OCCURRENCE, ATTENUATION AND DYNAMIC MODELING OF PESTICIDES TRANSPORT ALONG PAMPANGA RIVER BASINS

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Abstract

The purpose of this research is to determine the presence of pesticide, chlorpyrifos in Pampanga River basin and to develop or modify existing model to make it useful in predicting concentration levels of micro contaminants along the river channel. Sampling is done within a period of one year to cover the entire dry and wet seasons. Method of analysis include the preparation of samples in accordance with the standard test available using GC-MS. The analyses were conducted at the National Sciences Research Institute- Research Analytical Services Laboratory. The widely acceptable water quality model (WASP8) provided by the USEPA is used with an added feature like Monte Carlo Program is incorporated in this model to predict future concentration results. Risk assessment is also added in the study where target/non target organisms are points of concern.

Initial samples were obtained from identified sampling sites with high concentration of target pollutants from nearby farmlands and tributaries. Identified sampling sites with high concentrations of target pesticides (chlorpyrifos, endosulfan and malathion) are subject areas for the model. A dynamic box model was used in the Pampanga River channel with loads based on the laboratory results. Actual test results from GC-MS revealed that the model, with parameters and constants provided, can predict concentrations of pesticides at the downstream of the river water. Cross validation is done on the model that resulted a mean error of 0.0263% using the tributaries and an error of 0.65% when used in the main channel.

Assessing the risks for aquatic organisms observed that for most of the selected pesticides, the calculated exposure concentrations were higher than the regulatory acceptable concentration. To implement the exposure scenarios and models for pesticide authorization in the Philippines, further research on the acceptable concentrations is needed. Further studies are also recommended to develop top-tier model and risk management that can be applied in the Philippine setting.

This model is needed to aid people in their decisions on the proper management of micro-pollutants, pesticides. The results of this analysis can be used as a basis of social and industrial policies.
Keywords: Water Quality Modeling, Pesticides, Solid Phase Extraction, Elution, Cross Validation, Monte Carlo Simulation

1. Introduction

Many of our river systems today are polluted with pesticides and other contaminants. Even though pesticides improve crop/food yield and reduce vector-borne diseases among others, they pose a threat to our freshwater ecosystems. Agricultural lands, as one the major contributors of pesticides continuously bring run off residuals and dump to the mouth of the river. In Midwest, where farming is prevalent, water utility companies spend over 400 million USD per year just to treat water for one chemical, atrazine (UnadKat, 2017). In the Philippines, where farming is also a major source of income, generates more than 120 million USD worth of pesticides (Adapon, 2006).

Prevention and abatement became popular among existing solutions. Identification of source of contaminant is essential to efficiently manage the micro-pollutants. Therefore, the monitoring of our river system through infrastructure modeling the fate and transport of these contaminants may guarantee the maintenance of our natural river water system.

So far, the conducted study on the Pampanga River water quality is only on the chemical characteristics of the river water quality using some parameters such as pH, temperature, dissolved oxygen, ammonia, nitrates, and phosphates. None of the studies conducted in the Pampanga River water focus on the fate and transport of micro pollutants such as antibiotics, pesticides, and other endocrine disrupting compounds. The study being proposed is considered new and will significantly contribute to global measures by providing important data in micro pollutants present in river systems. Numerous models have been developed to address the problem. These models are generally categorized into three namely: Spatially explicit (e.g. LDC, SELECT, SPARROW), Mass Balance Methods (BLEST, BSLC, BIT) and Deterministic or Mechanistic Hydrologic/Water Quality Bacteria Models (HSPF, SWAT, SWIM, and WASP). Recently, several water quality mathematical models have been established and applied to the study of organic contaminants (O'Driscoll et al., 2011; Rygwelski et al., 2012; Xu et al., 2017). The application of mathematical models can provide quantitative insight into processes that influence the fate of organic pollutants (O'Driscoll et al., 2013; O'Driscoll, 2014). The Water Quality Analysis Simulation Program (WASP), developed by the US Environmental Protection Agency, is a widely used program for modeling aquatic systems (Ambrose et al., 1993). Multiple studies have demonstrated the performance of WASP as a water quality model (Cheng et al., 2014a; Quijano et al., 2017). It has been used to simulate the transport and fate of a variety of organic contaminants, including polychlorinated biphenyls and the pesticide atrazine (Vuksanovic et al., 1996; Rygwelski et al., 2012).

The main objective of this study is to develop or modify existing model on water quality to make it useful for predicting pesticides levels. This model is needed to aid people in their decisions on the proper management of micro-pollutants, pesticides. The results of this analysis can be used as a basis of social and industrial policies.

2. Methodology

River water samples from identified sampling sites along Pampanga River were collected from October 2018 to October 2019 to complete the one-year-round sampling for both dry and wet seasons. Two representative samples were collected in a 1-liter dark bottle with duplicates from each sampling site and sealed with labels for proper identification. The samples were placed in the iced box filled with iced cubes during shipping and stored at low temperature setting in laboratory for testing. Method of analysis include the preparation of samples in accordance with the standard test available using GC-MS. The analyses were conducted at the Research Analytical Services Laboratory, National Sciences Research Institute.

After screening the several water quality model, the widely acceptable water quality model (WASP version 8) provided by the USEPA (United States Environmental Protection Agency) was selected to model the prediction of pesticides. The Water Quality Analysis Simulation Program is an enhancement of the original WASP (Di Toro et al., 1983; Connolly and Winfield, 1984; Ambrose, R.B. et al., 1988). This model helps users interpret and predict water quality responses to natural phenomena and manmade pollution for various pollution management decisions. WASP is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. was used with an added feature like Monte Carlo Program is incorporated in this model to predict future concentration results. Risk assessment is also added in the study where target/non target organisms are points of concern.

Target analytes used were chlorpyrifos, endosulfan and malathion. Malathion is also common insecticide used by farmers because of its cheaper value and lesser impact to the environment. Endosulfan, known as old but persistent pesticide still exist in aquatic environment present in detectable concentration in the Pampanga River water system. Data from PalayStat provided the distribution data of farmers (%) by active ingredients of pesticide applied serve as basis in estimating the amount of pesticides consumption/usage. Initial samples were obtained from identified sampling sites with high concentration of target pollutants from nearby farmlands and tributaries. Identified sampling sites with high concentrations of target pesticides (chlorpyrifos, endosulfan and malathion) are subject areas for the model. Method validation and recovery were done using a 500-ml sample (Ultra-Pure Water). Surrogate solutions are added to 6 samples coded as Blank A, Blank B, MV1, MV2, MV3 and MV4. Mean recoveries from initial validation should be within the range 70–120%, with an associated repeatability RSDr ≤ 20%, for all analytes within the scope of a method. In exceptional cases, mean recovery rates outside the range of 70-120% can be accepted if they are consistent (RSD ≤ 20%) and the basis for this is well established (e.g., due to analyte distribution in a partitioning step), but the mean recovery must not be lower than 30% or above 140%. Additional 20 microliters of pesticide mixed are added to MV1 to MV4 labels for testing the accuracy and precision in testing. The extracted samples were run in a Shimadzu GCMS QP2010 or Shimadzu GCMS QP5000 equipped with capillary column DB5 (0.32 id x 30 m and 0.25μm thickness), Shimadzu GCMS AOC-20i Auto injector, data station, software and NIST library of mass spectral data with BUCHI or HEIDOLPH evaporator.

Figure 1. Sampling sites along Pampanga River

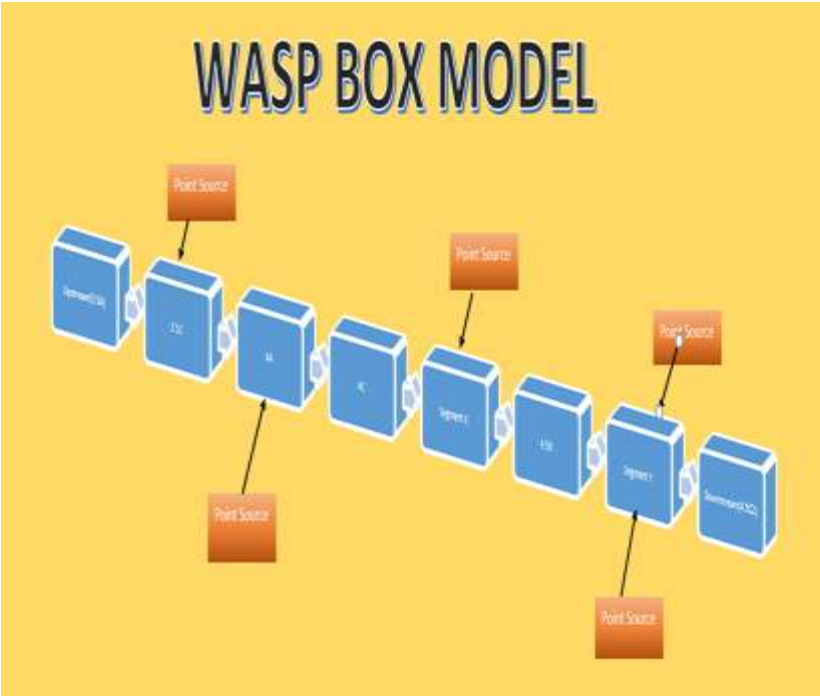

Figure 2. The WASP Box Model representing the selected water sampling stations

A dynamic box model represented by WASP (Water Quality Analysis Program) was used in the Pampanga River channel with the selected sampling stations (as shown in Figure 1) that are loaded based on the laboratory test results. Below is the simplified process flow of laboratory works.

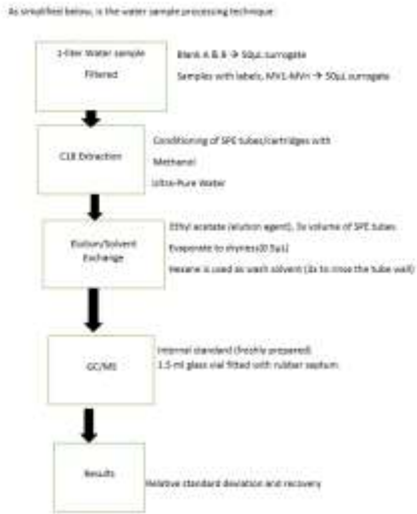

Figure 3. Method Validation of Samples applied in the Lab

Selected sites along the channel served as segments with corresponding distances from each other. Channel widths and segment distances were measured using the Google Distance Measuring feature needed as input data in the box model (Figure 2). Actual test results from the laboratory using method in GC-MS revealed that the model, with parameters and constants provided, can predict concentrations of pesticides at the downstream station of the river water.

Risk Assessment Scenarios

For the fish scenario, the peak concentration of pesticides in the water is calculated while ignoring losses due to the diffusion of pesticides into the soil and the adsorption of pesticides to the organic matter present in the soil. The exposure concentration was calculated from a series of applications while keeping a fixed time interval between the application.

Formulas:

$$5.4.1\ PEC = [0.1*(1 - CI)*M]/d$$

Where:

PEC = predicted exposure concentration for a single application (µg/L).

CI = crop interception fraction at the time of application (−).

M = application rate (g a.i./ha).

0.1 = correction factor to convert g/ha to mg/m2

d = depth of the paddy water (m).

For the fish scenario, the peak concentration of pesticides in the water is calculated while ignoring losses due to the diffusion of pesticides into the soil and the adsorption of pesticides to the organic matter present in the soil. The exposure concentration was calculated from a series of applications while keeping a fixed time interval between the application.

$$TER = PNEC;[(LC50 \text{ or } EC50)/SF]/PEC_{peak}$$

Where:

TER = toxicity exposure ratio (−).

PNEC = predicted no-effect concentration for aquatic organisms–fish (including mudfish), Daphnia and algae (µg/L).

SF = safety factor (−).

PEC_{peak} = the maximum predicted environmental concentration for the protection goal (μg/L).

The risks associated with the pesticides were classified by the calculated TER. If the TER is lower than 1, the exposure is deemed to be higher than the PNEC. These risks are considered unacceptable. If the TER is higher than 1, the risks associated with pesticide use are considered acceptable.

Other Scenarios: Estimating the pesticide concentration in rice paddies.

The USEPA suggest a model version on Rice Model that estimate the concentration of pesticides in rice paddies. This the “Tier I Rice Model - Version 1.0 - Guidance for Estimating Pesticide Concentrations in Rice Paddies”

$$Cw = mai' / (0.00105 + 0.00013Kd)$$

where, in this case:

Cw = water concentration [μg/L]

mai′ = mass applied per unit area [kg/ha]

Kd = water-sediment partitioning coefficient [L/kg]

= 0.01Koc

Assumptions

Most of the assumptions used in this model help ensure that the outputs are protective of most environments associated with rice agriculture. The model assumptions include the following:

a. Movement of pesticide on suspended sediment is not considered.

b. Degradation does not occur.

c. Volatilization and other dissipation processes are not considered.

d. Partitioning to sediment is instantaneous.

e. Water is available for human or wildlife exposure instantaneously.

f. Water column depth is 10 cm.

g. Sediment depth is 1 cm.

h. All pore space is saturated with water.

i. Organic carbon fraction is 0.01.

j. Bulk density is 1300 kg/m^3.

k. Grain density is 2650 kg/m^3.

Estimates from the Tier I model generally do not represent typical concentrations found in human drinking water, as they represent paddy discharge water. However, these concentrations may be a reasonable estimate of acute concentrations for use in ecological assessment where exposure occurs at or near the rice paddy. In both cases, human drinking water and ecological exposure, the chronic concentrations as well as offsite concentrations are expected to be conservative. A higher tier rice model should be used to estimate chronic exposure to compounds that degrade rapidly into degrades that are not of risk concern.

3. Results And Discussion

The results showed that there is a high concentration of malathion on the selected sampling sites where 4.5A gives the highest above 30 ppb followed by 5A along the downstream channel. This is because of the point sources where other pollutants are coming in. The pesticide malathion is known to be cheaper and has low effects on aquatic life, as compared to other target pesticides, endosulfan and chlorpyrifos. Figure 3 below shows average concentrations of pesticides tested from the laboratory.

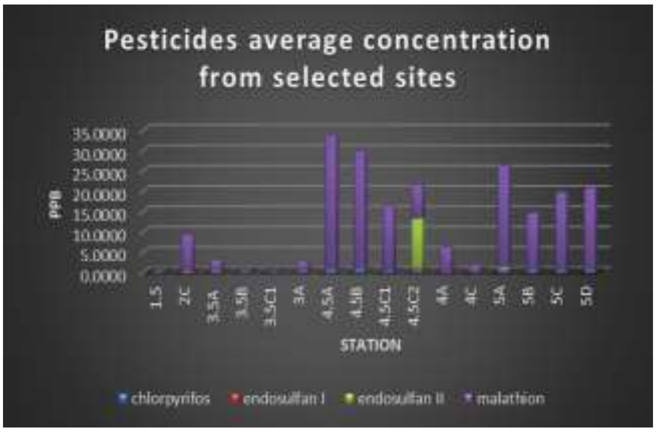

Figure 4. Mean concentrations of target analytes per sample code on the selected segment

Based on the WASP model results, the range from the tests runs catches some concentrations results from the laboratory. Figure 4 showed the predicted concentrations at the downstream of the three contaminants with respect to time in a daily basis.

Mean, Variance and Standard Deviation: Cross Validation using other data from other data sources (e.g., main channel, tributaries)

The values shown in table 4.10 indicates that the WASP model gave an acceptable value for endosulfan and chlorpyrifos which within the acceptable range of less than SD 2.0 while the value of malathion, SD 5 is far from the observed value. This may be due to the high concentration difference of malathion from the tested reference sample. The mean error is computed as 0.65% when data from malathion is not used.

The use of other data from the tributaries gives the cross validation of the WASP model. Another set of entries used on the interface, but values and segmentation were change. Table 1 summarizes the results of cross validation with a very minimal error.

Pesticides	Endosulfan	Malathion	Chlorpyrifos
Mean	0.19243716	13.93899	0.3137923
Variance	8.75E-03	2.51E+01	4.28E-03
Standard deviation	0.09354989	5.01048	0.0654399

Table 1 Calculated results of mean, variance, and standard deviation from the WASP model output

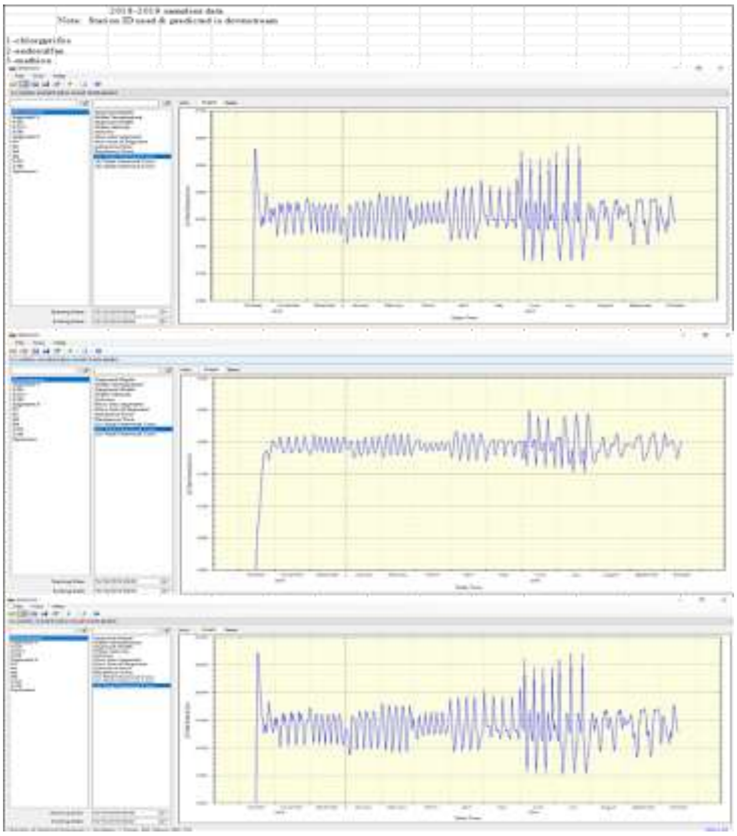

Figure 5. Graphical Representation Output WASP predicted results at the downstream

Montecarlo Simulation

In this study, the Montecarlo simulation is used to show predicted pesticide concentrations in varying scenarios considering the peak values in daily, yearly or depending on user's preferences. The model is linked to the simulations to help management decisions in pesticides' regulations and policies.

Results of risk assessment for aquatic organisms

As shown in Table 2 and based on the risk calculated results, majority of the fish species given are unacceptable.

These results are for pesticides that are specifically selected for this study because they are expected to pose risks for the aquatic ecosystem based on the pesticide sales, volume, frequency of application, number of products, and toxicity.

Among many fish species given exposed to malathion, the TER are acceptable to catfish, carp, and goldfish with values greater than 1. Malathion has proven to have less impact to aquatic organisms compared to the chlorpyrifos and endosulfan which are highly toxic.

Target Chemicals	Fish Species	LC50 (ppb)	TER
Chlorpyrifos	cyprinodon variegatus	136	0.0408
	menidia menidia	3	0.0009
	M. peninsulae	1.3	0.00039
	M. beryllina	4.2	0.00126
	Lauresthes tenuis	1.3	0.00039
	Opsanus beta	520	0.156
	Mugil cephalus	5.4	0.00162
	Fundulus heteroclitus	4.7	0.00141
	Morone saxatilis	0.58	0.000174
Endosulfan	Nile tilapia	12.795	0.003839
	Tilapia	1.42	0.000426
	Catfish	1.5	0.00045
	Spotted Snakehead fish	7.75	0.002325
	Bluegill sunfish	1.2	0.00036
	Penaeid shrimp	199.3	0.05979
	Bluegills	1	0.0003
	Striped dwarf catfish	2	0.0006
Malathion	Bluegill sunfish	30	0.009
	Redear sunfish	62	0.0186
	Rainbow trout	30	0.009
	Yellow perch	263	0.0789
	Largemouth bass	250	0.075
	Carp	6590	1.977
	Fathead minnow	8650	2.595
	Channel catfish	7620	2.286
	Salmon	170	0.051
	Cutthroat trout	174	0.0522
	Brown trout	101	0.0303
	Lake trout	76	0.0228
	Black bullhead catfish	11700	3.51
	Green sunfish	146	0.0438
	Walleye	64	0.0192
	Tilapia	2000	0.6
	Gold fish	10700	3.21

Table 2 Fish Samples Exposed to Selected Pesticides

These results are for pesticides that are specifically selected for this study because they are expected to pose risks for the aquatic ecosystem based on the pesticide sales, volume, frequency of application, number of products, and toxicity.

Among many fish species given exposed to malathion, the TER are acceptable to catfish, carp, and goldfish with values greater than 1. Malathion has proven to have less impact to aquatic organisms compared to the chlorpyrifos and endosulfan which are highly toxic.

On the other scenario as on the rice paddies as suggested by the USEPA, if Tier I estimate calculated by this screening method do not exceed the level of concern in a risk assessment, there is high confidence that there will be little or no risk above the level of concern from exposure through water resources. However, because of the uncertainties associated with a screening method, when a level of concern is exceeded, it cannot be determined whether the exceedance will in fact occur or whether this method has overestimated the exposure.

4. Conclusion/Remarks

Occurrence of significant concentration levels of pesticides has posed high risk in the aquatic organisms and other biota. Values ranges for chlorpyrifos, endosulfan, and malathion to be 0.20663-0.95150 ppb, 0.00825-1.30221 ppb and 6.60834-10.20278 ppb respectively at the downstream.

In this study, the Water Quality Assessment Program (WASP) has predicted the downstream pesticides concentrations along the selected segments of the Pampanga River with a mean error of 0.0263% taken from the three analytes using the data from the cross-validation method. This would mean that the model is more precise in predicting concentrations when sample is taken from a direct path along the tributaries. Output and downstream concentrations from the different sampling stations like that of the point sources from X1, X2 and X3 were provided with concentrations for chlorpyrifos, endosulfan A, Endosulfan B and malathion as 0.00047, 0.000401, 0.0000452, and 0.0171 ppb respectively when used as data in cross validation of the WASP model. Differential errors are higher, 0.65% when it was used in the main channel. This model may be efficient for predicting and calculating the pesticides levels and residues along the Pampanga River basin especially when the data collection and inputs are systematized.

Risk assessment scenarios presented the TER where in most of the introduced species were not acceptable. Fish species like carp, mudfish and goldfish passed and received an acceptable total exposure ratio of more than 1 when malathion is used. Computational values vary depending on the safety factor used, frequency of application, crop interception fraction at the time of application, depth of the paddy water and the LC50 used.

Montecarlo simulation aided the prediction of pesticides levels in determining the highest peaks for the 90-day, monthly, or even yearly period in the future. A dynamic program chart may be developed to monitor and alarm the concerned stakeholders when threshold concentrations is already reach.

Tier I Rice Model - Version 1.0 from the USEPA is an effective model to be included in the overall study because the regulation of loading/application of pesticides rice paddies causally linked to the pollutant concentrations of nearby surface streams. Important data from this model will help monitor the conservative values in the receiving surface water just like that of Pampanga River water system.

With all the models work together, it may facilitate the implementation of policies on the regulation of pesticides' sales, distribution, loading and application in the country.

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References

[1] A. Beketova, Matthias Hundtd, Coretta Bauere, Gerrit Schüürmanncg, Monika Mödere, Matthias Liessah, R. (2015). Pesticide impact on aquatic invertebrates identified with Chemcatcher® passive samplers and the SPEARpesticides index. Science of The Total Environment, 69-80.

[2] Ginebredaa, L.Sabater-Liesaa, A. Ricob A.Focksc, D.Barcelóad. (2018). Reconciling monitoring and modeling: An appraisal of river monitoring networks based on a spatial autocorrelation approach - emerging pollutants in the Danube River as a case study. Science of The Total Environment, 323-335.

[3] A. Ngc, A. E. (2018). Tracking pesticide fate in conventional banana cultivation in Costa Rica: A disconnect between protecting ecosystems and consumer health. Science of The Total Environment, 1250-1262.

[4] A. Vanrolleghemac1, K. M. (2007). Monitoring and modeling pesticide fate in surface waters at the catchment scale. Ecological Modelling, 53-64.

[5] Aldaa Damià Barcelóade, M.-S. L. (2012). Analysis of the occurrence and risk assessment of polar pesticides in the Llobregat River Basin (NE Spain). Chemosphere, 8-16.

[6] Alexander Ccanccapaa, Ana Masiáa Alícia, Navarro-Ortegab Yolanda, Picóa Damià Barcelóbc. (2016). Pesticides in the Ebro River basin: Occurrence and risk assessment. Environmental Pollution, 414-424.

[7] Alícia Navarroa, Romà Taulera, Sílvia Lacortea, Damià Barcelóab. (2010). Occurrence and transport of pesticides and alkylphenols in water samples along the Ebro River Basin. Journal of Hydrology, 18-29.

[8] Ana Masiáa, Julián Campoa, Alícia Navarro-Ortegab, Damià Barcelóbc, Yolanda Picóa. (2015). Pesticide monitoring in the basin of Llobregat River (Catalonia, Spain) and comparison with historical data. Science of The Total Environment, 58-68.

[9] Beshare Hashemia, Parvin Zohrabib, Ki-Hyun Kimc, Mojtaba Shamsipura, Akash Deepd, Jongki Honge. (2017). Recent advances in liquid-phase microextraction techniques for the analysis of environmental pollutants. Elsevier, 83-95.

[10] Brinkac, B. M. (2016). Monitoring and risk assessment of pesticides in irrigation systems in Debra Zeit, Ethiopia. Chemosphere, 280-291.

[11] C. Deschampsb, Charrid Resgalla Jr. a, D. C. (2016). Ecological risk analysis of pesticides used on irrigated rice crops in southern Brazil. Chemosphere, 48-54.

[12] D. Ngo-Conga, F.J. Mohammeda, D.V. Strunina, A.T. Skvortsovb, N.Mai-Duya, T.Tran-Conga. (2015). Higher-order approximation of contaminant transport

Online Resources:

[13] USEPA, 2007, Tier I Rice Model - Version 1.0 - Guidance for Estimating Pesticide Concentrations in Rice Paddieshttps://www.epa.gov

[14] Ron Gardner, National Water-Quality Assessment (NAWQA), Understanding the Fate of Pesticides after Application, Program https://pesticidestewardship.org

[15] Kyung et. Al., 2021, Science of The Total Environment, Development of surface water exposure scenarios for risk assessment of pesticides in Koreahttps://www.sciencedirect.com/
[16] Harsimran Kaur Gill and Harsh Garg, IntechOpen Limited, 2014, https://www.intechopen.com/
[17] European Food Safety Authority (EFSA), 2017, EFSA Guidance Document for predicting environmental concentrations of active substances of plant protection products and transformation products of these active substances in soil, https://www.intechopen.com/
[18] Sante, 2019, Analytical Quality Control and Method Validation Procedures for Pesticides Residues Analysis in Food and Feed, https://www.eurl-pesticides.eu/
[19] Zahan et. Al., 2019, TOXICITY BIOASSAY OFCHLORPYRIFOS ON SOMELOCAL FISH SPECIES OF NORTHERN BANGLADESH, http://oaji.net/
[20] Okoya et. Al., 2013, Organochlorine Pesticide Residues in Sediments and Waters from Cocoa Producing Areas of Ondo State, Southwestern Nigeria, https://www.hindawi.com/
[21] PalayStat, Results from our nationwide survey of rice farm households conducted every 5 years since 1996https://dbmp.philrice.gov.ph/
[22] NASA Prediction of Worldwide Energy Resources, Data Access, https://power.larc.nasa.gov/