIS samplers were used for TCP, and data were collected during six and five sampling campaigns, respectively.

3.5.2.1.1 Characterization of sediment exposure. In order to assess sediment toxicity, it is necessary to convert the concentration of pesticides in sediments into the concentration of pesticides in the interstitial water, using equation 17 as proposed by (Schwarzenbach and Westall, 1981)

$$C_{pw} = \frac{C_s}{k_d} \tag{Eq. 17}$$

Where Cs is the concentration of pesticides measured in the sediments and linear Kd is the sorption coefficient. The value of Kd is calculated from the partition coefficient between organic carbon and water (K_{oc}) and the fraction of organic carbon in the sediments (f_{oc}), using equation 18.

$$k_d = K_{oc} \times f_{oc} \tag{Eq. 18}$$

The values of K_{oc}, f_{oc} were taken from available literature as presented in Table 13.

Table 13

Values for Ecological risk calculation

	Koc	Kof	log Kd	LC$_{50}$ [µg/L]	PNEC [µg/L]	NOAEL [mg/kg bw/day]	ADI [mg/kg bw/day]	ARfD [mg/kg bw]
CPF	5509[a]	149[a]	7.33[*]	0.1[a] 0.24[e]	0.014[c**]	0.1[d]	0.001[d]	0.005 [d]
TCP	149[a]	845[a]	5.1[*]	12000[b]	120[**]	0.05[d]	0.03 [d]	0.25 [d]

Note. [a](Sabzevari and Hofman, 2022), [b] LC$_{50}$ in Aqueous Media(US EPA, 2018a),[c] (San Juan et al., 2023a), [d] (European Food Safety Authority (EFSA), 2014), [e] LC$_{50}$ in sediments (Cáceres et al., 2007)[*] calculated from Eq. 17 and Eq.18. [**]The factor was used AF=100 (Pacini, n.d.).

3.5.2.2 Characterization of effects. The characterization of ecological effects was performed through a stressor-response factor analysis, using a bioassay with *Daphnia pulex*, a strain originating from La Fe reservoir and cultured in the GAIA Group laboratory at the University of Antioquia, in elutriates of sediment extracted from the reservoir. The characterization of ecological effects was performed through a stressor-response factor analysis, using a bioassay with *Daphnia pulex*, a strain originating from La Fe reservoir and cultured in the GAIA Group laboratory at the University of Antioquia, in elutriates of sediment extracted from the reservoir. Since the experiments with *Daphnia pulex* yielded non-significant results for assessing the effects of TCP and CPF on the organism, it became necessary to consult available literature to compile the ecological effects of these stressors, as well as their potential effects on the ecosystem as a whole.

3.5.3 Risk Characterization

Based on the data previously obtained, risk estimation was performed using the Single Point Exposure and Effects Comparison approach, using both the Hazard Quotient method and probabilistic methods for risk assessment. In addition, for acute exposure risk estimation, the use of toxic units was implemented, allowing for the comparison of exposure levels to levels associated with acute toxic effects.

3.5.3.1 Acute Exposure Risk Characterization. The method of Toxic Units (Könemann and Pieters, 1996; Rasmussen et al., 2015) was proposed to calculate acute risk using equation 19 for the analysis of water and sediment samples.

$$TU = \frac{C_i}{LC_{50}} \qquad \text{(Eq. 19)}$$

To calculate the accumulated toxicity at each site (equation 20)

$$\sum TU_{site} = \sum_{i=1}^{n} TU_i \qquad \text{(Eq. 20)}$$

If the sum of the TUs is greater than 1, this indicates the potential ecological risk in that site due to exposure to the present contaminants. On the other hand, if the sum of the TU is less than 1, the risk is considered low or insignificant.

3.5.3.2 Chronic Exposure Risk Characterization. To conduct a chronic risk assessment, a deterministic approach called Risk Quotient (RQ) method (Vryzas et al., 2009) was employed by applying equation 21. This method calculates the ratio of the predicted environmental concentration (PEC) to the predicted no-effect concentration (PNEC) of a specific contaminant. The PEC is estimated based on the exposure concentration, while the PNEC is determined by using ecotoxicological data from laboratory or field studies. An RQ value of less than 1 indicates a low risk, while an RQ value greater than 1 suggests a potential risk of adverse effects on organisms in the ecosystem.

$$RQ = \frac{MEC}{PNEC} \qquad \text{(Eq. 21)}$$

The concentration measured in the environment is denoted by MEC, while the predictive no-effect concentration (PNEC) is defined as the concentration below which no harmful effects are expected to occur. To estimate the PNEC values, available data on the lowest observed effect concentration (LOEC) or the no-observed effect concentration (NOEC) of a toxic substance on sensitive organisms over short- or long-term exposure periods are used (San Juan et al., 2023a) previously presented in Table 13. Subsequently, this value is divided by an assessment factor (AF=100), as described in equation 22.

$$PNEC = \frac{NOEC}{AF} \qquad \text{(Eq. 22)}$$

As stated by (Merga et al., 2021) if the sum of the Risk Quotients (∑RQs) is less than 1, the risk of chronic toxicity at the evaluated site is considered minimal. Sum values ranging from 1 to 10 indicate a medium risk, while values exceeding 10 represent a high risk of chronic toxicity.

3.5.3.3 Human Health Risk Characterization. To evaluate the risk to human health, the Risk Quotient (RQ) methodology was applied, which is used to estimate non-carcinogenic hazards for humans. Considering that the Joint Meeting on Pesticide Residues (JMPR) concluded that it is unlikely that chlorpyrifos poses a risk for tumor formation in humans (WHO, 2011). Studies conducted in the laboratory and on living animals indicate that chlorpyrifos is not harmful to genetic material, while long-term studies show a reduction in cholinesterase activity as the main toxicological concern observed in all species. RQ is calculated as shown in equation 23.

$$RQ = \frac{CDI}{RfD} \qquad \text{(Eq. 23)}$$

Where the *CDI* is the Chronic Daily Intake [mg/kg/day] and it is given by equation 24.

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \qquad \text{(Eq. 24)}$$

Where *C* is the concentration of the contaminant in the water [mg/L] as seen in (Table 17 y Table 21), *IR* is the water intake, *EF* is the exposure frecuency , *ED* is the exposure time for adults and children, *BW* is the body weight for adults and children; *AT* is the average lifespan, ARfD is the Acute Reference Dose, according to the (European Food Safety Authority (EFSA), 2014) for Chlorpyrifos *ARfD* is 0.005 mg/kg/day and for TCP *ARfD*= 0.25 mg/kg/day. Values presented in Table 14.

Table 14

Human exposure and health-risk parameter values calculations

	IR [L/day]	**BW [kg]**	**ED [years]**	**AT [days]**	**CF [µg to mg]**	**EF [days]**	**ARfD CPF [mg/kg/ day]**	**ARfD TCP [mg/kg/ day]**
Adult	2[a]	70[b]	70[b]	2190[c]	0,0001	365[c]	0,005[d]	0,25[d]
Child	1[a]	15[b]	6[b]	25550[c]				

[a] (WHO, 2011); [b] (Smegal, 2000); [c] (Papadakis et al., 2015), [d](European Food Safety Authority (EFSA), 2014)

Although the model was designed for a single compound, it is well known that pollutants in nature occur in mixtures (Dar et al., 2023; Shi et al., 2011), and the same is true for chlorpyrifos and its degradation product. As a result, it is proposed that the Hazard Quotient be estimated as the sum (equation 25) of the Risk Quotients for each compound.

$$HQ = \sum_{i=1}^{n} RQ_i \qquad \text{(Eq. 25)}$$

An HQ < 1 implies a low risk to human health, while an HQ = 1 indicates a high risk. On the other hand, if HQ > 1, it implies a very high risk and warrants immediate action to mitigate exposure to the contaminant. Therefore, the HQ and RQ values serve as key indicators of the potential health risks associated with exposure to pollutants, and they provide critical information that can aid in making informed decisions to safeguard public health and the environment.

Chapter 4. Results and discussion

In the previous chapter, the methodology used in data collection to estimate the concentrations of Chlorpyrifos and TCP necessary for modeling and simulating the behavior of these substances in the La Fe reservoir was presented. Additionally, an assessment of the risk associated with the presence of the pesticide in the water column and surface sediments was conducted. In this chapter, the results obtained during the study are presented, and corresponding analyses and discussions are carried out.

The analysis and discussion of the results focus on the evaluation of the distribution and concentration of Chlorpyrifos and TCP in the La Fe reservoir, as well as the identification of possible sources of contamination and the potential environmental and public health consequences associated with them.

4.1 Physical-Chemical Parameters of Water at Monitoring Points

Table 15 presents the La Fe reservoir's average physical and chemical characteristics, summarizing water composition and quality properties through mean values. This data is essential for assessing the reservoir's environmental condition.

Table 15

Physicochemical characteristics of the reservoir

Parameter	Sampling Site					
	EBP	**EBT**	**EPE**	**ESB**	**TPE**	**TSB**
pH	7.9-8.2	6.7-7.0	6.3-6.8	6.4-6.7	6.3-6.8	6.0-6.5
Temperature (°C)	21.9±0.6	20.9±2.1	21.9±0.2	20.6±2.3	16.4±0.1	16.6±0.5
Conductivity (µS/cm)	45±0.0	50.7±9.0	46±1.7	42. 3±2.5	86.3±0.6	26±0.0
Oxygen Saturation (%)	97.3±12.7	62.8±23.5	76±2.6	72.1±14.6	86.3±1.2	45±0.2
Turbidity (NTU)	23±0.0	25±4.4	23±0.0	24.3±4.9	44±0.0	13.3±0.6
DO (ppm)	6.9±0.9	4.6±1.6	5.2±0.2	4.8±1.4	5.8±0.1	3.9±0.0

Note. mean ± standard deviation

The pH values found in La Fe reservoir (6.3-8.2) meet the requirement for bodies of water used for human consumption and recreation (Eboagu et al., 2019; Lukubye and Andama, 2017). It is important to mention that pH is not a parameter that directly affects human health, however, it is an important parameter due its role in the physicochemical and biological processes that occur in the aquatic ecosystems, besides its effects on the infrastructure of water treatment plants. The conductivity values collected (26 to 86.3 µS/cm) at the monitoring stations indicate that the total dissolved solids are within the acceptable range (<1000 µS/cm), according to Colombian regulations (Resolution 2115 of 2007) for water intended for human consumption. The turbidity parameter shows that the values in the reservoir area are relatively consistent, however, the differences found between NTU 44 in TPE and 13.3 NTU in TBS, indicates in the Palmas-Espíritu Santo tributary a strong anthropogenic intervention, as previously evidenced by (Amaringo Villa et al., 2019), which observed untreated wastewater is discharged into the stream near its point of confluence with the reservoir.

Regarding water temperature, moderate variations are observed among the sites, with EBP, EBT, and EPE showing higher temperatures (approximately 21.9°C) compared to TPE and TSB, which are notably cooler (approximately 16.5°C). This variation could reflect differences in solar exposure, water depth, or water inputs at the sampling sites.

Regarding oxygen saturation, these values indicate considerable variability, ranging from relatively high values in EBP (97.3%) to significantly lower values in TSB (45%). This variability can be explained by the fact that at the EBP site, which is the discharge point of the Pantanillo pumping, there is water agitation, increasing air exposure and promoting the mixing of water layers with different oxygen levels. Conversely, at the San Luis-Boquerón tributary discharge point, this reduced value suggests water contamination from chemical or agricultural runoff, where substances such as chemicals, heavy metals, or organic waste may be affecting water quality. Furthermore, is noticeable that the sampling point at the EBT water intake tower shows an average DO concentration of 4.6 ppm and an oxygen saturation of 62.8%, indicating a decrease in available oxygen. This could be due to factors such as the presence of cyanobacterial blooms or reduced oxygen renewal at this site.

4.2 Determination of Chlorpyrifos and TCP in La Fe Reservoir

Taking into account the previous research carried out by Narvaez in 2015, where the existence of the compounds chlorpyrifos and TCP in the La Fe reservoir was corroborated through passive sampling, the same methodology was used in this investigation to determine the concentrations and distribution of these compounds.

4.2.1 Concentrations and Distribution of Chlorpyrifos in La Fe Reservoir Water

Chlorpyrifos concentrations were estimated based on the sampling rates of the Semipermeable Membrane Devices (SPMDs), utilizing the dissipation of a Performance Reference Compound (PRC) - in this study, the compound PCB-14, which was spiked (100ng) into the triolein contained within the membrane (Appendix 10). The remaining PRC compound in the SPMDs after deployment was quantified via gas chromatography-mass spectrometry. The calibration curve exhibited an R^2 value of 0.99 and %RSD=11.4, see Appendix 19. The final PRC concentrations were then used to estimate the sampling rate by employing the publicly available spreadsheet from the US Geological Services. Table 16 displays the average concentrations of PCB-14 found within the SPMDs at each sampling point.

Table 16

Average PRC dissipation percentage and Sampling Rates by sampling site

Sampling Site	PRC final concentration Average [N, ng/SPMD]	Average PRC dissipation %	Rs average [L/day]
EBP	13,06	86,94	64,06
EBT	13,39	86,61	63,21
EPE	14,16	85,84	62,16
ESB	13,86	86,14	62,50
TPE	17,35	82,65	56,43
TSB	15,20	84,80	60,11

Data showed an average dissipation of the PCR in the study area of 85.5%, this percentage ensured that the capture of the contaminant occurred during the linear phase of the sampling kinetics, which is crucial for reliable sampling results. In this study, the average sampling rate was estimated to be 61.5 L/day, which appears lower than 72.6 L/day reported by Narvaez Valderrama et al.

(2023). However, considering the range of sampling rates found in this previous study conducted in La Fe reservoir spanned from 27.8 to 72.7 L/day, the rate observed in this present study agreed within this reported range, indicating consistency with the prior findings. Despite the differences in average rates, the employed sampling methodologies in both studies are equivalent and robust, thus providing reliable insights into the contaminant levels in aquatic environments.

Table 17 displays the average Chlorpyrifos estimated concentrations obtained by the SPMD devices passive monitoring technique. A total of six field deployments were conducted during the second rainy season of the years 2017, 2018, and 2019 to acquire the results. The calculated mean of the estimated concentration was calculated using results acquired from the six sampling campaigns conducted within a span of three years. The GC/MS quantification technique was used to estimate the mass chlorpyrifos in the SPMD, to estimate the TWA of chlorpyrifos in the La Fe reservoir.

Table 17

Descriptive Statistics of Chlorpyrifos TWA in La Fe Reservoir

	Concentration SPMD CFP[µg/L]					
	EBP	**EBT**	**EPE**	**ESB**	**TPE**	**TSB**
n	6	6	6	6	6	5
Median	0.004	0.004	0.010	0.024	0.010	0.012
Mean	0.009	0.006	0.033	0.030	0.063	0.010
Std. Deviation	0.011	0.007	0.054	0.032	0.122	0.006
Minimum	ND	ND	0.002	6.000×10^{-4}	4.600×10^{-4}	0.002
Maximum	0.028	0.018	0.140	0.076	0.310	0.015

Note. ND: no detectable. Averages obtained from the 6 deployments that were made during the 3 years of the campaign. Data processed with JASP statistical software (Wagenmakers, 2018)

During this investigation, average concentrations of chlorpyrifos were observed to be 0.015 µg/L in 2017, 0.041 µg/L in 2018, and 0.019 µg/L in 2019. The increase in concentrations can be attributed to elevated precipitation levels, which consequently lead to increased surface runoff into the reservoir influents. This favors the mobility and absorption to the sediments transported into the reservoir (Gebremariam et al., 2012a).

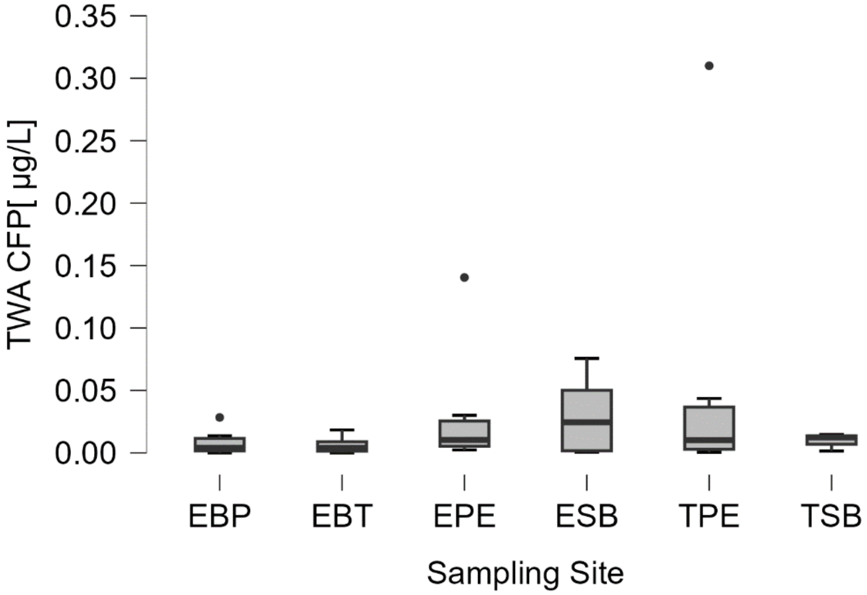
Statistical analysis showed the lowest averages concentrations of CPF were observed in EBP 0.009 µg/L and EBT 0,006 µg/L. In contrast, TPE presented the highest concentrations among all measured sampling points, with relatively high standard deviations, showing considerably variability in the Chlorpyrifos concentrations throughout the sampling deployments. The total average concentration of Chlorpyrifos observed in La Fe reservoir water was 0,0195 µg/L while the mean concentration of the Chlorpyriphos entry by its tributaries was 0.0365µg/L, with the highest average concentrations found in the TPE (0.063µg/L), and the lowest at the reservoir's intake tower, which corresponds to EBT point (0.006 µg/L). These observed values suggested active degradation processes in the reservoir, attributable to hydrolysis, photolysis and biodegradation processes. This variability in Chlorpyrifos concentrations in the La Fe reservoir and its inflows, not only highlight the dynamic nature of pollutant behavior in this aquatic environment but also set the stage for comparing these findings with global benchmarks, such as the study conducted by McCarthy (2008) where they estimated a time-weighted average concentrations of Chlorpyrifos using SPMD, ranging from 0.1 to 2 ng/L in the Columbia Slough, Portland, USA, values under the ranges estimated by this study. On the other hand, our observed data concentrations are close the TWA estimated by Zhang et al. (2016) in a rage of concentration <0.02-14.24 ng/L in the River Ugie, Scotland.

The higher concentrations in the TPE (Palmas Espiritu Santo creek) could be explained due to the presence of crops and livestock grazing in the tributary's surroundings in addition to the urbanization processes happening in the area and the indiscriminate use of Chlorpyrifos for flea control, these activities collectively contribute to diffuse pollution of the contaminant, as highlighted by Correa Z et al. (2018). Additionally, the reduction in CPF concentrations within the reservoir is likely due to a 28-day water residence time, facilitating natural transformation processes (Román-Botero, Gómez-Giraldo, and Toro, 2013).

An ANOVA test was performed on the CPF concentrations at all sampling points with a p-value of >0.05 (p=0.187), indicating that there is insufficient evidence to claim that there is a significant difference in CPF concentrations between the sampling points. This means that CPF concentrations may be similar at all sampling points and there may not be one point with significantly higher or lower levels, as can be seen in Figure 19.

Figure 19

Distribution of the estimated concentration of chlorpyrifos in the La Fe Reservoir



Note. Distribution of estimated time-weighted median concentrations (TWA) from passive sampling of Chlorpyrifos using SPMD devices at each sampling point.

Although high concentrations of CPF that were estimated in all tributaries y La Fe reservoir water, they did not exceed the allowable concentrations (0.1μg/L) in bodies of water intended for consumption according to EU Directive 2008/105/EC (Gvozdenac et al., 2013). It is noteworthy that the concentrations of CPF in the La Fe reservoir remained relatively stable over time and within a similar range, as expected for lentic water bodies such as La Fe reservoir. This consistency in the concentrations is in accordance with the natural processes and characteristics of such water bodies, which exhibit slow turnover rates and a tendency to accumulate pollutants. This suggests that the source of CPF contamination in the tributary is likely diffuse rather than point-source, meaning that it is coming from various sources and not from a single identifiable source such as a factory or wastewater treatment plant. As an study carried in Argentine Patagonia Dufilho and Falco (2020), where they highlights that the transport of chlorpyrifos to water systems is influenced by various factors such as soil properties, preferential flow pathways, and agricultural practices, indicating the contamination of water systems with chlorpyrifos is not solely attributed to a single point source but rather to multiple diffuse sources associated with agricultural activities and soil-water interactions.

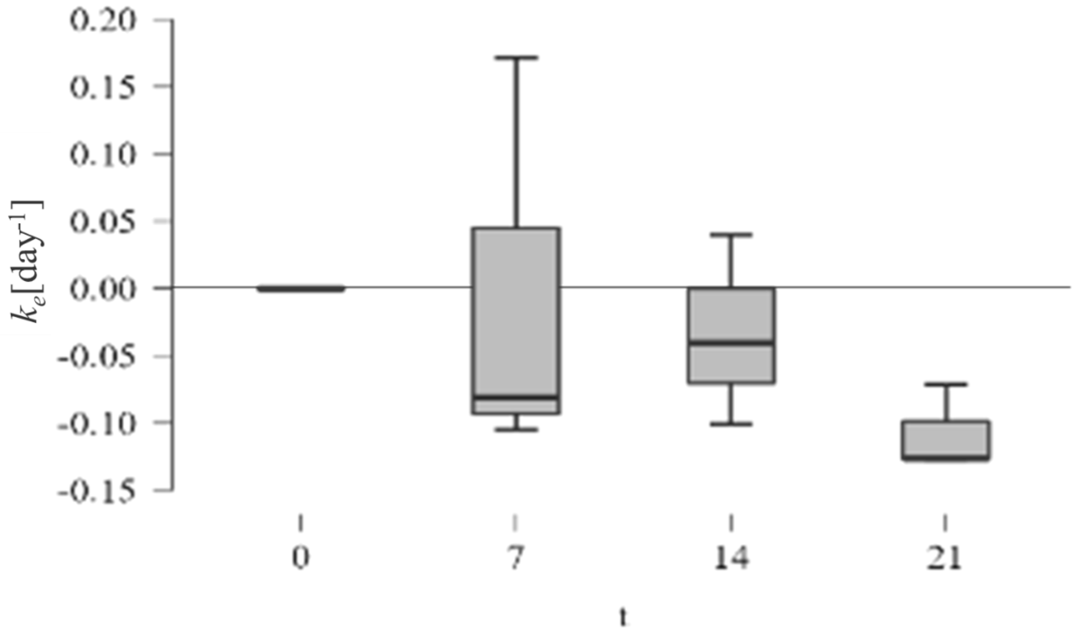
4.2.2 TCP on POCIS devices

In order to estimate TCP concentrations in the reservoir, an in-situ calibration was performed using the desorption kinetics of DIA-d5, a compound used as a Performance Reference Compound (PRC), to calculate the sampling rate Rs. This rate was used as a reference for estimating the time-weighted average concentrations of this degradation product.

4.2.2.1 In-situ calibration of POCIS using PRC approach. The desorption kinetics of DIA-d5 Figure 20 were used in situ at La Fe reservoir to estimate the sampling rate at the EBT point. Samples (n=3) were collected on days 7, 14, and 21 using POCIS doped with an initial concentration of 33 ng/g of DIA-d5 on the sorbent material of the POCIS, applying the equations presented in section 2.3.2

Figure 20

Distribution of DIA-d5 PRC concentrations in POCIS



Note: Boxplot of the concentrations found for the in-situ calibration using the PRC approach for estimating TCP sampling rates in La Fe reservoir.

A linear regression model was proposed using the *ke* values (Table 18) according to equation (9) to calculate the desorption rate of DIA-d_5. The intercept of the regression line (R^2 = 0.83) was used to establish *k*e=0.0516/d.

Table 18

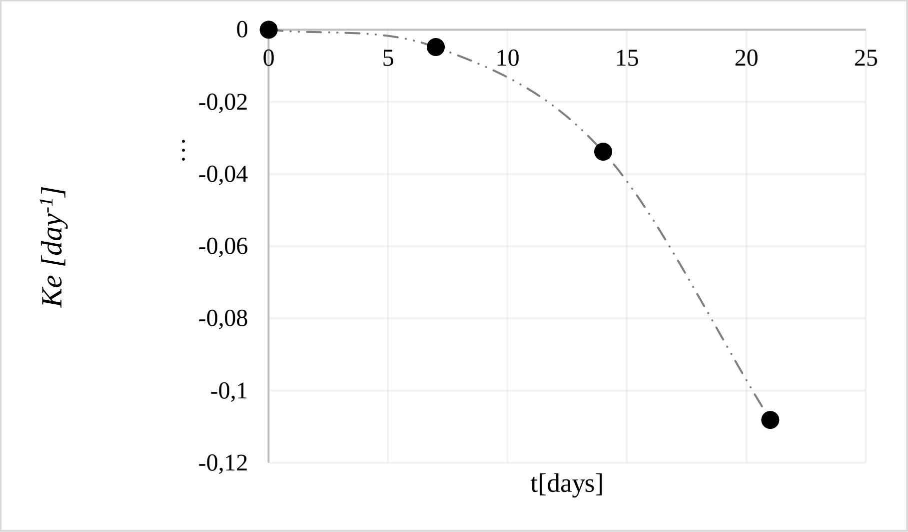
k_e in situ values of DIA-d_5

	k_e [day^{-1}]			
	t=0	**t=7**	**t=14**	**t=21**
n	3	3	3	3
mean	0.000	-0.005	-0.034	-0.108
Std Deviation	0.000	0.153	0.070	0.032

These data indicate a curvilinear elimination kinetics for the desorption of the PRC DIA-d_5, as seen in Figure 21, where a 94% elimination is observed at t=21, in response to the high desorption rate expected for the PRC approach (Mazzella et al., 2007).

Figure 21

DIA-d5 Elimination Kinetics



After obtaining the slope (k_e) and intercept (R_s) values through regression analysis, the in-situ sampling rate of DIA-d5 is calculated. This process is carried out using the k_e and Rs values previously obtained in laboratory conditions, as presented in Table 19.

Table 19

Values of k_e and R_s for sampling rate *calculation*

Parameter		Source
$k_{e\ (lab)}$	0.057	(Mazzella et al., 2010)
$R_{s\ lab}$ [L/day]	0.016	(Mazzella et al., 2010)
$k_{e\ (insitu)}$	0.0516	Calculated in this study
$R_{s\ (corre)}$ [L/day]	0.0145	Calculated in this study

The in-situ Rs value of 0.0145 L/day was used to estimate the time-weighted concentrations of TCP at each sampling point distributed throughout the reservoir. The mean of these concentrations during the deployment time is presented in Table 21.

Although the exchange of the PRC in POCIS is not completely isotropic, as confirmed by the present study and previous research by (Christopher Harman et al., 2012) , this approach allows for the most accurate estimate of chemical concentrations over time as it takes into account the actual flow velocity conditions at the sampling site. Moreover, an adsorption rate constant (ku) was obtained from the slope of the in-situ TCP concentrations shown in Table 20 estimated from the POCIS deployed for calibration with the PRC. These results provide a more comprehensive understanding of the spatial and temporal variability of TCP concentrations in the reservoir, and can inform future monitoring and management efforts.

Table 20

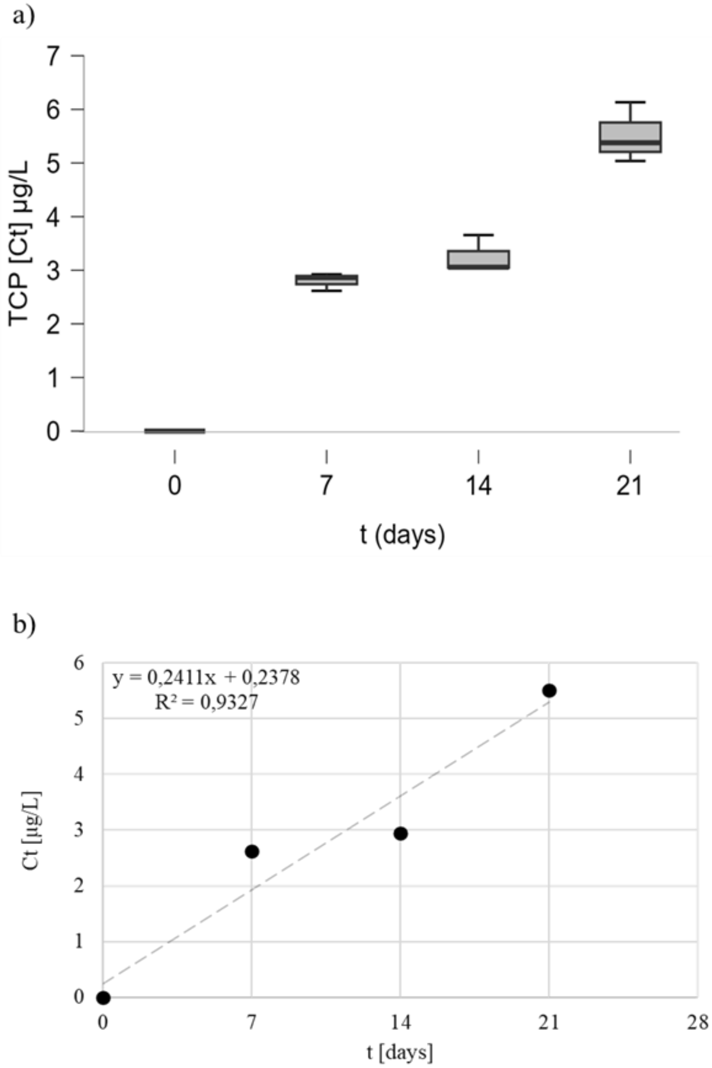
TCP concentrations for calculation of k_u

Deployement time [day]	**TCP [Ct] µg/L**			
	0	**7**	**14**	**21**
n	3	3	3	3
Median	0.000	2.863	3.056	5.378
Mean	0.000	2.801	3.251	5.516
Std. Deviation	0.000	0.163	0.351	0.560
Minimum	0.000	2.616	3.040	5.037
Maximum	0.000	2.923	3.656	6.132

With the purpose of establishing a potential relationship between the behavior of DIA-d5 and TCP in the reservoir, the TCP sampling rate in the POCIS devices was evaluated, and subsequently, a correlation analysis was conducted. In Figure 22 can be observed that the slope obtained in the analysis indicates an isotropic exchange rate between POCIS and the TCP compound. An R^2 fit of 0.93 was achieved, suggesting an appropriate correlation between the obtained data. From the obtained slope value, an exchange rate constant (k_u) of 0.241 $Lg^{-1}day^{-1}$ for the TCP compound was established. This value was used in equation 1, to estimate time-weighted concentrations of TCP in the water.

Figure 22

TCP Uptake rate in POCIS



Note. a) Distribution of TCP concentrations found in the POCIS during the field deployment. b) Graph of the linear regression obtained in the calibration based on the concentrations found in the POCIS.

Furthermore, it is important to consider the kinetics of degradation of most pesticides follow a first-order function; the degradation rate decreases proportionally to the concentration of the pesticide (Wirsching et al., 2020) as the found in this study. Besides, *in-situ* calibration played a crucial role in environmental monitoring of TCP as it allows for more accurate estimation of concentrations and reduces the uncertainty associated with extrapolating laboratory data to real-world environmental conditions.

A Pearson correlation analysis indicates a strong correlation between the uptake rate of TCP and the elimination rate of DIA-d5 (Pearson's r = -0.942) with fitting significance ($p<0.001$). This suggests that DIA-d5 is an appropriate performance reference compound (PRC) for estimating the sampling rate of TCP in POCIS devices. Once the sampling rate calculation was completed, estimations of TCP concentrations were made at different sampling points located in the reservoir and its tributaries, these estimations are provided in Table 21.

Table 21

Time-Weighted Average of TCP in La Fe Reservoir

	TCP TWA in POCIS [µg/L]					
	EBP	**EBT**	**EPE**	**ESB**	**TPE**	**TSB**
n	5	5	5	5	4	3
Median	0.539	0.221	0.305	0.342	0.596	0.246
Mean	0.700	0.309	0.299	0.345	0.589	0.291
Std. Deviation	0.524	0.219	0.082	0.240	0.321	0.115
Minimum	0.133	0.187	0.184	0.096	0.193	0.205
Maximum	1.546	0.699	0.376	0.683	0.973	0.421

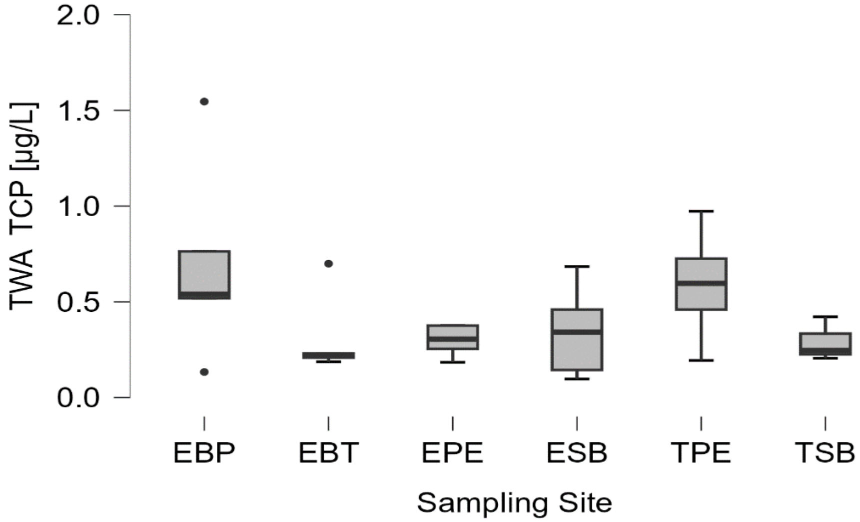
Note. averages an median obtained from the 5 deployments that were made during 2 years of campaign. Data processed with JASP statistical software (Wagenmakers, 2018).

The findings demonstrate that for Station EBP, the standard deviation for the TCP concentration is highest at is 0.524 µg/L. This elevated standard deviation signifies a considerable dispersion of data, suggesting that some values may notably deviate from the mean. Such substantial variation in TCP concentrations at this particular sampling site can be attributed to the intermittent nature of the pumping activity conducted to maintain a constant reservoir volume. Consequently, this intermittent Pantanillo river pumping activity could cause fluctuations in the TCP concentrations, leading to more scattered data as well its median as seen in Figure 23.

On average, the EBP site exhibits higher TCP concentrations compared to other sampling locations (0.7 µg/L). This observation implies that within the Pantanillo pumping basin, the parent compound undergoes transformation and subsequently is transported to the reservoir as a degradation product rather than in its original form. This suggests a potential underlying chemical process at play in this specific geographic context.

Figure 23

Distribution of time-weighted average concentrations of TCP in La Fe Reservoir



Note. Distribution of TCP time-weighted average concentrations estimated from passive sampling using POCIS devices per sampling point.

Monitoring degradation products that are often overlooked in regular monitoring programs is crucial for a complete understanding of environmental contamination, assessing risks, and implementing effective management strategies to protect water ecosystems (Akhtar et al., 2021). TCP has been extensively studied in soil (Lei et al., 2018), but just recently in water systems

After performing an analysis of variance (ANOVA) of 3,5,6-trichloro-2-pyridinol (TCP) concentrations at different monitoring points, it was determined that there were no statistically significant differences ($p>0.05$; $p=0.633$) in the estimated concentrations. However, TCP concentrations were observed to be in the range of 0.096 to 1.546 µg/L, which are notably higher than the concentrations of chlorpyrifos in the reservoir (ND-0.31 µg/L). As the main and more stable degradation product of Chlorpyrifos, TCP leach into the soil and eventually reach water bodies through runoff or percolation (John & Shaike, 2015b).

The findings of this research suggest a high rate of chlorpyrifos degradation to TCP in the tributaries and reservoir water column. It is also plausible that in a lentic water body, as la Fe reservoir a higher concentration of degradation products as TCP may be present compared to the original contaminant compound, the chlorpyrifos due the formation of degradation products can emerge in any water body containing contaminants, regardless of water movement. Lentic water bodies may be of particular concern due to their typically lower water renewal rates (Ulrich et al., 2018), which can elevate the concentration of degradation products and extend their persistence in the system. Chai et al., (2009) found that tropical environments have higher rates of substance degradation for Chlorpyrifos compound, mainly due to higher levels of photodegradation. High temperatures and solar radiation intensity in tropical climates lead to faster chemical reactions and degradation of compounds, including pesticides like chlorpyrifos. Environmental factors like humidity and rainfall patterns also impact the fate of these pollutants in tropical environments (Lewis et al., 2016).

4.2.3 CPF and TCP in sediments.

A significant proportion of chemical compounds that are released in the surrounding area of surface waters ultimately become deposited in sediment. Chlorpyrifos and TCP have the potential to be conveyed to surface aquatic systems via precipitation and runoff events, even following a considerable period of time since their initial application (San Juan et al., 2023b).

Table ***22*** displays the average concentrations, expressed in dry weight, of the target analytes found in the sediment samples.

Table 22

Chlorpyrifos and TCP concentrations in reservoir sediments

	CPF [μg/kg]						**TCP [μg/kg]**					
	EBP	**EBT**	**EPE**	**ESB**	**TPE**	**TSB**	**EBP**	**EBT**	**EPE**	**ESB**	**TPE**	**TSB**
n	2	2	2	2	2	2	2	2	2	2	2	2
Mean	0.77	0.91	0.70	0.51	1.02	1.89	8013.17	1773.97	2378.56	3581.45	3623.83	3727.53
Std. Deviation	0.13	0.13	0.36	0.21	0.44	0.06	8412.42	994.77	1996.51	187.07	2028.20	1230.03
Minimum	0.69	0.81	0.45	0.36	0.71	1.85	2064.68	1070.57	966.82	3449.17	2189.68	2857.77

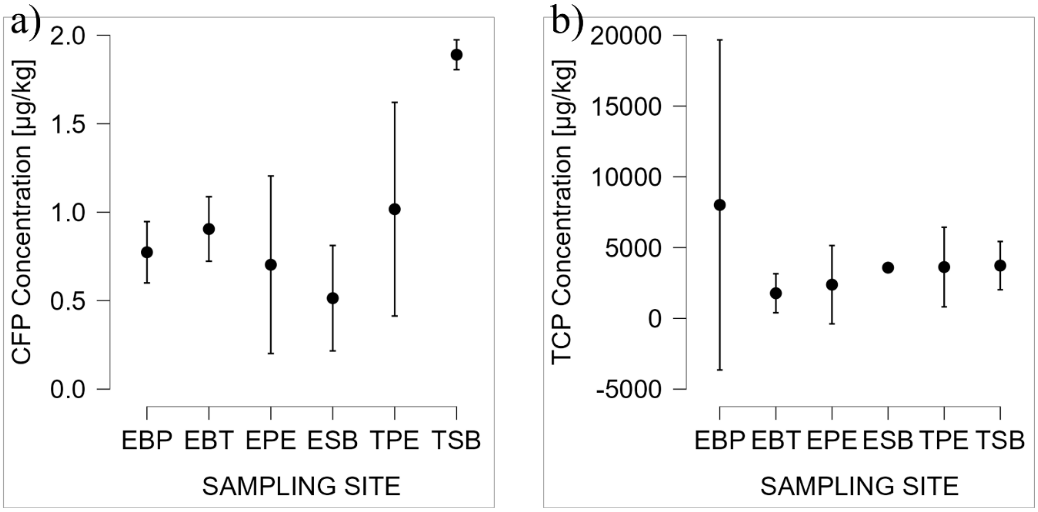
Maximum	0.86	1.00	0.96	0.67	1.32	1.93	13961.65	2477.38	3790.30	3713.73	5057.99	4597.29

Note. Data processed with JASP statistical software (Wagenmakers, 2018)

The average concentrations of CPF in sediments collected from the tributaries and La Fe reservoir range between 0.36 - 1.93 µg/kg and 966.82 - 13961.65 µg/kg for TCP respectively. Data suggests that the most substantial contributor of CPF in sediments is the San Luis Boquerón tributary, with an average concentration of 1.89 µg/kg. Notably, a 73% decrease in CPF concentration is observed in the sediment at the discharge and mixing area of the small stream, indicating the presence of degradation processes within the reservoir sediments. This degradation is further evidenced by a 30% decrease in CPF concentration from the TPE site towards the discharge and confluence zone in EPE. However, a highest CPF concentration is observed at the EBT site, which can be attributed to the effects of the water tower intake. The flow of water towards the gates of the capture tower carries along surface sediments and accumulates them. This phenomenon suggests that the hydromechanical processes in the reservoir might significantly influence the distribution and concentration of CPF in sediments. Furthermore, the results display a significant disparity, spanning several orders of magnitude, between the quantities of CPF and TCP detected in the sediments of the tributaries and the reservoir as seen in Figure 24. The concentrations of TCP are considerably higher than Chlorpyrifos, indicating that degradation processes are also occurring within the sediments. The EBP sampling site exhibits the highest average concentrations of the degradation product, a trend that is also as in the water column. This indicates that the Pantanillo River basin and its influents are the primary hotspots of activities involving CPF use in comparison to other tributaries feeding into the reservoir. Consequently, it suggests that this region may warrant further investigation to gain a more comprehensive understanding of the processes and factors influencing the occurrence and distribution of CPF and its degradation products.

Figure 24

Distribution of CPF and TCP in Sediments



Note. Interval plots. a) Distribution of the CPF mean concentrations in La Fe sediments. b) Distribution of the TCP mean concentrations in La Fe sediments. The dot indicates the average of the concentrations measured.

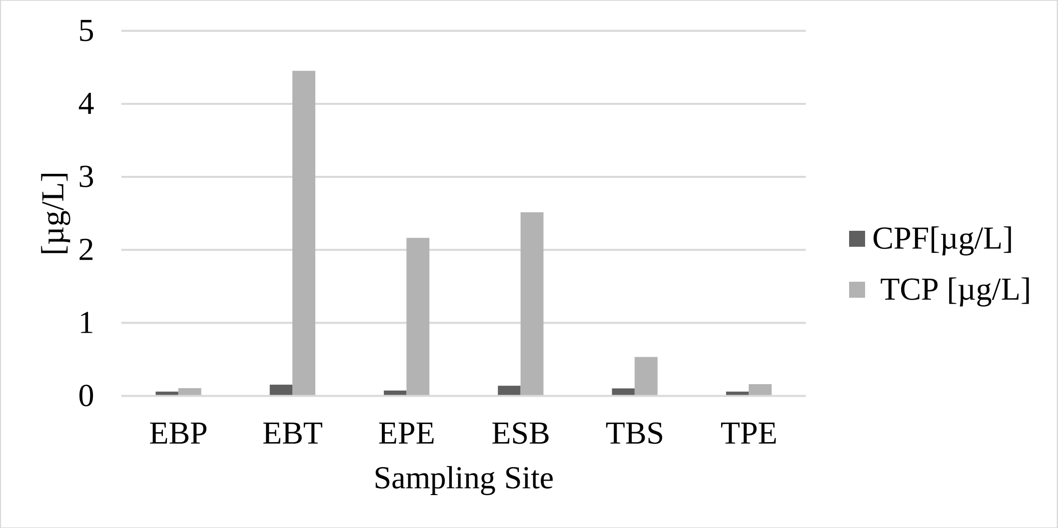
Although CPF exhibits a higher inclination towards sediments than the soil (Gebremariam et al., 2012b), it is prone to undergoing degradation and conversion into TCP as a result of alkaline hydrolysis (Narvaez Valderrama et al., 2014), and biodegradation (Tiwari and Guha, 2014). This finding may provide a plausible explanation for the notable disparity in concentrations of CPF and TCP. As well, this phenomenon in the La Fe reservoir could be attributed to the fact that, due to its solubility, TCP has a more extensive distribution in the environment compared to chlorpyrifos (Y. Zhao et al., 2017), which exhibits a greater affinity for solid particles, also its persistence in natural environments. Consequently, the mobility of chlorpyrifos is more limited, leading to differences in their respective concentrations and distribution patterns.

4.2.4 Chlorpyrifos and TCP in Elutriates

A conducted Pearson correlation test presented an R-value of 0.803 and a p-value of less than 0.001, indicating a substantial positive correlation between Chlorpyrifos and TCP concentrations in the elutriates analyzed in the Daphnia assay. Figure 25 depicts a comparison of the amounts of TCP and chlorpyrifos.

Figure 25

Comparison of CPF and TCP Concentrations in Elutriates



The observed phenomenon can be attributed to the fact that, during the resuspension process, the TCP being more water-soluble than its parent compound chlorpyrifos, undergoes a shift in its environmental compartment from sediment to water (Agudelo Echavarría et al., 2013). This shift can potentially have significant consequences for the mobility and availability of TCP in the aquatic environment, ultimately affecting its exposure and bioavailability to aquatic organisms present in the environment.

4.3 Model Calibration and verification

The model was calibrated using data from two 2018 samplings and validated its predictive accuracy with data from 2017 and 2019 samplings. This method ensured the model's effectiveness over time and different conditions. Table 23 presents the calibration results of a US EPA WASP model for the compounds chlorpyrifos and its degradation product, TCP. For each station and compound, statistics for both measured and simulated values are provided, along with error metrics.

Table 23

Statistical calibration of the WASP model for Chlorpyrifos and TCP

		Measured		Simulated					
Station	**Parameter**	**Mean**	**Median**	**Mean**	**Median**	**R^2**	**Mean Abs Err**	**RMS Err**	**IOA**
D1	CPF	0	0	0.097	0.114	1	0.097	0.112	0.46
D2	CPF	0	0	0.631	0.744	1	0.631	0.735	0.47
D3	CPF	0	0	0.096	0.113	1	0.096	0.111	0.46
D4	CPF	0	0	0.337	0.405	1	0.337	0.406	0.48
S1	CPF	0	0	0	0	0.03	0	0	0.47
S2	CPF	0	0	0	0	0.02	0	0	0.41
S3	CPF	0	0	0	0	0.12	0	0	0.37
S4	CPF	0	0	0	0	0.01	0	0	0.4
D1	TCP	0.466	0.549	0.391	0.459	1	0.075	0.091	0.97
D2	TCP	0.348	0.389	0.255	0.301	1	0.093	0.094	0.91
D3	TCP	0.702	0.71	0.386	0.453	1	0.316	0.372	0.52
D4	TCP	1.571	1.921	1.35	1.623	1	0.254	0.337	0.97
S1	TCP	0	0	0.01	0.01	0.05	0.009	0.009	0
S2	TCP	0	0	0.014	0.016	0.14	0.014	0.014	0.24
S3	TCP	0	0	0.005	0.005	0	0.005	0.005	0
S4	TCP	0.001	0.001	0.03	0.036	0.02	0.029	0.03	0.33

Note. The water column segments were identified as S1=EPE, S2=EBT, S3=ESB, and S4=EBP. Sediment segments were identified as U1=TPE, U3=TSB, D1=EPE, D2=EBT, D3=ESB, and D4=EBP.

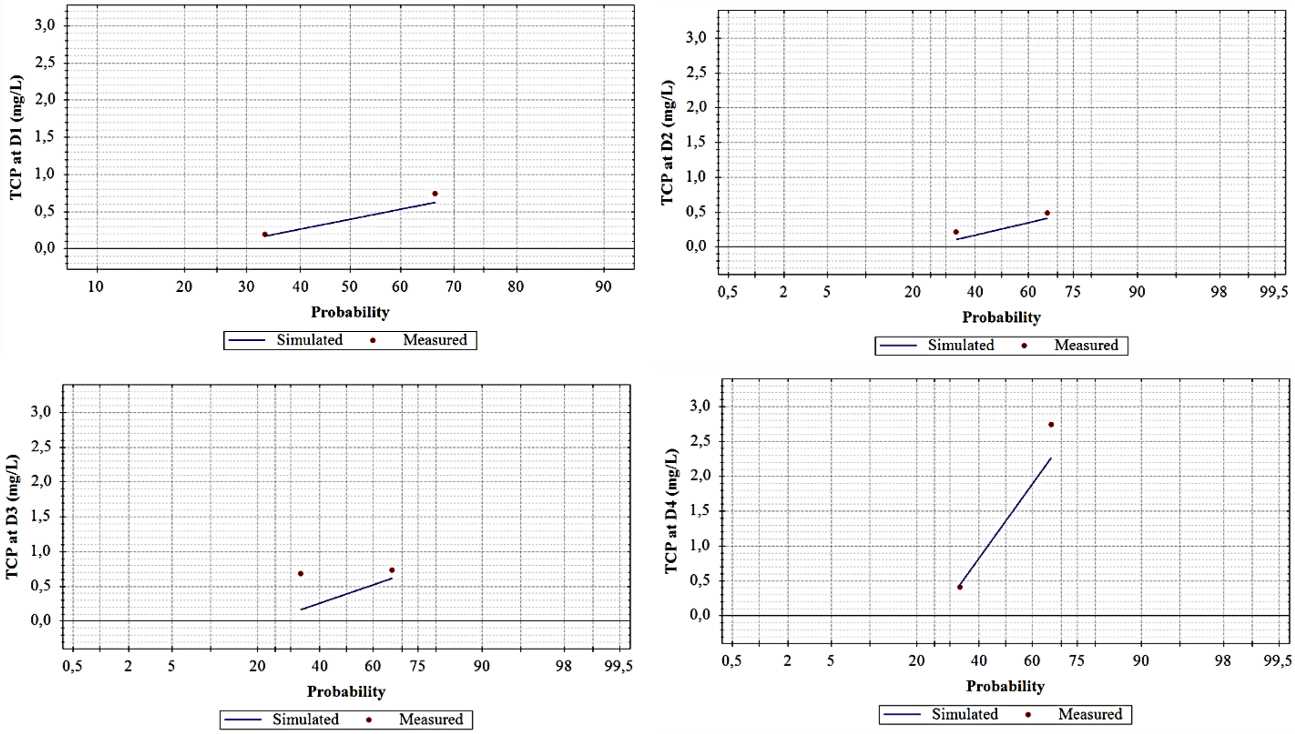
In the application of the model, it was found that it has a limitation in the data processing capabilities, which prevents it from providing an accurate representation of the concentrations of Chlorpyrifos (CPF) within the water column, due to the model excluded concentrations that were below the established threshold, leading to insufficient data for statistical analysis. The chlorpyrifos measurements in stations S1 to S4 were all zero, similar to the simulated values, indicating that the model accurately predicted the absence of chlorpyrifos in these locations. The coefficient of determination R^2 exhibits a range of values from 0.01 to 0.12, suggesting the presence of residual variability within the dataset. However, despite the fact that the model ignored the observed values of CPF in sediments, it was able to make simulations and present data showing simulated CPF values showing variability between sampling points. As at D1, the simulated mean value is 0.097, while in D2 is 0.631, in D3 is 0.096 and in D4 is 0.337. Even though they exhibit a correlation of

(R^2=1), the IOA of 0.46 to 0.48 at all sediment segments, the values are below the acceptance to 0.6 as suggested by Willmott et al. (2012). The findings suggest that the model has limitations in replicating the presence of chlorpyrifos at ng/L concentration levels.

On the other hand, the model appears to perform differently for TCP, which exhibits correlation of 1 in sediment segments and with MAE values of 0.075, 0.043, and 0.254, as well an IOA values of 0.97, 0.91, and 0.97 for D1, D2, and D4 respectively as shown in Figure 26. Although segment D3 displays an R2 value of 1, the error is greater than 30%, and the agreement index is lower than 0.6. Additionally, it is noted that there is not an appropriate correlation for TCP in the water column portions, which could be explained by the low concentrations that the model would not have been able to calculate. This suggested that it could be useful to review the model and/or the input data regarding TCP concentrations in order to improve the predictions.

Figure 26

Probability plots for TCP at sediment segments



Nevertheless, due to the limited dataset of the of TCP concentrations in the sediments of the reservoir, and its tributaries, there was a scarcity of information to performed further modeling. In light of this, the model results con be employed as a tool to explore the possible sources of this Chlorpyrifos's degradation product. By investigating the origin of TCP, the model could facilitate the identification of specific conditions or processes that may be contributing to its presence in the reservoir. This approach is fundamental as it allows for a deeper understanding of the dynamics of TCP as a tracer of contamination due to the presence of Chlorpyrifos.

In the La Fe reservoir basin, there is a significant influence of erosive processes on sediment accumulation in the reservoir. This phenomenon is intrinsically linked to the geographic and climatic characteristics of the region. It is important to highlight that 92% of the land in the tributary basins is composed of mountains and hills, which is a critical factor considering its steep relief (GAIA et al., 2016), this rugged topography exacerbates the susceptibility of the basin to soil erosion. Additionally, the area experiences significant rainfall, with an annual average of approximately 3,000 mm (Amaringo Villa, 2022), categorizing the region as torrential. The high precipitation contributes to accelerated erosion, as intense rains mobilize sediments and transport them to the reservoir.

In view of this, the model results can be utilized as a tool to explore the potential sources of this chlorpyrifos degradation product. By investigating the origin of TCP, the model could facilitate the identification of specific conditions or processes that may be contributing to its presence in the reservoir, given that the transport of chlorpyrifos to watercourses is related to surface runoff, as it is strongly adsorbed, especially to soils and sediments with a high content of organic matter (Echeverri-Jaramillo et al., 2020b; Solomon et al., 2014a). Previous researches conducted by Florez-Molina, Parra Sánchez, et al. (2017) and Gallo Sánchez et al. (2014) has revealed that in the reservoir, inorganic sediments make up the majority at 53.1%, while organic sediments account for 9.49%. The samples utilized in this study (Appendix 8) have indicated a maximum percentage of 2.65% of total organic carbon. It is important to consider that the sediment half-life of CPF ranges from 0.8-16 days (X. Yu et al., 2019a), suggesting that CPF undergoes rapid transformation into TCP, which has a half-life of 360 days (Maya et al., 2011), indicating its persistence and high mobility in the environment. The variations observed in the concentrations of TCP and chlorpyrifos in the reservoir may be explained by certain environmental factors as the relatively slower degradation rate of TCP might result in its greater accumulation within the reservoir, potentially leading to a higher concentration of this compound.

4.4 Risk Assessment

Chlorpyrifos is a non-polar and hydrophobic organic compound with a high affinity for organic matter present in the soil. Their presence in aquatic systems is usually caused by runoff from contaminated soils or by erosion and transport of soil particles (Echeverri-Jaramillo et al., 2020a). This compound is considerably mobile in the soil due to its low or no sorption capacity. This feature, coupled with its log K_{ow}, can lead to widespread contamination in both soil and water (Y. Zhao et al., 2017). The presence of contaminant compounds in sediments can have a significant impact on water quality in the water column, which may be the result of various exchange processes, including resuspension, entrainment and human intervention. These processes can contribute to the release of contaminants into the water and increase pollution levels in the water column, which in turn can have a negative impact on the health of aquatic organisms and overall water quality. In addition, the presence of contaminant compounds in sediments can also be an ongoing source of contamination, which may be of particular concern in areas of high human activity where contamination may be more prevalent. Regarding the degradation processes of Chlorpyrifos, it has been observed that hydrolysis and photolysis are the predominant processes (Giesy, et al., 2014).

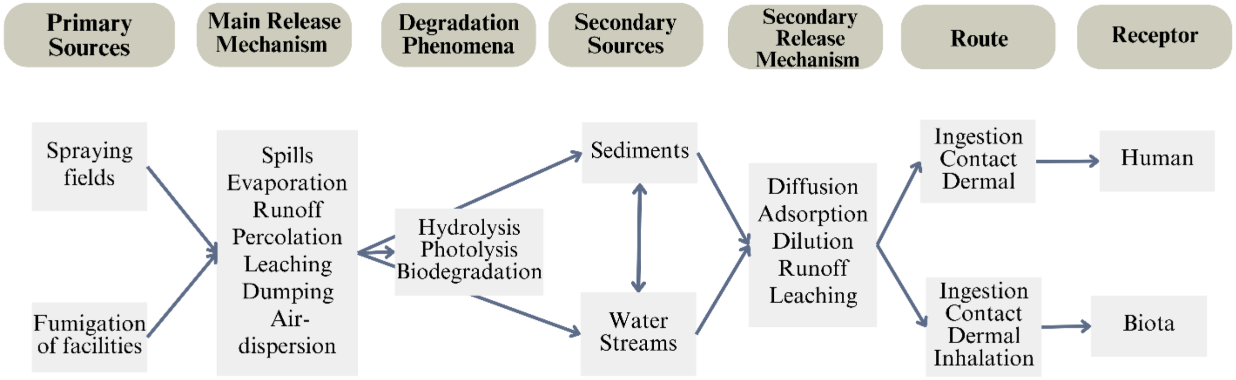
4.4.1 Problem Formulation

In a characterization of the basins of the main tributaries of the La Fe reservoir conducted by (Narvaez Valderrama, 2015), is described that chlorpyrifos is used in pastures for livestock, as well as in crops such as tree tomatoes, flowers, and beans in the areas surrounding the water bodies that feed the reservoir. However, due to soil characteristics and precipitation levels, both chlorpyrifos and its degradation products can reach the water body through different transport phenomena. The conceptual model illustrating the pathways of Chlorpyrifos and its degradation products is depicted in

Figure **27**. This model was formulated based on a thorough review of existing literature. It aims to elucidate how degradation processes impact and determine the fate of Chlorpyrifos and its by-products in the environment. By delineating the routes, the model providing a comprehensive overview of the lifecycle of Chlorpyrifos, from its introduction into the environment to its eventual degradation and dispersion. This conceptual framework serves as a valuable tool for understanding the dynamic interplay between Chlorpyrifos and various environmental factors and for predicting its potential environmental and ecological implications.

Figure 27

Conceptual model of CFP and TCP transport and fate in La Fe reservoir



Note. This model builds upon the previous work of (Adriaanse et al., 2022; European Food Safety Authority (EFSA), 2014; Giesy, et al., 2014; Luo et al., 2008; Mackay et al., 2014; Tsaboula et al., 2016; US EPA, 2006)

Since its initial application in various environments such as agricultural fields, industrial facilities, and households, chlorpyrifos begins its movement through different environmental compartments, driven by transport processes such as evaporation, runoff, leaching, and atmospheric dispersion(Dollinger et al., 2018; Dores et al., 2016). Concurrently, chlorpyrifos degradation processes commence. Due to its physicochemical properties, chlorpyrifos tends to reach water bodies either as a compound adhered to soil and sediment particles or as a compound not dissolved in water(Gebremariam and Beutel, 2010). This facilitates compound migration between these two environmental matrices through secondary release mechanisms, including diffusion, dilution, and adsorption (B. Wang et al., 2018; X. Yu et al., 2019b).

Once chlorpyrifos and TCP compounds enter ecosystems, organisms are exposed through ingestion, inhalation, or dermal contact, leading to risks associated with these substances. Human exposure in these ecosystems also implies potential risks from these interactions. It's crucial to note that chlorpyrifos' mobility in soil and presence in aquatic systems may pose significant risks to aquatic organisms and human health (Dar et al., 2019; Tudi et al., 2023). Therefore, a rigorous environmental risk assessment associated with this compound is necessary, and appropriate measures for its management and control must be taken. In this study, the standard method for designing biological tests with sediments ASTM E1525 was employed. The elutriation method used is widely recognized in scientific literature due to its high precision and reproducibility. This extraction process is based on the mobilization of contaminants present in sediment towards water, allowing for the collection of a representative sample of the soluble fraction of contaminants in sediment. This enables the evaluation of contaminant toxicity in the water column and their possible impact on aquatic organisms.

4.4.2 analysis Phase

After to obtain elutriates, as described in chapter 3, item 3.3.5, following the method validated by Poveda-Saenz, (2012), various physical and chemical variables of sediment elutriate were measured in this study, as shown in Table 24. These variables included dissolved oxygen concentration, oxygen saturation, temperature, pH, and conductivity. These variables were measured at both the start and end of the test to track changes in environmental factors that may affect sample quality.

Twenty *Daphnia pulex* specimens were exposed to different concentration fractions at each sampling site (100%, 50%, 25%, 12.5%, 6.25%), the results of the acute toxicity bioassay with *Daphnia pulex* are presented in Appendix 12. Regarding the reference CPF and TCP concentrations determined for the elutriates depicted in Figure 25. A descriptive statistical analysis was conducted based on the percentage of mean mortality in each of the elutriate samples presented in Table 25.

Sampling point	***I DO [mg/L]***	***F DO [mg/L]***	***I O_2 Saturation [%]***	***F O_2 Saturation [%]***	***I pH***	***F pH***	***I Temperature [°C]***	***F Temperature [°C]***	***I Conductivity (µS/cm)***	***F Conductivity (µS/cm)***
TSB	*6.45*	*5.14*	*93.8*	*67.8*	*7.35*	*7.65*	*22.8*	*22.8*	*314*	*315*
TPE	*8.23*	*5.33*	*100*	*69.8*	*7.23*	*7.63*	*22.9*	*22.7*	*278*	*284*
EPE	*6.26*	*5.34*	*93.5*	*70.8*	*7.12*	*7.68*	*22.7*	*22.8*	*337*	*340*
EBT	*7.8*	*5.12*	*99.2*	*68.9*	*7.02*	*7.24*	*21*	*22.3*	*432*	*386*
ESB	*5.2*	*5.31*	*66.7*	*68.8*	*6.87*	*7.69*	*20.8*	*22.5*	*390*	*356*
EBP	*6.13*	*5.29*	*75.8*	*67.5*	*6.75*	*7.34*	*21.5*	*22.5*	*405*	*389*

Table 24

Physicochemical parameters during the toxicity test of elutriates

Note. I: initial, F: final

In the course of this investigation, a decline in dissolved oxygen levels was noted across all samples, with the exception of the ESB station. At this particular location, a 2% increase in dissolved oxygen concentration was observed relative to the initial measurement. This anomaly may be attributed to the interaction of two primary factors: microbial respiration sourced from the elutriates and the oxygen consumption of Daphnia (Poveda-Saenz, 2012). The initial pH ranged from 6.75 to 7.35, indicating slightly acidic to neutral water at the sampling points. At the end of the test, the pH increased in most of the sampling points, suggesting possible alkalization of the water during the test, with station ESB showing the highest increase of 11.9%. Considering the stability of laboratory conditions, particularly temperature, the average temperature in the analyzed samples and replicates was found to be 21.95°C. However, a higher variation was identified at station ESB, with an 8.2% increase in the final temperature compared to the initial temperature. The initial oxygen saturation indicates that most of elutriates samples have well-oxygenated water, with values close to 100%. However, at the end of the test, the saturation decreased in all sampling points. The initial conductivity ranged from 278 to 432 µS/cm, with an increase in the samples corresponding to EPE (0.89%), TPE (2,16%) sampling points at the end of the test. This increase could be related to the release of ions during the test. Overall, the data suggest a possible decrease in water quality during the biological test, due the influence of minerals (see Appendix 9) and the metabolism of the Daphnia and microorganisms in the elutriate.

Table 25

Dead or Immobile Daphnia Specimens

Sample Fraction [%]	**100**	**50**	**25**	**12,5**	**6,25**	**Negative Control**	**Positive Control**
n (samplin points)	6	6	6	6	6	6	6
Mean	3.500	1.667	1.667	2.000	1.333	0.833	10.000
Std. Deviation	1.871	1.366	1.751	3.033	1.506	0.408	1.265
Minimum	1.000	0.000	0.000	0.000	0.000	0.000	8.000

Maximum	6.000	4.000	5.000	8.000	4.000	1.000	11.000

Note. The calculations were performed based on the exposure of 20 individuals per sample fraction per sampling point.

It was found that at the EBP point, 40% with a maximum of 8 immobile or dead specimens was the station with the highest percentage, followed by TSB = 30%; EPE = 25%; TPE = 15%; EBT = 10%; ESB = 10%.

An ANOVA statistical analysis conducted on the CPF concentrations in the elutriate samples revealed that the statistical values (F = 0.491 and p = 0.781) did not indicate a significant difference in the incidence of dead or immobile specimens across the elutriates corresponding to the sampling sites. Similarly, for TCP concentrations, the F-value (F = 0.066) and the high p-value (p = 0.997) suggest no significant association between samples and the number of dead or immobile specimens.

Considering that the standard requires finding that 50% or more of observed individuals have died or are immobile, it was not possible to calculate the LC_{50} for CPF and TCP with the elutriate samples from sediment. This could be explained because the CPF and TCP concentrations in the elutriates did not exceed the LC_{50} reference values of 0.1 μgL^{-1} and 12000 μgL^{-1} respectively (US EPA, 2018b). As the experimental results did not yield sufficient data for the determination of the LC_{50}, it was necessary to employ ecological risk assessment models to evaluate the potential risks associated with acute and chronic exposure to CPF and TCP in both aquatic environments and sediments.

4.4.3 Risk Characterization

Risk assessment models have been widely used to estimate the potential adverse effects of chemical substances on ecosystems. These models allow for a quick evaluation of the toxicological effects that can occur shortly after exposure to a substance. In this context, we present the results obtained from the acute risk assessment models applied to the chemical substances CPF and TCP in water and sediment.

4.4.3.1 Acute Ecological Risk Assessment of CPF and TCP Exposure in Water.

Table 26 and Table 27 displays the toxic units (TU) values for the aquatic ecosystem at each sampling point during the monitoring campaign results. The values were obtained by assessing the toxicity potential of the studied contaminants presented in Appendix 14.

Table 26

CPF Toxic Units in La Fe Reservoir Water

Sampling Point	**2017**	**2018**	**2019**	ΣTU_i
EBP	0.30	0.06	0.19	0.54
EBT	0.15	0.01	0.22	0.37
EPE	0.39	**1.45**	0.14	**1.98**
ESB	0.78	0.02	**0.98**	**1.78**
TPE	0.16	**3.15**	0.46	**3.77**
TSB	0.08	0.26	0.15	0.49
ΣTU_{annual}	**1.86**	**4.94**	**2.13**	**8.93**

The Toxic Units values vary over time and space, where in EPE (1.45 TU), ESB (0,98 TU) and TPE (3.77 TU) sampling points were showing highest levels of toxicity, suggesting a high risk for the aquatic organisms in those areas of the reservoir. Results allowed us to infer that the main concentration of Chlorpyrifos input to the reservoir is from Palmas Espiritu Santo creek. The ΣTU_{annual} values indicate an overall increase in CPF toxicity over the years, with the highest value recorded in 2018. Meanwhile, the annual aggregate assessment suggested an elevated risk of acute chlorpyrifos exposure within the reservoir. This finding has significant implications, as it highlights the substantial CPF input from the TPE source into the basin. Given that acute exposure to chlorpyrifos has been associated with detrimental effects on the metabolic processes and proliferation of fish species (Majumder and Kaviraj, 2019; Paracampo et al., 2015), significantly impacted larval development, causing abnormalities and defects in later stages in tadpoles (Bernabò et al., 2011). It is crucial to pay attention to these findings, because the presence of pesticides in water intended for human consumption is associated with high treatment costs, potential toxicological incidents, and water use prohibition (De Gerónimo et al., 2014; X. Huang et al., 2020).

Table 27

TCP Toxic Units in La Fe Reservoir Water

Sampling Point	2018	2019	ΣTU$_i$
EBP	2.3E^{-05}	3.5E^{-05}	5.8E^{-05}
EBT	7.3E^{-06}	1.9E^{-05}	2.6E^{-05}
EPE	1.3E^{-05}	4.6E^{-05}	5.9E^{-05}
ESB	1.7E^{-05}	1.5E^{-05}	3.1E^{-05}
TPE	1.4E^{-05}	2.5E^{-05}	3.9E^{-05}
TSB	8.0E^{-06}	8.3E^{-06}	1.6E^{-05}
Σ$_{annual}$	8.3E^{-05}	1.5E^{-04}	2.3E^{-04}

The risk analysis for TCP indicates that no significant exposure risk detected at any of the evaluated sampling points, nor in the cumulative assessment. The TSB station presented the lowest potential risk of exposure to TCP. However, the total annual sum of TU in 2019 is higher than in 2018, which may indicate an increase in the probability of exposure of ecosystem organisms to the risk of toxicity.

Given the model's suggestion that the primary source of Chlorpyrifos and particularly TCP mare the sediments entering the reservoir, we proceeded to evaluate the acute exposure to these substances within the sediment, as outlined in Table 28. However, in the face of an absence of sediment toxicity data for CPF and TCP, pesticide concentrations in the sediment were converted to pore water concentrations (Cpw) by employing Equation 17, results are presented in Appendix 13 and Appendix 16.

Table 28

CPF and TCP Toxic Units in La Fe Reservoir Sediments

	ΣTU CPF		ΣTU TCP		ΣTU$_i$ CPF	ΣTU$_i$ TCP
Sampling Point	**2017**	**2018**	**2017**	**2018**		
EBP	0.058	0.046	0.034	0.228	0.104	0.262
EBT	0.067	0.055	0.017	0.040	0.121	0.058
EPE	0.064	0.030	0.016	0.062	0.094	0.078
ESB	0.045	0.024	0.056	0.061	0.069	0.117

	ΣTU CPF		**ΣTU TCP**		**ΣTU_i CPF**	**ΣTU_i TCP**
Sampling Point	**2017**	**2018**	**2017**	**2018**		
TPE	0.048	0.089	0.036	0.083	0.137	0.118
TSB	0.124	0.130	0.047	0.075	0.254	0.122
ΣTU_{Annual}	***0.405***	***0.373***	***0.206***	***0.549***	***0.779***	***0.755***

The Total Toxic Units of chlorpyrifos (CPF) and 3,5,6-trichloro-2-pyridinol (TCP) were found to be higher in 2018 compared to 2017. The highest ΣTU values for both CPF and TCP were observed at the TSB sampling point. EBT showed the lowest ΣTU values for both CPF and TCP. When evaluating individual toxic units (ΣTUi), the highest values were observed for TCP at EBP, whereas the highest values for CPF were observed at TPE. However, all the values obtained were less than 1. This indicates that the ecological acute risk associated with the presence of these compounds concerning benthic organisms is minimal (Merga et al., 2021).

4.4.3.2 Chronic Ecological Risk assessment of CPF and TCP exposure in water. This section presents the results of the evaluation of the chronic exposure risk of CPF and TCP TWA concentrations estimated in water (Table 29, Table 30 y Table 31), based on the calculation of Risk Quotients in different sampling points in la Fe Reservoir presented in Appendix 14 and Appendix 15.

Table 29

Chlorpyrifos Chronic Risk Quotients in La Fe Reservoir Water

Sample Point	**2017**	**2018**	**2019**	**ΣRQ_i**
EBP	2.956	*0.586*	1.878	5.420
EBT	1.454	*0.061*	2.219	3.734
EPE	3.907	**14.453**	1.405	**19.765**
ESB	7.823	0.198	**9.767**	**17.788**
TPE	1.614	**31.453**	4.589	**37.656**
78TSB	*0.843*	2.608	1.467	4.918
ΣRQ_{Annual}	**18.598**	**49.359**	**21.325**	**89.281**

The sum of RQs at all sampling points was found to be greater than 1, indicating potential risk for the ecosystem exposed to chlorpyrifos. However, TPE point indicate the higher risk among the reservoir. Sampling points EBP, EBT, and TSB showed medium potential risk, The EBT demonstrates the smallest RQ value, which suggests that the concentrations of CPF entering the Ayurá potabilization plant could be effectively reduced post-treatment. On the other hand, sampling point TPE showed a significantly higher risk quotient with an RQ greater than 10. The total risk sum for the reservoir was RQ=89.3. These results were compared with a similar study conducted (Dar et al., 2023) in Baratagi Lake in India, and similar chronic exposure risk quotient values for chlorpyrifos were found in both ecosystems. This indicates that the presence of chlorpyrifos in the reservoir could be detrimental to the ecosystem's health. It is widely acknowledged that long-term exposure to pesticides, such as chlorpyrifos, induces substantial changes in the invertebrate and fish communities. Specifically, it causes a decline in sensitive species, an increase in resistant species, and an inhibition of algal growth. The cumulative effect of these changes is a discernible decline in biodiversity (San Juan et al., 2023a), highlighting the potential environmental hazard posed by these contaminants.

Table 30 presents the results of the Toxic Units analysis, regarding exposure to the Time-Weighted Average estimates of TCP, over the deployment duration of the Passive Organic Compound Integrative Samplers (POCIS).

Table 30

TCP Risk Quotient in La Fe Reservoir Water

Sample Point	**2018**	**2019**	**ΣRQ_i**
EBP	0.002	0.003	0.006
EBT	0.001	0.002	0.003
EPE	0.001	0.005	0.006
ESB	0.002	0.001	0.003
TPE	0.001	0.003	0.004
TSB	0.001	0.001	0.002
ΣRQ_{Annual}	0.008	0.015	0.023

Based on the information provided, it can be concluded that in 2018 and 2019, all sampling points had a potential risk (RQ) of less than 1, indicating a low potential risk to the ecosystem.

However, the total annual RQ value increased from 0.008 in 2018 to 0.015 in 2019, suggesting an increase in potential risk to the ecosystem.

These results indicate that none of the evaluated sampling points, their site sum, or the annual sum present potential risk to the ecosystem. This is in line with the postulates regarding TCP, which is considered less toxic than chlorpyrifos. However, it is important to note that TCP degradation products could be more toxic than the initial compound, such as the 5,6-dichloro-2,3-dihidroxypyridine, which still unknown its toxic profile and its impact on the environment (Žabar et al., 2016), and thus continuous monitoring of degradation products in future studies is necessary.

Table 31 presents the risk assessment quotient for chronic exposure to sediments, data presented in Appendix 16, which implies a possible impact on predominant benthic organisms or those located in the interstitial water zone. It was found that the presence of chlorpyrifos in sediments represents a medium to high risk for the ecosystem, with the TPE and TSB stations indicating the highest potential risk to the health of the ecosystem.

Table 31

CPF and TCP Risk Quotients in La Fe reservoir sediments

Sample Point	**CPF**			**TCP**		
	2017	**2018**	***ΣQRi***	**2017**	**2018**	***ΣQRi***
EBP	5.8	4.6	**10.4**	3.4	**22.8**	**26.2**
EBT	6.7	5.5	**12.1**	1.7	4.0	5.8
EPE	6.4	3.0	9.4	1.6	6.2	7.8
ESB	4.5	2.4	6.9	5.6	6.1	**11.7**
TPE	4.8	8.9	**13.7**	3.6	8.3	**11.8**
TSB	**12.4**	**13.0**	**25.4**	4.7	7.5	**12.2**
ΣQR_{Annual}	**40.5**	**37.3**	**77.9**	**20.6**	**54.9**	**75.5**

The risk quotients (ΣQRi) for both compounds are generally highest in the TSB and EBP sampling points. However, it should be noted that the risk quotient for TCP in the EBP station increased from a medium risk to a high risk from 2017 to 2018, indicating a potential trend of increasing risk for this compound. The ΣQRannual values indicate that the overall risk posed by both compounds has decreased slightly from 2017 to 2018, but is still significant.

Regarding TCP, an increase in risk was observed in 2018 compared to 2017, with the EBP station changing from medium to high risk. However, when comparing the sums of chlorpyrifos and TCP, both compounds were found to be in the same risk range, which implies that both substances pose a danger to the health of the ecosystem in contact with sediments. This is because significant effects of chlorpyrifos on non-target organisms can alter the dynamics of the ecosystem (Bertrand et al., 2017; X. Huang et al., 2020). Besides, according to a quantitative activity structure-related hypothesis (QSARs), anaerobic conditions in the sediments increase in the CPF and TCP to undergo reductive dehalogenation processes, which may lead to the creation of pyridine, a substance with a high carcinogenic potential (Narvaez Valderrama, 2015).

4.4.3.3 Human Health Risk Assessment of CPF and TCP Exposure in Water. An assessment of human health risks associated with ingestion and dermal contact with raw water from the reservoir and its tributaries was conducted.

Table ***32*** showcases the hazard quotients pertaining to exposure to CPF and TCP at each respective sampling site and an exploratory statistics shown in Table 33 from the data presented in Appendix17 and Appendix 18.

Table 32

Hazard Quotient of Chlorpyrifos and TCP by Sampling Site

Sampling Point	**Chlorpyrifos**			**TCP**		
	n	**Adults**	**Children**	**n**	**Adults**	**Children**
EBP	6	5,14E-06	2,06E-03	5	8,00E-06	1,87E-05
EBT	6	3,43E-06	9,32E-04	5	3,53E-06	8,24E-06
EPE	6	1,89E-05	5,01E-04	5	3,42E-06	7,97E-06
ESB	6	1,71E-05	9,11E-04	5	3,94E-06	9,20E-06
TPE	6	3,60E-05	1,30E-03	4	6,73E-06	1,57E-05
TSB	5	5,71E-06	5,61E-04	3	3,33E-06	7,76E-06
ΣRQi		8,63E-05	6,26E-03		2,89E-05	6,75E-05
HQ compound	6,35E-03			9,64E-05		

Note. Risk assessment was performed for two scenarios infant = 6 years and adult = 70 years

Table 33

Total Hazard Quotients comparation by group age

	Chlorpyrifos		**TCP**	
	HQ Adults	**HQ Children**	**HQ Adults**	**HQ Children**
n	35	35	27	27
Mean	1,45E-02	3,39E-02	4,86E-03	1,14E-02
Std. Deviation	3,24E-02	7,55E-02	3,62E-03	8,44E-03
Minimum	0.000	0.000	1,10E-03	2,57E-03
Maximum	1,77E-01	4,13E-01	1,77E-02	4,12E-02

An analysis of variance (ANOVA) was conducted to determine if there were statistically significant differences between sampling locations and age groups in order to determine if there were differences in the hazard quotient (HQ) for ingestion and contact between adults and children at the various sampling locations. The results indicate that there is no statistically significant difference between the HQ for ingestion between adults and minors at the various sampling locations (F = 0.850, p = 0.526). In a similar way there were no statistically significant differences in the HQ between adults and minors (F = 0.850, p = 0.52. The assessment of non-cancer risks related to CPF and TCP through human water ingestion reveals that both Hazard Quotient (HQ) and Hazard Index (HI) were less than 1 in both children and adults. This suggests a negligible Non-Cancer Risk (NCR) for these groups.

Although Chlorpyrifos does not possess a classification as a potential carcinogen, it is considered a significant health risk due to its various toxic effects, such as genotoxicity, immunotoxicity, and neurotoxicity (ur Rahman et al., 2021). Although information about toxicological effects of TCP in human health is scarce (J. Wang et al., 2014), emerging research suggests it may disrupt thyroid function and cause DNA damage (Makris et al., 2022; Meeker et al., 2004, 2006), highlighting the need for further investigation into its toxicological effects.

Chapter 5. Conclusions y recommendations

Monitoring of parental chemical compounds is common in environmental assessments to determine the presence and level of contamination in the ecosystem. Some chemical compounds, however, can degrade into their degradation products, giving the impression that the parent compound is no longer present in the environment. Taking this into account that degradation products can be just as toxic as parent compounds, posing a risk to human health and the environment. As a result, monitoring of substance degradation products is critical for determining the presence and impact of substances on the ecosystem. Monitoring degradation products can also help identify potential sources of contamination, leading to better environmental regulation and management.

The conversion of chlorpyrifos into its degradation product TCP at reservoir monitoring stations is consistent with theory, given that its residence time in the reservoir water favors chlorpyrifos hydrolysis and photolysis, increasing the proportion of TCP. This conversion is attributable to the reservoir's environmental conditions, particularly the elevated pH, which promotes the hydrolysis of chlorpyrifos to TCP. The main degradation mechanism of chlorpyrifos in aqueous environments is hydrolysis, and an increase in pH in aquatic environments favors chlorpyrifos hydrolysis. Furthermore, the formation of TCP as a degradation product is expected in high pH environments and serves as an indicator of chlorpyrifos exposure.

It is recommended for future research in the La Fe reservoir to carry out monitoring through the use of passive samplers, with the purpose of comparing the concentrations of contaminants present in the water during the flood season and the dry season. This is because it simplifies the collection of samples in a continuous way and does not interfere with the natural dynamics of the water, allowing for a more precise evaluation of exposure to contaminants in the aquatic ecosystem during both seasons. Additionally, the application of passive sampling techniques in sediments represents an opportunity for effective monitoring of polluting organic compounds in aquatic ecosystems that may indicate the presence of pollutants in the long term.

The modeling study of chlorpyrifos and its degradation product (TCP), in the La Fe reservoir basin reveals valuable insights, albeit with some limitations. Specifically, the model struggles to accurately represent CPF concentrations in the water column, particularly when these fall at ng/L or pg/L concentration levels, leading to data scarcity for robust statistical analysis. Nonetheless, the model accurately predicts the absence of CPF in certain stations, illustrating its proficiency under specific conditions. When examining CPF in sediment, the model exhibits variability between sampling points and, despite a perfect Index of Agreement (IOA), it falls short of the accepted value, suggesting room for improvement. In contrast, the model demonstrates improved performance in predicting TCP concentrations within sediment segments, although this success does not extend to water column portions, potentially due to low TCP concentrations. Furthermore, the model serves as a useful tool to explore potential sources of TCP, a critical aspect given TCP's role as a tracer of contamination. An analysis of the geographical and climatic characteristics of the reservoir basin points towards the influence of significant erosion and high rainfall in the region, contributing to CPF transport via surface runoff and sediment accumulation. This transport is further enhanced by the propensity of CPF to bind strongly to soils and sediments rich in organic matter. CPF's rapid transformation into TCP, coupled with TCP's persistence and high environmental mobility, may explain the observed variations in their reservoir concentrations. Collectively, these findings underscore the need for further refinement of the model and an enhanced understanding of the factors influencing CPF and TCP behavior in such an ecosystem.

A bioassay with *Daphnia pulex* was carried out in order to characterize the risk from acute exposure to elutriates from the La Fe reservoir. *Daphnia pulex* is a species of aquatic microcrustacean that is commonly used as a model organism in bioassays to assess the toxicity of contaminants present in the water. In this study, this model organism was used to assess the risk of acute exposure to the elutriates from the La Fe reservoir. However, the results obtained were not satisfactory to allow an adequate characterization, since the concentrations found in the elutriates did not exceed the LC_{50} values reported by different investigators. Alternative approaches were employed to evaluate the ecological risk and the risk to human health as a result of the bioassay's inability to produce results that were satisfactory. For acute exposure, Toxic Unit (TU) methods and Risk Quotient (RQ) are used. The Hazard Quotient (HQ) technique was also used to measure the danger to human health.

Concerning acute exposure to chlorpyrifos, it was determined que at the EPE, ESB and TPE sampling points, a high risk for aquatic organisms was estimated due to acute exposure to chlorpyrifos, the results indicated that the sum of the toxic units ($\sum TU>1$), which suggests that the levels of exposure to chlorpyrifos in water are potentially hazardous to aquatic life and may have adverse health effects on exposed organisms. On the other hand, it could be concluded that the risk associated with TCP in all monitoring stations was extremely low or negligible, as an estimate of the risk $\sum TU<1$ indicates a very low or negligible risk to human health and the environment even when the TCP concentration are significatively higher that the parental compound.

Furthermore, the acute risk associated with acute exposure to reservoir sediments was also estimated. It was calculated that at in all sampling points for the two compounds, the TU were less than 1 ($\sum TU_{CPF}= 0.78$ and $\sum TU_{TCP}= 0.76$), which indicates that there is no risk to the benthic population of the reservoir due to exposure to these two compounds. However, more research is needed to estimate the sublethal effects of these compounds.

The risk assessment for chronic exposure to Chlorpyrifos indicates a medium and high risk in all sampling points, especially in the Palmas Espiritu Santo Tributary ($\sum RQ=37.7$). which requires priority attention in risk management. Chronic exposure to Chlorpyrifos can have serious and long-term consequences for the health of the aquatic ecosystem, so it is necessary to take measures to reduce exposure to this compound and promote safer and more sustainable alternatives for pest control. While for chronic risk assessment for exposure to the compound 3,5,6-trichloro-2-pyridinol (TCP) was carried out and the results indicated values of $\sum RQ<1$, which suggests that at all sampling points where the assessment was carried out, this substance does not pose a significant danger to aquatic organisms. However, the risk assessment for chronic exposure to reservoir sediments could suggest that benthic organisms are potentially at risk of hormesis, which is a process that describes the beneficial biological responses that occur from exposure to low levels of a substance that is usually toxic in higher concentrations (Agathokleous et al., 2023); This merits further exploration to fully understand the drivers behind this phenomenon.

Although the concentrations are low, the RQ indicates that at all sampling points for the two compounds, CPF and TCP, they represent medium to high risk with a range of ∑RQ between (5.8 and 12.2). There is no appreciable health risk from Chlorpyrifos and TCP via water ingestion, due Children and Adults exposure to single non-carcinogenic pesticides (HQ) and total hazard (HI) were <1. Nonetheless, further research is needed into the risks to human health associated with the presence of these compounds in combination with other contaminants in drinking water, thus will it be possible to obtain a more complete and accurate assessment of the potential risk posed by these chemicals to human health.

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Appendixes

Appendix 1

Conditioned Sampling Points

Note.Points installed in infrastructure located in the tributaries of the reservoir a) under *box coulver* in the tributary San Luis-Boquerón b) under a bridge in the tributary Palmas Espíritu Santo. Source: Authors.

Appendix 2

Scheduling campaigns for deployment, monitoring and collection of SPMD devices

Sampling Points	Deployment Date	Date of Collection	Exposure time (days)
4	4-oct-17	31-oct-17	27
2	5-oct-17	31-oct-17	26
6	31-oct-17	23-nov-17	23
6	26-sep-18	18-oct-18	21
6	18-oct-18	8-nov-18	21
5	9-oct-19	30-oct-19	21
5	30-oct-19	20-nov-19	21
6	20-nov-19	11-dic-19	21

Appendix 3

Scheduling campaigns for deployment, monitoring and collection of POCIS devices

Sampling Points	**Deployment Date**	**Date of Collection**	**Exposure time (days)**
6	26-sep-18	18-oct-18	21
6	18-oct-18	8-nov-18	21
5	9-oct-19	30-oct-19	21
5	30-oct-19	20-nov-19	21
5	20-nov-19	11-dic-19	21

Appendix 4

Scheduling sediment collection campaigns

Sampling Points	**Date of Collection**
6	4-oct-17
6	26-sep-18
6	9-oct-19

Note. Samples were taken at the same sites where the passive samplers were located.

Appendix 5

Location of devices within the reservoir

Appendix 6

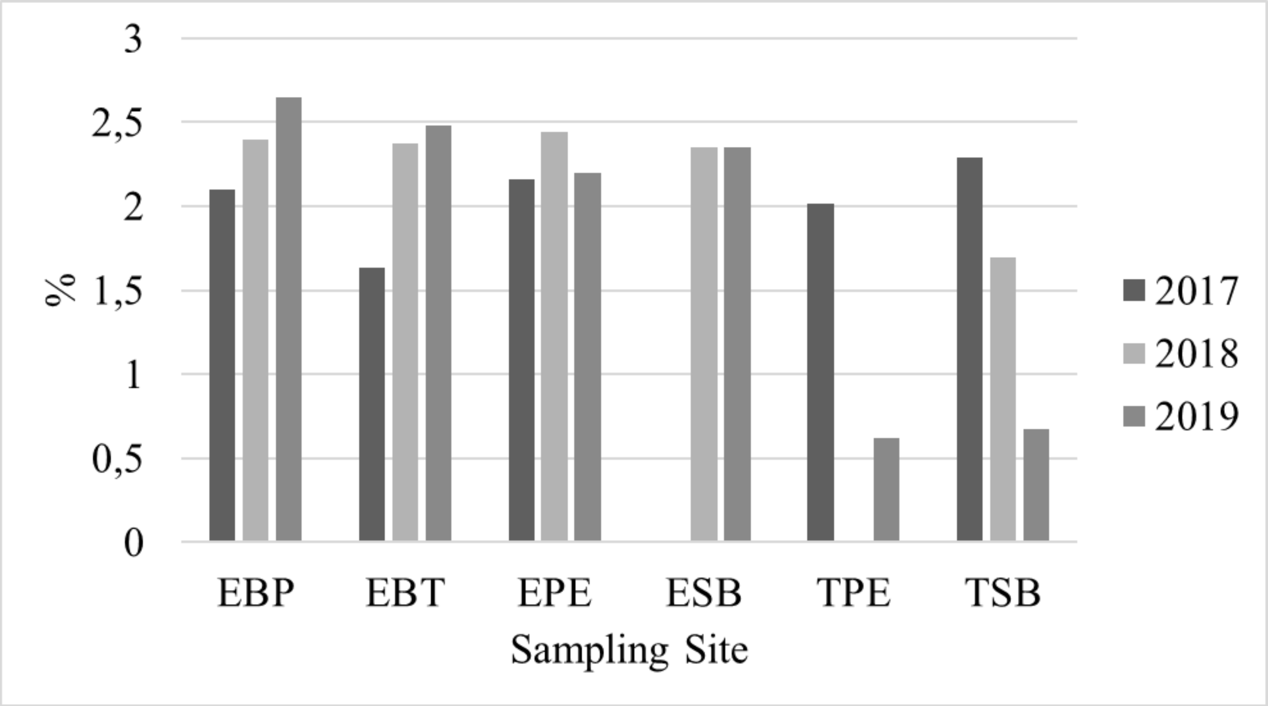
Flotation device at the EBP monitoring point

Appendix 7

Sediment Collection

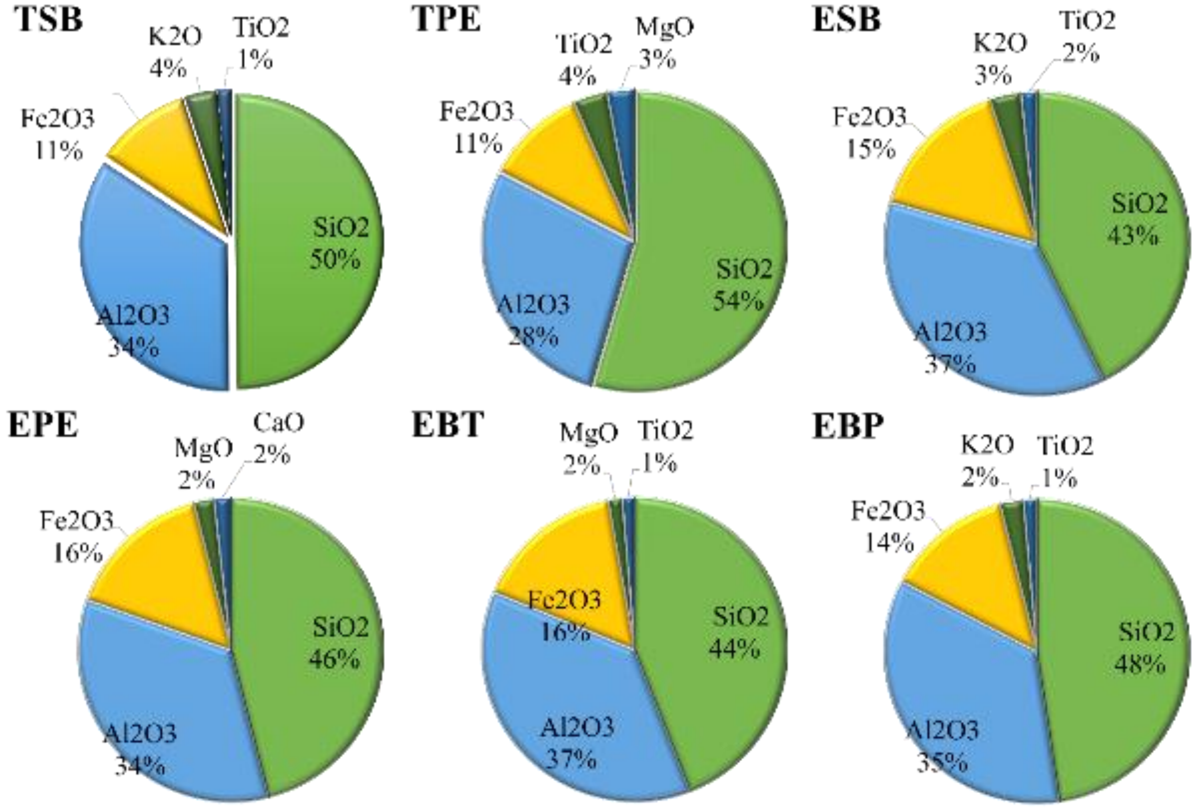
Appendix 8

Total Organic Carbon



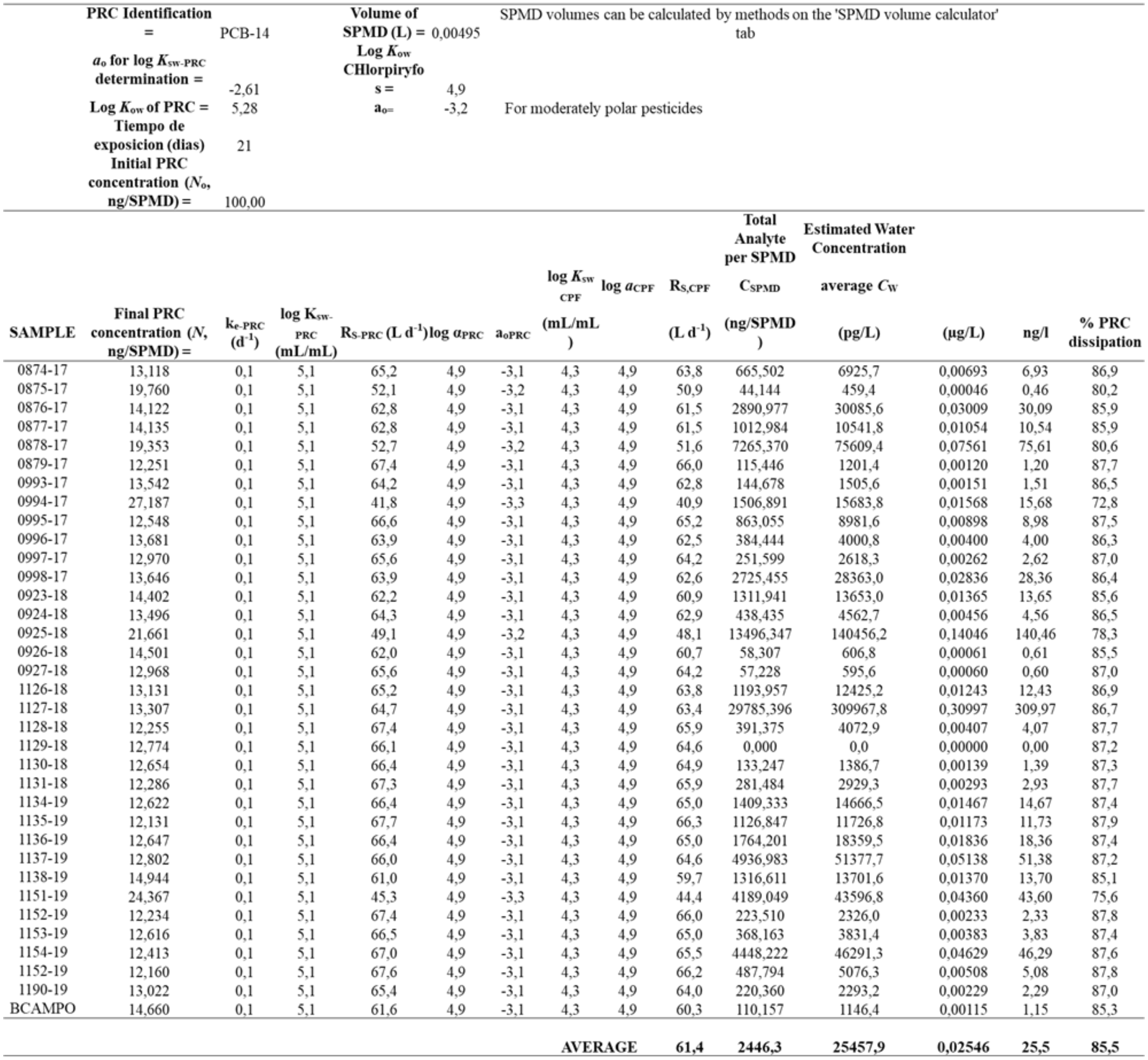
Appendix 9

Mineralogical characterization of sediments



Appendix 10

CPF Concentration and Sampling Rate with PRC Approach using the USGS calculation sheets



PRC Identification =	PCB-14	**Volume of SPMD (L) =**	0,00495	SPMD volumes can be calculated by methods on the 'SPMD volume calculator' tab
a_o for log $K_{sw\text{-}PRC}$ determination =	-2,61	**Log K_{ow} CHlorpiryfos =**	4,9	
Log K_{ow} of PRC =	5,28	**$a_{o=}$**	-3,2	For moderately polar pesticides
Tiempo de exposicion (dias)	21			
Initial PRC concentration (N_o, ng/SPMD) =	100,00			

SAMPLE	**Final PRC concentration (N, ng/SPMD) =**	**$k_{e\text{-}PRC}$ (d^{-1})**	**log $K_{sw\text{-}PRC}$ (mL/mL)**	**$R_{S\text{-}PRC}$ (L d^{-1})**	**log α_{PRC}**	**a_{oPRC}**	**log K_{sw} CPF (mL/mL)**	**log a_{CPF}**	**$R_{S,CPF}$ (L d^{-1})**	**Total Analyte per SPMD C_{SPMD} (ng/SPMD)**	**Estimated Water Concentration average C_W (pg/L)**	**(µg/L)**	**ng/l**	**% PRC dissipation**
0874-17	13,118	0,1	5,1	65,2	4,9	-3,1	4,3	4,9	63,8	665,502	6925,7	0,00693	6,93	86,9
0875-17	19,760	0,1	5,1	52,1	4,9	-3,2	4,3	4,9	50,9	44,144	459,4	0,00046	0,46	80,2
0876-17	14,122	0,1	5,1	62,8	4,9	-3,1	4,3	4,9	61,5	2890,977	30085,6	0,03009	30,09	85,9
0877-17	14,135	0,1	5,1	62,8	4,9	-3,1	4,3	4,9	61,5	1012,984	10541,8	0,01054	10,54	85,9
0878-17	19,353	0,1	5,1	52,7	4,9	-3,2	4,3	4,9	51,6	7265,370	75609,4	0,07561	75,61	80,6
0879-17	12,251	0,1	5,1	67,4	4,9	-3,1	4,3	4,9	66,0	115,446	1201,4	0,00120	1,20	87,7
0993-17	13,542	0,1	5,1	64,2	4,9	-3,1	4,3	4,9	62,8	144,678	1505,6	0,00151	1,51	86,5
0994-17	27,187	0,1	5,1	41,8	4,9	-3,3	4,3	4,9	40,9	1506,891	15683,8	0,01568	15,68	72,8
0995-17	12,548	0,1	5,1	66,6	4,9	-3,1	4,3	4,9	65,2	863,055	8981,6	0,00898	8,98	87,5
0996-17	13,681	0,1	5,1	63,9	4,9	-3,1	4,3	4,9	62,5	384,444	4000,8	0,00400	4,00	86,3
0997-17	12,970	0,1	5,1	65,6	4,9	-3,1	4,3	4,9	64,2	251,599	2618,3	0,00262	2,62	87,0
0998-17	13,646	0,1	5,1	63,9	4,9	-3,1	4,3	4,9	62,6	2725,455	28363,0	0,02836	28,36	86,4
0923-18	14,402	0,1	5,1	62,2	4,9	-3,1	4,3	4,9	60,9	1311,941	13653,0	0,01365	13,65	85,6
0924-18	13,496	0,1	5,1	64,3	4,9	-3,1	4,3	4,9	62,9	438,435	4562,7	0,00456	4,56	86,5
0925-18	21,661	0,1	5,1	49,1	4,9	-3,2	4,3	4,9	48,1	13496,347	140456,2	0,14046	140,46	78,3
0926-18	14,501	0,1	5,1	62,0	4,9	-3,1	4,3	4,9	60,7	58,307	606,8	0,00061	0,61	85,5
0927-18	12,968	0,1	5,1	65,6	4,9	-3,1	4,3	4,9	64,2	57,228	595,6	0,00060	0,60	87,0
1126-18	13,131	0,1	5,1	65,2	4,9	-3,1	4,3	4,9	63,8	1193,957	12425,2	0,01243	12,43	86,9
1127-18	13,307	0,1	5,1	64,7	4,9	-3,1	4,3	4,9	63,4	29785,396	309967,8	0,30997	309,97	86,7
1128-18	12,255	0,1	5,1	67,4	4,9	-3,1	4,3	4,9	65,9	391,375	4072,9	0,00407	4,07	87,7
1129-18	12,774	0,1	5,1	66,1	4,9	-3,1	4,3	4,9	64,6	0,000	0,0	0,00000	0,00	87,2
1130-18	12,654	0,1	5,1	66,4	4,9	-3,1	4,3	4,9	64,9	133,247	1386,7	0,00139	1,39	87,3
1131-18	12,286	0,1	5,1	67,3	4,9	-3,1	4,3	4,9	65,9	281,484	2929,3	0,00293	2,93	87,7
1134-19	12,622	0,1	5,1	66,4	4,9	-3,1	4,3	4,9	65,0	1409,333	14666,5	0,01467	14,67	87,4
1135-19	12,131	0,1	5,1	67,7	4,9	-3,1	4,3	4,9	66,3	1126,847	11726,8	0,01173	11,73	87,9
1136-19	12,647	0,1	5,1	66,4	4,9	-3,1	4,3	4,9	65,0	1764,201	18359,5	0,01836	18,36	87,4
1137-19	12,802	0,1	5,1	66,0	4,9	-3,1	4,3	4,9	64,6	4936,983	51377,7	0,05138	51,38	87,2
1138-19	14,944	0,1	5,1	61,0	4,9	-3,1	4,3	4,9	59,7	1316,611	13701,6	0,01370	13,70	85,1
1151-19	24,367	0,1	5,1	45,3	4,9	-3,3	4,3	4,9	44,4	4189,049	43596,8	0,04360	43,60	75,6
1152-19	12,234	0,1	5,1	67,4	4,9	-3,1	4,3	4,9	66,0	223,510	2326,0	0,00233	2,33	87,8
1153-19	12,616	0,1	5,1	66,5	4,9	-3,1	4,3	4,9	65,0	368,163	3831,4	0,00383	3,83	87,4
1154-19	12,413	0,1	5,1	67,0	4,9	-3,1	4,3	4,9	65,5	4448,222	46291,3	0,04629	46,29	87,6
1152-19	12,160	0,1	5,1	67,6	4,9	-3,1	4,3	4,9	66,2	487,794	5076,3	0,00508	5,08	87,8
1190-19	13,022	0,1	5,1	65,4	4,9	-3,1	4,3	4,9	64,0	220,360	2293,2	0,00229	2,29	87,0
BCAMPO	14,660	0,1	5,1	61,6	4,9	-3,1	4,3	4,9	60,3	110,157	1146,4	0,00115	1,15	85,3
							AVERAGE		**61,4**	**2446,3**	**25457,9**	**0,02546**	**25,5**	**85,5**

Appendix 11

3,5,6-trichloro-2-pyridinol Values in POCIS Devices

Sampling Site	ID Sample	Sampler Mass (Ms) [g]	Concentration in sampler (Cs) [µg/g]	Cw (TWA) [ug/L]	TWA (Average) [n=3]	Standar Deviation
	0911-18A	0,2804	0,11465869	0,13312753		
TBS	0911-18B	0,2311	0,48472042	0,46384633	0,24555006	0,18907847
	0911-18C	0,2687	0,12553714	0,13967632		
	0912-18A	0,0966	1,3436248	0,53744992		
TPE	0912-18B	0,2987	0,64314005	0,7954697	0,64344354	0,13502888
	0912-18C	0,8795	0,16404179	0,597411		
	0913-18A	0,1642	0,45125887	0,30681866		
EPE	0913-18B	0,2482	0,30987436	0,31847129	0,25441418	0,10102683
	0913-18C	0,1425	0,23379336	0,1379526		
	0914-18A	0,2655	0,07979352	0,08772331		
EBT	0914-18B	0,2614	0,24403434	0,26414318	0,22959018	0,12813349
	0914-18C	0,2191	0,37134792	0,33690405		
	0915-18A	0,2352	0,37556476	0,36576742		
ESB	0915-18B	0,229	0,32458491	0,30778445	0,34160176	0,03017237
	0915-18C	0,2505	0,33863353	0,35125341		
	0916-18A	0,2289	0,48040813	0,45534336		
EBP	0916-18B	0,2657	0,57604481	0,63376855	0,51851526	0,09996619
	0916-18C	0,2637	0,42716641	0,46643389		
	1120-18A	0,2332	0,327655	0,31639398		
TBS	1120-18B	0,1366	0,2839272	0,16059816	0,20519831	0,09692423
	1120-18C	0,303	0,11047054	0,13860278		
	1121-18A	0,3167	0,14919476	0,1956521		
TPE	1121-18B	0,2959	0,11993257	0,14694844	0,19315403	0,04500858
	1121-18C	0,2997	0,19086442	0,23686155		
	1122-18A	0,1516	0,48166302	0,30236072		
EPE	1122-18B	0,2426	0,2833814	0,28467216	0,30499636	0,02176205
	1122-18C	0,1306	0,60644273	0,3279562		
	1123-18A	0,2653	0,24777687	0,27219545		
EBT	1123-18B	0,2433	0,22182498	0,22347833	0,22084349	0,05271879
	1123-18C	0,2546	0,15827137	0,16685669		
	1124-18A	0,1842	0,58345762	0,44502234		
ESB	1124-18B	0,1837	0,62272069	0,47368029	0,45933921	0,01432899
	1124-18C	0,1473	0,75305211	0,45931501		
	1125-18A	0,2511	0,67012822	0,69676686		
EBP	1125-18B	0,208	0,94487101	0,81380195	0,76299214	0,06002108
	1125-18C	0,1669	1,12633577	0,77840762		
	1123-19A	0,1869	0,5851002	0,45281668		
TBS	1123-19B	0,2119	0,26643618	0,23377982	0,42116709	0,17373818
	1123-19C	0,2129	0,65440349	0,57690477		
EPE	1124-19A	0,2158	0,34256675	0,3061114	0,37555219	0,06604128

Sampling Site	**ID Sample**	**Sampler Mass (Ms) [g]**	**Concentration in sampler (Cs) [µg/g]**	**Cw (TWA) [ug/L]**	**TWA (Average) [n=3]**	**Standar Deviation**
	1124-19B	0,2068	0,44724109	0,38297912		
	1124-19C	0,2314	0,45666466	0,43756605		
EBT	1125-19A	0,1862	1,13397906	0,87431429	0,69904794	0,28025169
	1125-19B	0,2338	0,388203	0,37582552		
	1125-19C	0,2621	0,78043291	0,847004		
ESB	1126-19A	0,2472	0,77784605	0,79620515	0,68339115	0,19588938
	1126-19B	0,2443	0,78763846	0,7967705		
	1126-19C	0,2374	0,46509381	0,45719781		
EBP	1127-19A	0,2432	0,54848645	0,55234743	0,53915932	0,03213556
	1127-19B	0,1919	0,7080175	0,56260272		
	1127-19C	0,1476	0,82222536	0,5025278		
TPE	1156-19A	0,2559	1,0385334	1,10045838	0,97290482	0,17716254
	1156-19B	0,2249	0,82750125	0,77062125		
	1156-19C	0,2484	1,01853386	1,04763483		
EPE	1157-19A	0,2332	0,32103225	0,30999885	0,18381084	0,10968378
	1157-19B	0,2324	0,11569711	0,11133751		
	1157-19C	0,239	0,131457	0,13009617		
EBT	1158-19A	0,2637	0,28659509	0,31294048	0,20791899	0,0909557
	1158-19B	0,2318	0,16097715	0,1545114		
	1158-19C	0,265	0,14244406	0,15630508		
ESB	1159-19A	0,2605	0,13074626	0,14103271	0,14420426	0,01452577
	1159-19B	0,2549	0,12461202	0,13152631		
	1159-19C	0,3169	0,12197218	0,16005376		
EBP	1160-19A	0,2375	0,15019075	0,14770312	0,1330793	0,01266975
	1160-19B	0,2393	0,12728824	0,12612868		
	1160-19C	0,2624	0,11541758	0,1254061		
TPE	1191-19A	0,226	0,35859254	0,33557729	0,54807928	0,3721069
	1191-19B	0,2462	0,95907762	0,9777429		
	1191-19C	0,2292	0,34867633	0,33091766		
EPE	1192-19A	0,0211	6,05132645	0,52870803	0,37533157	0,32685027
	1192-19B	0,2731	0	0		
	1192-19C	0,27	0,53423976	0,59728668		
EBT	1193-19A	0,2298	0,1632275	0,15531958	0,1865961	0,09541444
	1193-19B	0,2424	0,1103341	0,11074528		
	1193-19C	0,2437	0,29107183	0,29372342		
ESB	1194-19A	0,2545	0,11527446	0,12147971	0,09634357	0,02707155
	1194-19B	0,2318	0,07051429	0,06768204		
	1194-19C	0,1959	0,12311564	0,09986896		
EBP	1195-19A	0,2741	0,12232981	0,13884307	1,54574079	1,32044371
	1195-19B	0,2977	1,41169966	1,74021941		
	1195-19C	0,2896	2,30005391	2,75815988		

Appendix 12

Daphnia Pulex Bioessay with Elutriates

Sampling Site	CPF Concentration [mg/L]	TCP Concentration [mg/L]	Fraction of the Sample	Exposed Specimens	Dead or Immobile Specimens	Percentaje
TSB	0,0001	0,0005	6,25	20	1	5
			12,5	20	0	0
			25	20	1	5
			50	20	1	5
			100	20	6	30
			Positive control	20	8	40
			control negativo	20	1	5
TPE	0,00006	0,0002	6,25	20	1	5
			12,5	20	2	10
			25	20	2	10
			50	20	1	5
			100	20	3	15
			Positive control	20	9	45
			Negative Control	20	1	5
EPE	0,00007	0,0022	6,25	20	0	0
			12,5	20	0	0
			25	20	0	0
			50	20	2	10
			100	20	5	25
			Positive control	20	10	50
			Negative Control	20	0	0
EBT	0,00015	0,0045	6,25	20	0	0
			12,5	20	1	5
			25	20	1	5
			50	20	0	0
			100	20	2	10

Sampling Site	CPF Concentration [mg/L]	TCP Concentration [mg/L]	Fraction of the Sample	Exposed Specimens	Dead or Immobile Specimens	Percentaje
			Positive control	20	11	55
			Negative Control	20	1	5
ESB	0,00014	0,0025	6,25	20	2	10
			12,5	20	1	5
			25	20	1	5
			50	20	2	10
			100	20	1	5
			Positive control	20	11	55
			Negative Control	20	1	5
EBP	0,00006	0,0001	6,25	20	4	20
			12,5	20	8	40
			25	20	5	25
			50	20	4	20
			100	20	4	20
			Positive control	20	11	55
			Negative Control	20	1	5

Appendix 13

Pore Water Concentrations from sediment samples

Year	Sampling Site	CPW CPF [µg/L]	CPW TCP [µg/L]
	TSB	0,01240	560,346
	TPE	0,00476	429,348
	EPE	0,00644	189,572
	EBT	0,00670	209,915
	ESB	0,00447	676,307
2017	EBP	0,00578	404,840
	TSB	0,01297	901,429
	TPE	0,00889	991,763
	EPE	0,00300	743,197
	EBT	0,00545	485,761
	ESB	0,00243	728,182
2018	EBP	0,00459	2737,578

Appendix 14

Calculations for Toxicity Unit (TU) and Risk Quotient (RQ) of Chlorpyrifos in Water

Year	Sampling Point	CFP TWA [µg/l]	LC50 [µg/L]	CPF TU Water	CPF PNEC [µ/L]	CPF RQ TWA
2017	TSB	0,007	0,1	0,07	0,014	0,069
2017	TPE	0	0,1	0	0,014	0,005
2017	EPE	0,03	0,1	0,3	0,014	0,301
2017	EBT	0,011	0,1	0,11	0,014	0,105
2017	ESB	0,076	0,1	0,76	0,014	0,756
2017	EBP	0,001	0,1	0,01	0,014	0,012
2017	TSB	0,002	0,1	0,02	0,014	0,015
2017	TPE	0,016	0,1	0,16	0,014	0,157
2017	EPE	0,009	0,1	0,09	0,014	0,090
2017	EBT	0,004	0,1	0,04	0,014	0,040
2017	ESB	0,003	0,1	0,03	0,014	0,026
2017	EBP	0,028	0,1	0,28	0,014	0,284
2018	TSB	0,014	0,1	0,14	0,014	0,137
2018	TPE	0,005	0,1	0,05	0,014	0,046
2018	EPE	0,14	0,1	1,4	0,014	1,405
2018	EBT	0,001	0,1	0,01	0,014	0,006
2018	ESB	0,001	0,1	0,01	0,014	0,006
2018	EBP	0	0,1	0	0,014	0,000
2018	TSB	0,012	0,1	0,12	0,014	0,124
2018	TPE	0,31	0,1	3,1	0,014	3,100
2018	EPE	0,004	0,1	0,04	0,014	0,041
2018	EBT	0	0,1	0	0,014	0,000
2018	ESB	0,001	0,1	0,01	0,014	0,014
2018	EBP	0,003	0,1	0,03	0,014	0,029
2019	TSB	0,015	0,1	0,15	0,014	0,147
2019	EPE	0,012	0,1	0,12	0,014	0,117
2019	EBT	0,018	0,1	0,18	0,014	0,184
2019	ESB	0,051	0,1	0,51	0,014	0,514
2019	EBP	0,014	0,1	0,14	0,014	0,137
2019	TPE	0,044	0,1	0,44	0,014	0,436
2019	EPE	0,002	0,1	0,02	0,014	0,023
2019	EBT	0,004	0,1	0,04	0,014	0,038
2019	ESB	0,046	0,1	0,46	0,014	0,463
2019	EBP	0,005	0,1	0,05	0,014	0,051
2019	TPE	0,002	0,1	0,02	0,014	0,023

Appendix 15

Calculations for Toxicity Unit (TU) and Risk Quotient (RQ) of TCP in Water

Year	Sampling Point	TWA TCP POCIS[µg/L]	LC50 [µg/L]	TU TWA TCP	PNEC [µg/L]	RQ TWA TCP
2018	TSB	0,048	12000	4,00E-06	120	4,00E-06
2018	TPE	0,142	12000	1,19E-05	120	1,19E-05
2018	EPE	0,066	12000	5,48E-06	120	5,48E-06
2018	EBT	0,046	12000	3,83E-06	120	3,83E-06
2018	ESB	0,069	12000	5,73E-06	120	5,73E-06
2018	EBP	0,098	12000	8,18E-06	120	8,18E-06
2018	TSB	0,048	12000	3,98E-06	120	3,98E-06
2018	TPE	0,030	12000	2,54E-06	120	2,54E-06
2018	EPE	0,091	12000	7,56E-06	120	7,56E-06
2018	EBT	0,042	12000	3,46E-06	120	3,46E-06
2018	ESB	0,130	12000	1,08E-05	120	1,08E-05
2018	EBP	0,181	12000	1,51E-05	120	1,51E-05
2019	TSB	0,100	12000	8,30E-06	120	8,30E-06
2019	EPE	0,082	12000	6,87E-06	120	6,87E-06
2019	EBT	0,152	12000	1,27E-05	120	1,27E-05
2019	ESB	0,134	12000	1,12E-05	120	1,12E-05
2019	EBP	0,137	12000	1,15E-05	120	1,15E-05
2019	TPE	0,191	12000	1,59E-05	120	1,59E-05
2019	EPE	0,038	12000	3,13E-06	120	3,13E-06
2019	EBT	0,039	12000	3,25E-06	120	3,25E-06
2019	ESB	0,025	12000	2,08E-06	120	2,08E-06
2019	EBP	0,026	12000	2,17E-06	120	2,17E-06
2019	TPE	0,110	12000	9,18E-06	120	9,18E-06
2019	EPE	0,436	12000	3,63E-05	120	3,63E-05
2019	EBT	0,037	12000	3,11E-06	120	3,11E-06
2019	ESB	0,020	12000	1,70E-06	120	1,70E-06
2019	EBP	0,254	12000	2,11E-05	120	2,11E-05

Appendix 16

Calculation Chlorpyrifos and TCPof Risk Quotients (RQ) and Toxic Units (TU) in Sedimemts

Year	**Sampling Site**	**CFP [µg/kg]**	**TCP [µg/kg]**	**CPW CPF [µg/L]**	**CPW TCP [µg/L]**	**TU CPF**	**TU TCP**	**QR CPF**	**QR TCP**
2017	TSB	1,85	2857,77	0,0124	560,35	0,52	0,05	12,40	4,67
2017	TPE	0,71	2189,68	0,0048	429,35	0,20	0,04	4,76	3,58
2017	EPE	0,96	966,81	0,0064	189,57	0,27	0,02	6,44	1,58
2017	EBT	1,00	1070,57	0,0067	209,92	0,28	0,02	6,70	1,75
2017	ESB	0,67	3449,17	0,0045	676,31	0,19	0,06	4,47	5,64
2017	EBP	0,86	2064,68	0,0058	404,84	0,24	0,03	5,78	3,37
2018	TSB	1,93	4597,29	0,0130	901,43	0,54	0,08	12,97	7,51
2018	TPE	1,32	5057,99	0,0089	991,76	0,37	0,08	8,89	8,26
2018	EPE	0,45	3790,30	0,0030	743,20	0,13	0,06	3,00	6,19
2018	EBT	0,81	2477,38	0,0055	485,76	0,23	0,04	5,45	4,05
2018	ESB	0,36	3713,73	0,0024	728,18	0,10	0,06	2,43	6,07
2018	EBP	0,68	13961,65	0,0046	2737,58	0,19	0,23	4,59	22,81

Appendix17

Calculation of Hazard Quotients in Human Risk Assessment for Chlorpyrifos in Water

TWA CPF Sampling Point	TWA CPF [µg/L]	APDR	TWA CPF Di adults [µg/kg/dia]	TWA CPF Di Children [µg/kg/dia]	TWA CPF Dd adult [µg/kg/dia]	TWA CPF Dd Children [µg/kg/dia]	TWA CPF HQ ingestion Adults	TWA CPF HQ contact adults	TWA CPF HQ ingestion children	TWA CPF HQ contact children
TSB	0,00693	1,98E-08	1,98E-04	4,62E-04	1,01E-06	2,51E-07	3,96E-02	2,02E-04	9,24E-02	5,01E-05
TPE	0,00046	1,31E-09	1,31E-05	3,07E-05	6,69E-08	1,66E-08	2,63E-03	1,34E-05	6,13E-03	3,33E-06
EPE	0,03009	8,60E-08	8,60E-04	2,01E-03	4,38E-06	1,09E-06	1,72E-01	8,75E-04	4,01E-01	2,18E-04
EBT	0,01054	3,01E-08	3,01E-04	7,03E-04	1,53E-06	3,81E-07	6,02E-02	3,07E-04	1,41E-01	7,62E-05
ESB	0,07561	2,16E-07	2,16E-03	5,04E-03	1,10E-05	2,73E-06	4,32E-01	2,20E-03	1,01E+00	5,47E-04
EBP	0,0012	3,43E-09	3,43E-05	8,00E-05	1,75E-07	4,34E-08	6,86E-03	3,49E-05	1,60E-02	8,68E-06
TSB	0,00151	4,31E-09	4,31E-05	1,01E-04	2,20E-07	5,46E-08	8,63E-03	4,39E-05	2,01E-02	1,09E-05
TPE	0,01568	4,48E-08	4,48E-04	1,05E-03	2,28E-06	5,67E-07	8,96E-02	4,56E-04	2,09E-01	1,13E-04
EPE	0,00898	2,57E-08	2,57E-04	5,99E-04	1,31E-06	3,25E-07	5,13E-02	2,61E-04	1,20E-01	6,50E-05
EBT	0,004	1,14E-08	1,14E-04	2,67E-04	5,82E-07	1,45E-07	2,29E-02	1,16E-04	5,33E-02	2,89E-05
ESB	0,00262	7,49E-09	7,49E-05	1,75E-04	3,81E-07	9,48E-08	1,50E-02	7,62E-05	3,49E-02	1,90E-05
EBP	0,02836	8,10E-08	8,10E-04	1,89E-03	4,13E-06	1,03E-06	1,62E-01	8,25E-04	3,78E-01	2,05E-04
TSB	0,01365	3,90E-08	3,90E-04	9,10E-04	1,99E-06	4,94E-07	7,80E-02	3,97E-04	1,82E-01	9,87E-05
TPE	0,00456	1,30E-08	1,30E-04	3,04E-04	6,63E-07	1,65E-07	2,61E-02	1,33E-04	6,08E-02	3,30E-05
EPE	0,14046	4,01E-07	4,01E-03	9,36E-03	2,04E-05	5,08E-06	8,03E-01	4,09E-03	1,87E+00	1,02E-03
EBT	0,00061	1,74E-09	1,74E-05	4,07E-05	8,87E-08	2,21E-08	3,49E-03	1,77E-05	8,13E-03	4,41E-06
ESB	0,0006	1,71E-09	1,71E-05	4,00E-05	8,73E-08	2,17E-08	3,43E-03	1,75E-05	8,00E-03	4,34E-06
EBP	0	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00
TSB	0,01243	3,55E-08	3,55E-04	8,29E-04	1,81E-06	4,50E-07	7,10E-02	3,62E-04	1,66E-01	8,99E-05
TPE	0,30997	8,86E-07	8,86E-03	2,07E-02	4,51E-05	1,12E-05	1,77E+00	9,02E-03	4,13E+00	2,24E-03
EPE	0,00407	1,16E-08	1,16E-04	2,71E-04	5,92E-07	1,47E-07	2,33E-02	1,18E-04	5,43E-02	2,94E-05
EBT	0	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00
ESB	0,00139	3,97E-09	3,97E-05	9,27E-05	2,02E-07	5,03E-08	7,94E-03	4,04E-05	1,85E-02	1,01E-05
EBP	0,00293	8,37E-09	8,37E-05	1,95E-04	4,26E-07	1,06E-07	1,67E-02	8,52E-05	3,91E-02	2,12E-05
TSB	0,01467	4,19E-08	4,19E-04	9,78E-04	2,13E-06	5,31E-07	8,38E-02	4,27E-04	1,96E-01	1,06E-04
EPE	0,01173	3,35E-08	3,35E-04	7,82E-04	1,71E-06	4,24E-07	6,70E-02	3,41E-04	1,56E-01	8,48E-05
EBT	0,01836	5,25E-08	5,25E-04	1,22E-03	2,67E-06	6,64E-07	1,05E-01	5,34E-04	2,45E-01	1,33E-04
ESB	0,05138	1,47E-07	1,47E-03	3,43E-03	7,47E-06	1,86E-06	2,94E-01	1,49E-03	6,85E-01	3,72E-04
EBP	0,0137	3,91E-08	3,91E-04	9,13E-04	1,99E-06	4,95E-07	7,83E-02	3,99E-04	1,83E-01	9,91E-05
TPE	0,0436	1,25E-07	1,25E-03	2,91E-03	6,34E-06	1,58E-06	2,49E-01	1,27E-03	5,81E-01	3,15E-04
EPE	0,00233	6,66E-09	6,66E-05	1,55E-04	3,39E-07	8,43E-08	1,33E-02	6,78E-05	3,11E-02	1,69E-05
EBT	0,00383	1,09E-08	1,09E-04	2,55E-04	5,57E-07	1,39E-07	2,19E-02	1,11E-04	5,11E-02	2,77E-05
ESB	0,04629	1,32E-07	1,32E-03	3,09E-03	6,73E-06	1,67E-06	2,65E-01	1,35E-03	6,17E-01	3,35E-04
EBP	0,00508	1,45E-08	1,45E-04	3,39E-04	7,39E-07	1,84E-07	2,90E-02	1,48E-04	6,77E-02	3,67E-05
TPE	0,00229	6,54E-09	6,54E-05	1,53E-04	3,33E-07	8,28E-08	1,31E-02	6,66E-05	3,05E-02	1,66E-05

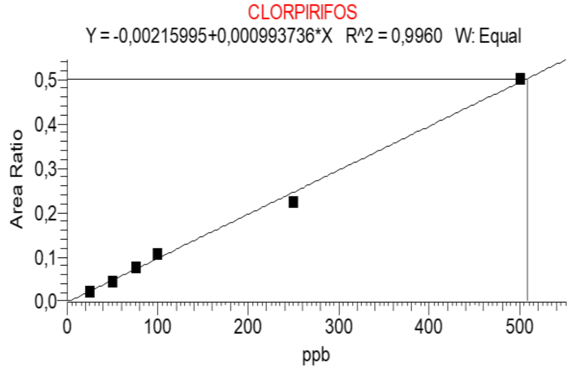
Appendix 18

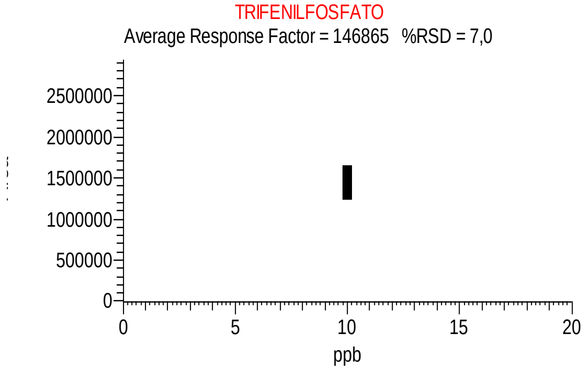
Calculation of Hazard Quotients in Human Risk Assessment for TCP in Water

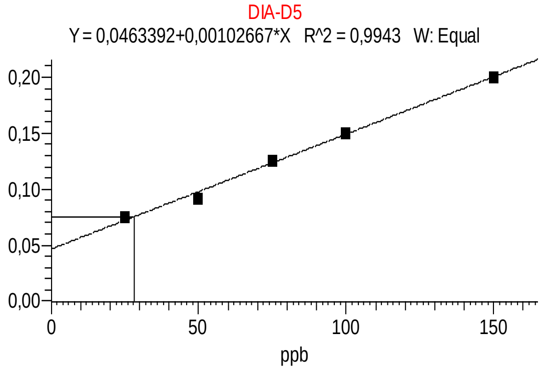
Sampling Point	TWA TCP [µg/L]	APDR	TWA TCP Di adults [µg/kg/dia]	TWA TCP Di Children [ug/kg/dia]	TWA TCP Dd adult [µg/kg/dia]	TWA TCP Dd Children [µg/kg/dia]	TWA TCP HQ ingestion Adults	TWA TCP HQ contact adults	TWA TCP HQ ingestion children	TWA TCP FHQ contact children
TSB	0,2456	7,0E-07	0,00702	0,01637	0,00004	0,00001	0,02807	0,00014	0,06549	0,00004
TPE	0,6434	1,8E-06	0,01838	0,04289	0,00009	0,00002	0,07353	0,00037	0,17157	0,00009
EPE	0,2544	7,3E-07	0,00727	0,01696	0,00004	0,00001	0,02907	0,00015	0,06784	0,00004
EBT	0,2296	6,6E-07	0,00656	0,01531	0,00003	0,00001	0,02624	0,00013	0,06123	0,00003
ESB	0,3416	9,8E-07	0,00976	0,02277	0,00005	0,00001	0,03904	0,00020	0,09109	0,00005
EBP	0,5185	1,5E-06	0,01481	0,03457	0,00008	0,00002	0,05926	0,00030	0,13827	0,00008
TSB	0,2052	5,9E-07	0,00586	0,01368	0,00003	0,00001	0,02345	0,00012	0,05472	0,00003
TPE	0,1932	5,5E-07	0,00552	0,01288	0,00003	0,00001	0,02208	0,00011	0,05152	0,00003
EPE	0,305	8,7E-07	0,00871	0,02033	0,00004	0,00001	0,03486	0,00018	0,08133	0,00004
EBT	0,2208	6,3E-07	0,00631	0,01472	0,00003	0,00001	0,02523	0,00013	0,05888	0,00003
ESB	0,4593	1,3E-06	0,01312	0,03062	0,00007	0,00002	0,05249	0,00027	0,12248	0,00007
EBP	0,763	2,2E-06	0,02180	0,05087	0,00011	0,00003	0,08720	0,00044	0,20347	0,00011
TSB	0,4212	1,2E-06	0,01203	0,02808	0,00006	0,00002	0,04814	0,00025	0,11232	0,00006
EPE	0,3756	1,1E-06	0,01073	0,02504	0,00005	0,00001	0,04293	0,00022	0,10016	0,00005
EBT	0,699	2,0E-06	0,01997	0,04660	0,00010	0,00003	0,07989	0,00041	0,18640	0,00010
ESB	0,6834	2,0E-06	0,01953	0,04556	0,00010	0,00002	0,07810	0,00040	0,18224	0,00010
EBP	0,5392	1,5E-06	0,01541	0,03595	0,00008	0,00002	0,06162	0,00031	0,14379	0,00008
TPE	0,9729	2,8E-06	0,02780	0,06486	0,00014	0,00004	0,11119	0,00057	0,25944	0,00014
EPE	0,1838	5,3E-07	0,00525	0,01225	0,00003	0,00001	0,02101	0,00011	0,04901	0,00003
EBT	0,2079	5,9E-07	0,00594	0,01386	0,00003	0,00001	0,02376	0,00012	0,05544	0,00003
ESB	0,1442	4,1E-07	0,00412	0,00961	0,00002	0,00001	0,01648	0,00008	0,03845	0,00002
EBP	0,1331	3,8E-07	0,00380	0,00887	0,00002	0,00000	0,01521	0,00008	0,03549	0,00002
TPE	0,5481	1,6E-06	0,01566	0,03654	0,00008	0,00002	0,06264	0,00032	0,14616	0,00008
EPE	0,3753	1,1E-06	0,01072	0,02502	0,00005	0,00001	0,04289	0,00022	0,10008	0,00005
EBT	0,1866	5,3E-07	0,00533	0,01244	0,00003	0,00001	0,02133	0,00011	0,04976	0,00003
ESB	0,0963	2,8E-07	0,00275	0,00642	0,00001	0,00000	0,01101	0,00006	0,02568	0,00001
EBP	1,5457	4,4E-06	0,04416	0,10305	0,00022	0,00006	0,17665	0,00090	0,41219	0,00022

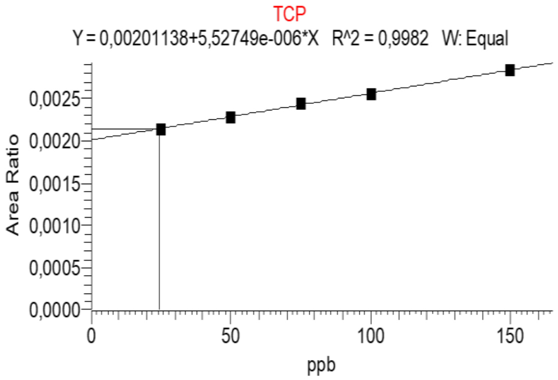
Appendix 19

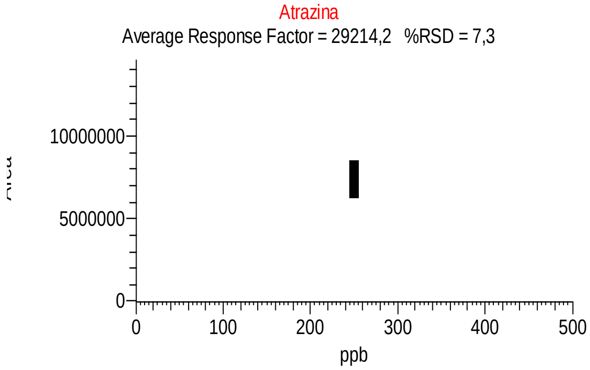
Method Verification

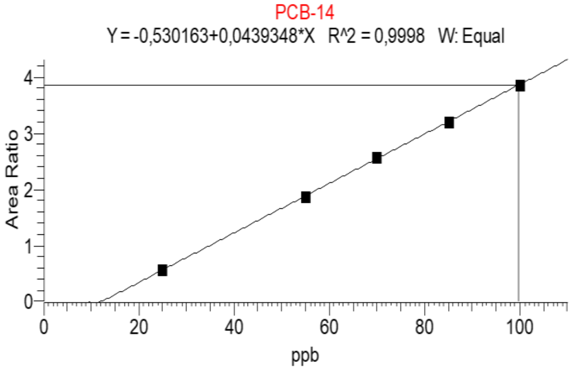


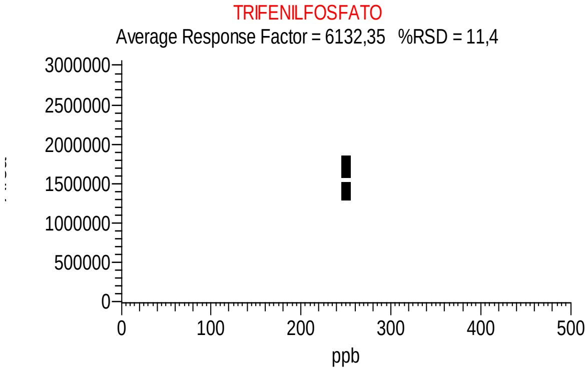












Outreach Products

- Amaringo Villa, F. A., Narvaez Valderrama, J. F., Gómez-Arguello, M. A., and Molina, F. (2019). Contaminación en agua y sedimentos por hidrocarburos aromáticos policíclicos: Revisión de la dinámica y los métodos analíticos. *Gestión y Ambiente*, *22*(1), 129–140. https://doi.org/10.15446/ga.v22n1.77874

DOI: https://doi.org/10.15446/ga.v22n1.77874

Contaminación en agua y sedimentos por hidrocarburos aromáticos policíclicos: Revisión de la dinámica y los métodos analíticos

Pollution in Water and Sediments by Polycyclic Aromatic Hydrocarbons: Review of Dynamics and Analytical Methods

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Mayra Alejandra Gómez-Arguello[a], Francisco Molina[c]

- Gomez Arguello, M. A., Narvaez Valderrama, J. F., Amaringo Villa, F. A., and Molina, F. (2020). Environmental Risk assessment of Chlorpyrifos and TCP in Aquatic Ecosystems. *Revista EIA*, *17*(34), 1–12. https://doi.org/10.24050/reia.v17i34.1313

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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.

- Gomez-Arguello, M. A., and Molina, F. (2023, March 29-31). Participation as a speaker in the II Congreso Internacional en Ingeniería Ambiental. Tecnologías para la sustentabilidad en tiempos de emergencia ambiental. San José de Cúcuta, Norte de Santander, Colombia. Paper titled " “Muestreo Pasivo De Chlorpyrifos y su Principal Producto de Degradación como Indicadores de Contaminacion del Agua”

LA UNIVERSIDAD FRANCISCO DE PAULA SANTANDER
Y
LA UNIVERSIDAD NACIONAL ABIERTA Y A DISTANCIA

CERTIFICAN QUE

MAYRA ALEJANDRA GOMEZ ARGUELLO

Participó como **PONENTE** en el **II CONGRESO INTERNACIONAL EN INGENIERÍA AMBIENTAL**, que se desarrolló del 29 al 31 de marzo del año 2023 en San José de Cúcuta, Norte de Santander, Colombia, con el trabajo de investigación titulado “MUESTREO PASIVO DE CLORPIRIFOS Y SU PRINCIPAL PRODUCTO DE DEGRADACIÓN COMO INDICADORES DE CONTAMINACIÓN DEL AGUA”.

Dorance Becerra M.
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DIRECTOR PROGRAMA INGENIERÍA AMBIENTAL, UFPS

VICTOR FABIAN FORERO
LIDER NACIONAL DE LA CADENA DE FORMACION AMBIENTAL, UNAD

Herrera-Gudiño, E J., Gomez-Arguello, M A., Molina, F. (2023). Toxicity of Glyphosate and its Degradation Products in Aquatic Ecosystems: A Review. *Revista de Investigación Agraria y Ambiental RIAA. 15(1). En prensa*

Gomez-Arguello, M A., Navarez-Valderrama, J F., Molina, F. (2023). Tracking of Clorpyrifos Degradate (3,5,6-Trichloro-2-Pyridinol) in a Tropical Mountain Reservoir Using Pocis by PRC Dissipation Modeling. *Water, air and Soil pollution.* (under revision)