Assessment of Pesticide Occurrence, Attenuation and Transport Dynamics in the Pampanga River Basin

AGUSTIN R.[1,*], ROLLON A.[2], KWAN C.[3], BALLESTEROS F.[4]

[1]Department of Environmental Engineering, University of the Philippines; Department of Environmental and Sanitary Engineering, Technological Institute of the Philippines; General Engineering Department, National University Philippines
[2]Department of Environmental Engineering, University of the Philippines
[3]Research and Analytical Services Laboratory, Natural Science Research Institute, University of the Philippines
[4]Department of Chemical Engineering, University of the Philippines

*Corresponding author:
email: rgagustin@national-u.edu.ph

Abstract. The goal of this study is to detect chlorpyrifos, a pesticide, in the Pampanga River basin and to create a new model, or improve upon an existing one, that can accurately predict the concentration levels of micro pollutants in the river bed. The complete dry and wet seasons are accounted for by taking samples within a single calendar year. Method of analysis include the preparation of samples in line with the standard test available utilizing GC-MS. The analyses were done 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. The research includes a risk analysis of potential hazards posed by both target and non-target organisms.

The first samples were taken from locations that had been previously determined to have a high concentration of the pollutants of interest, such as nearby farmlands and tributaries. Identified sampling sites with high concentrations of target pesticides (chlorpyrifos, endosulfan and malathion) constitute subject regions 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 demonstrated that the model, with parameters and constants provided, can estimate amounts of pesticides at the downstream of the river water. The model is cross-validated based on the fact that it produces a mean error of 0.0263% when applied to the tributaries and a mean error of 0.65% when applied to the main channel.

The predicted exposure concentrations for most of the identified pesticides were found to be greater than the regulation permissible value during the risk assessment for aquatic species. Additional study on safe pesticide concentrations is required before the Philippines can implement exposure scenarios and models for pesticide authorization. Further studies are also needed to build top-tier model and risk management that may be utilized in the Philippine scenario.

People will require this model to help them make educated choices about how to deal with micro-pollutants like pesticides. The results of this investigation can be used as a basis of social and industrial strategies.

Keywords: water quality modeling, pesticides, solid phase extraction, elution, method validation

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). Among various water quality models, the WASP model has gained significant prominence in recent years. Notably, publications using models like CE-QUAL-W2, EFDC, and MIKE have exceeded 10 records since 2015, while the other models have averaged over five records per year during the same period. However, when considering both recent years (2016-2020) and longer time spans (2001-2020), the WASP model consistently ranks among the top three models in terms of citations, alongside CE-QUAL-W2 and EFDC. This highlights the substantial attention and recognition received by these models from researchers over the past five years and the last two decades, emphasizing their importance in the field of water quality modeling (Bai, et.al., 2022)

The main objective of this study is to develop 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 November 2021 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 into the iced box filled with ice 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 selecting from the available water quality models, the widely acceptable water quality model (WASP version 8) provided by the USEPA (United States Environmental Protection Agency) was chosen 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 $\leq$ 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 $\leq$ 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 using the solid phase extraction method 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.

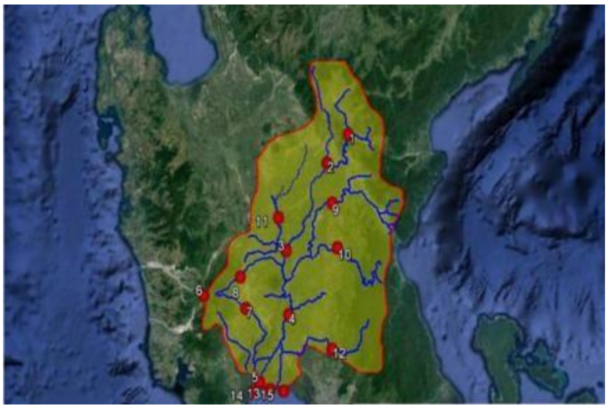


Figure 1. Sampling sites along Pampanga River

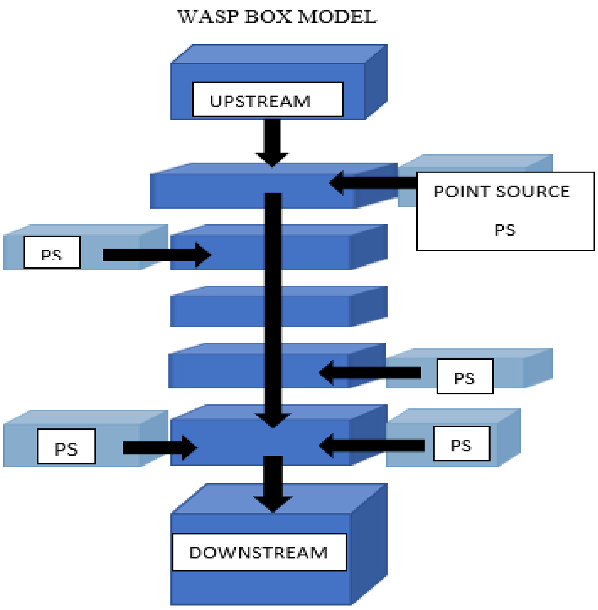
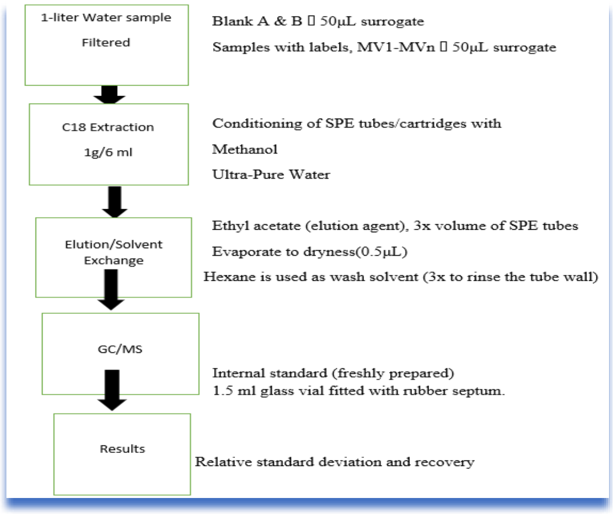


Figure 2. WASP Box Model representing the selected water sampling stations

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 obtained from the simplified water sample processing technique below:



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.

3. Results and Discussion

The results showed that there is a high concentration of malathion on the selected sampling site where 4.5C1 in 2018, endosulfan 2 in 2019 of 4.5C2 and almost all sampling sites in 2021 along the main channel. Higher number of population density is in this region and more agricultural crops are grown. The pesticide malathion is known to be cheaper and has low effects on aquatic life, as compared to other target pesticides, endosulfan and chlorpyrifos. Figures 3, 4 and 5 shows average concentrations of pesticides tested from the laboratory results.

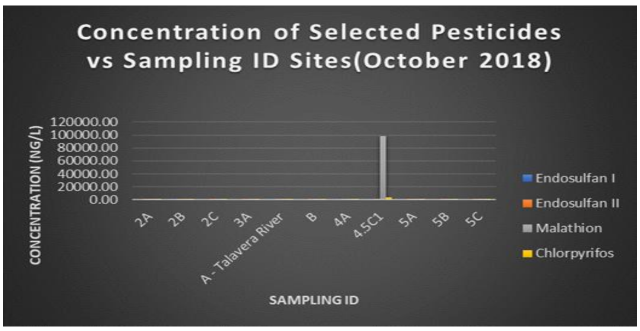


Figure 3. Mean concentrations of target analytes per sample code on the selected segment

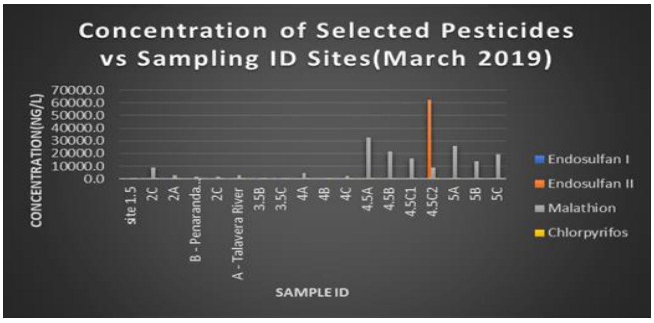


Figure 4. Mean concentrations of target analytes per sample code on the selected segment

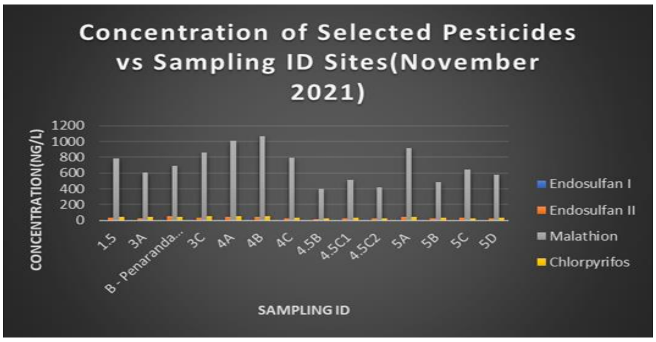


Figure 5. Mean concentrations of target analytes per sample code on the selected segment

Table 1. Summary of Results Comparing Predicted Results from the model and the actual values from lab

PESTICIDES	WASP MODEL	LAB RESULT	STANDARD ERROR
chlorpyrifos	36.5	22.4	0.64
endosulfan	27.6	22.6	0.28
malathion	507.9	415	5.07

Note: The standard error describes the variation between the calculated mean of the population and one which is considered known, or accepted as accurate.

Table 1 present the summary of WASP model and laboratory results. Concentrations in ng/L vary slightly with chlorpyrifos and endosulfan. Standard mean error of 1.994 was calculated using the three pesticides.

Based on the WASP model results, the range from the tests runs catches some concentrations results from the laboratory. Data showed the predicted concentrations at the downstream station of the three micropollutants daily with respect to time.

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

4. Conclusion/Remarks

Occurrence of significant concentration levels of pesticides has posed high risk in the aquatic organisms and other biota. 2021 data value for chlorpyrifos, endosulfan, and malathion to be 22.4 ng/L, 22.6 ng/L and 415 ng/L respectively at the downstream. These values are closed to the predicted results obtained from the WASP model with an average standard error of 1.994.

Overall, this study focuses on assessing the presence of pesticides in the Pampanga River basin and improving an existing model for predicting micro pollutant concentrations. By sampling both dry and wet seasons over a year and utilizing GC-MS analysis, the study provides valuable insights into the target pesticides' concentrations. The developed model, integrating WASP8 and the Monte Carlo Program, enables the forecast of future pesticide concentrations in the river. This research serves as a significant resource for decision-makers, facilitating informed judgments on proper pesticide handling. Additionally, it supports the development of social and industrial policies by evaluating risks and providing crucial data on pesticide presence in the Pampanga River basin.

Acknowledgements

This work was supported by the PCARI, Philippine California Advanced Research Institutes; ERDT, Engineering Research Development for Technology, and TIP, Technological Institute of the Philippines.

The authors gratefully acknowledge University of the Philippines Diliman and the Natural Science Research Institute.

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

[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

[18] E. Morillo et. Al., 2022, Science of Total Environment, Advanced technologies for the remediation of pesticide-contaminated soils //www.sciencedirect.com/