Pesticide Assessment Using Passive Samplers in Two River System of Cagayan De Oro River Basin, Philippines

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Pesticide assessment using passive samplers in two river systems of Cagayan de Oro River Basin, Philippines

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Abstract

Monitoring organic pesticides in surface water using grab water sampling method is ineffective in most cases due to pesticides' irregular emission and low solubility in water. To address the problem in water sampling method, this study used passive samplers (PS) composed of silicon rubber sheets (SR) and speedisk (SD). SR and SD were used respectively to measure hydrophobic and hydrophilic organic pesticides. These were submerged in river water uninterruptedly for 34 days. Pesticides in PS were extracted and analysed by sensitive analytical instruments HPLC, GC-MS MS and LC-MS MS. Pesticide assessment were conducted in two river systems in Cagayan de Oro River Basin, Philippines where agricultural run-off are unintentionally and continuously disposed from medium to huge plantations. The samplers were able to measure 105 emerging organic pollutants of which, 56 were organic pesticides and 22 organochlorine pesticides (OCP). Out of 56 pesticides, 11 were measured beyond the applied threshold level of 10ng/L. These were boscalid, carbendazim, dimethomorph, metalaxyl, propiconazole, pyrimethanil, diuron, monuron, simazine, dichlorvos and phenamiphos. The 22 OCP, despite being banned or restricted for almost two decades, were measured in ultra-traces of ng-pg/L. The data obtained in this study can be used to establish a baseline background level which is currently absent in most river systems in the Philippines. It is recommended that further study will be conducted using software PBPK or NORMTOX to assess health impacts and implications of the measured pesticides on the communities that are dependent, and continuously exposed to these constituents by these river waters.

Keywords:

Cagayan de Oro River Basin, GC-MS MS, LC-MS MS, passive samplers, pesticides

Water Impact

Organic pesticides from agricultural run-off in surface water is difficult to assess. Methodology used in this study, was able to measure organic and organochlorine pesticides in Cagayan de Oro River Basin, Philippines. Data can be used to evaluate health impacts and implications of the measured pesticides on the communities that are continuously exposed to these contaminants by these river waters.

**Pesticide assessment using passive samplers in two river systems of
Cagayan de Oro River Basin, Philippines**

1 Introduction

There has been an overwhelming interest to monitor chemical pollutants in water resources after the implementation the Clean Water Act in 1972. This awareness came after the publication of the Silent Spring of Rachel Carson in 1962 about the adverse effect of indiscriminating usage of pesticides. Much attention was given to the persistent organic pollutants, POPs, because of their great potential to bio-accumulate and bio-magnify in the food chain. POPs were banned by the international environmental treaty, Stockholm Convention ¹. The prohibition was agreed and signed by participating countries, including the Philippines, in the convention that took effect as of May 2004.

The main problems in monitoring POPs is their very low dissolved water concentrations in the ppb (10^{-9}) range or even lower. These low concentrations impose limitations on sensitive analytical instruments to measure potentially relevant organic pollutants in aqueous media and from irregular emission of organic pollutants which makes discrete or grab water sampling methods ineffective. Due to these limitations, POPs monitoring has been applied to sediments and tissues that excluded water samples. The tissue samples despite providing direct exposure measurements, failed to consider other chemical pollutants in the water, the organism's metabolism, bioaccumulation, avoidance and death ².

Due to these limitations mentioned, there was a need to develop an alternative sampling technique which provides an accurate estimate of POPs and other dissolved chemicals in water. Using passive samplers (PS) was an option to solve the problem ³. PS can detect and measure irregular emission of pollutants, like pesticides. Furthermore, it can detect more substances than grab method on water samples taken at the same time. It is considered cost-effective, practical, more reliable, suitable for routine monitoring and can even detect low concentrations of organic compounds in the nano to picogram per liter (ng/L-pg/L) range which is difficult to attain in grab sampling method ⁴.

This study aims to analyse pesticides unintentionally disposed and transported through surface runoff from farms in the upstream to receiving waters to assist in the establishment of baseline data. The pesticide assessment using the PS will be done in two river systems in Cagayan de Oro River Basin that headwaters to Mt. Kitanglad Mountain Range and head tails towards Cagayan de Oro River downstream.

For the review of literature in the advancement of passive sampling methods, the first passive sampling devices developed were air PS in the early 70s ³. Air PS was used to determine occupational exposure to volatile organic chemicals (VOC) in air. The extent of exposure was

measured through diffusion of the VOC into the air samplers that enables the estimation of time-weighted average concentrations⁵. Two decades after its introduction, there has been a growing interest to use PS of quantifying ambient air pollutant concentrations, mostly in remote and wilderness areas⁶⁻⁸.

Various type of PS for air monitoring have been developed depending on their purpose. For example, an air sampler made of glass fiber filter infused with 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid fixed into an aerosol-sampling cassette was used to monitor formaldehyde in air with sensitivity of 5 ppb for 15 minutes to eight hours sampling time⁹. Another air PS developed is the semipermeable membrane device (SPMD) filled with triolein that measured PCB and HCH in picogram per cubic meter (pg/m^3)⁷. Another air PS, Ogawa was developed with filter-discs impregnated with citric acid as a useful tool for monitoring atmospheric ammonia, NH_3 , in poultry houses⁸. These air PS were validated, calibrated and continuously modified to be able to come up with an accurate and efficient sampling technique in monitoring pollutants in air¹⁰⁻¹².

The first patented passive sampling method in water was made by Byrne and Aylott in the 80s that used a nonpolar solvent in nonporous membrane¹³. The concept of PS was introduced by Soedergren using dialysis membranes filled with hexane solvent to stimulate the bioaccumulation of persistent lipophilic pollutants, like DDT, DDE or PCB from water¹⁴. To optimize Soedergren's concept, samples were tested in combinations of solvents and nonporous membranes for monitoring of organic pollutants. Which led to the development of neutral lipid triolein enclosed in a low-density polyethylene, LDPE tube. This device filled with lipid is referred to as a semipermeable membrane device, SPMD¹⁵.

SPMD was proven to be effective in measuring traces of POPs in ppt (10^{-12}) in water. The estimated time-weighted average concentration of pollutants depends on the sampling rates and was determined in the laboratory under specific conditions¹⁶. To validate the effects of water temperature, turbulence and build-up of biofilm on membranes, SPMD were spiked with exposure standards which were not found in such environment, before deployment. The release rates of these standards were used as independent component for the kinetic exchange of SPMD and water¹⁷.

Results showed that standards added before deployment can predict the effect of environmental conditions on the uptake kinetics of hydrophobic organic compounds. The rate-limiting step in the diffusion process was the water boundary layer and not the membrane. The rate of diffusion through the SPMD is an isotropic process¹⁷. This findings laid to the foundation for the development of the performance reference compound approach, which is critical in improving the accuracy of time-weighted average concentration estimates from passive samplers¹⁸.

Since SPMD has been introduced, numerous sampling devices for nonpolar organic contaminants have been developed. Some of these are the LDPE strips, silicon strip, polymers on glass, and solid-phase micro extraction (SPME) devices. All these developed samplers have a specific niche and were proven useful in environmental monitoring¹⁹.

In the later part of the 90s, a passive sampler was developed to complement SPMD. This led to the development of the polar organic integrated sampler, POCIS. It contains triphasic admixture solid-phase adsorbents placed in between sheets of microporous polyethersulfone membrane. It was tested in hydrophilic compounds like atrazine, diazinon and 17- α -ethynylestradiol which were not readily measured in the other devices²⁰. The triphasic admixture was later replaced with the universal sorbent, Oasis® HLB (Waters Corp), which was necessary to estimate in the time-weighted average concentrations²¹.

After the development of POCIS, there was a paradigm shift that showed the potential to assess various pharmaceutical, hormones and other organic contaminants²². Various PS are used depending on target contaminants, like POCIS (pharma or pesticide version), Empore Disk, Chemcatcher, Membrane enclosed silicon collector, Polyoxymethylene sheet, and many more²³.

Passive sampler use in this study are developed for more than a decade by Deltares, a research institute in the Netherlands²⁴, that took into consideration the limitations and concerns of other PS previously tested. These PS consist of silicon rubber (SR) and speedisk sampler (SD) for nonpolar and polar organic compounds, respectively. These set of samplers are expected to give good estimates of ultra-trace organic pollutants in water at very concentrations of nanogram per liter (ng/L) to even picogram per liter (pg/L). SD is made of hard propylene cage. It has an adsorption material and a filter made of glass fibre to retain the sorption material in the sampler.

SR spiked with PAH and PCB compounds, was calibrated by using sheets of different surface area in two hydrodynamic conditions. Smaller surface area sheets were used to measure the uptake rate. In both hydrodynamic conditions, sampling rates R_s is inversely proportional to SR water partition coefficient, K_{pw} , with the equation $R_s \approx K_{pw}^{-0.08}$. Under experimental conditions, modelling validates that the uptake of test compounds was controlled by the diffusion in water phase. The dissipation of PRC to target hydrophobic compounds, model using $R_s \approx M^{-0.47}$ was suggested to estimate R_s by extrapolation²⁵.

The measurement of concentrations of dissolved organic contaminants depend on the knowledge of in-situ sampling rates. Nonlinear least-squares (NLS) methods were used to estimate the sampling rates that take into account the information stored in PRC data which was not considered in the traditional methods. Errors of the traditional methods and the weighted and unweighted NLS were examined. Results showed that sampling rates are best estimated with

unweighted NLS because of the availability of sampling rates estimates and uncertainties which the traditional method fails. Unweighted NLS also has smaller variability of sampling rate ²⁶.

The most important measurement is using PS in the sampler-water partition coefficients K_{pw} , which are determined in the laboratory under standard conditions of 20°C for freshwater. K_{pw} theoretically are dependent on environmental conditions like salinity and temperature. This Dutch SR was used to quantify the effects of these two factors. The location-specific SR-water partition coefficient, K_{sr-w} , adjusted for temperature and salinity can be calculated based on the Dutch passive sampling field monitoring database gathered for 10 years using PAH and PCB data established on various locations ²⁷.

In this paper, the study site is in the Philippines, where agricultural expansion and intensification are practiced for the last two decades. Agribusiness is an economic shift mandated by laws and policies that emphasis on high quality cash crop production ²⁸. Despite all these natural calamities of at least 20 typhoons annually that destroy crops, the country is currently the world leading producers in abaca (~87% of the world's market) and second, third and fourth respectively, in coconut, pineapple and banana. To produce these high quality cash crop for international market, it needs pesticides.

In agriculture, pesticides were developed and used for undeniable practical purposes. These are used to preserve crops and control infestations in order to have continuous production to cater the needs of the clients. But if pesticide application is mismanaged or overused it has the potential to cause harm to human and the environment. Worse, applied pesticides in farms are potential run-off in surface water of communities wherein pesticides were not even applied.

In Davao, Philippines, due to lack of awareness of banana planters on the adverse effect of pesticides and the lack of safety and protection, pesticides, dibromochloropropane, DBCP, was proven to cause sterility to about three thousand banana plantation workers ²⁹. In Northern Mindanao, Philippines, palm oil plantation owner was sued for not providing protective equipment to workers and the contamination of the water system experience by the communities near the plantations of pesticides furadan, glyphosate and paraquat ³⁰.

In order to avoid future pesticide-related dispute, baseline data on residual pesticides in some rivers along farms doing intensive agriculture is necessary. Northern Mindanao, is one of the regions where agricultural expansion and intensification are currently implemented. In some major rivers in the region, various funded researches on pesticide assessment were conducted for years using grab water sampling method ^{31, 32}. But data gathered could not be considered as baseline information because of fluctuating results. To solve the problem of assessing irregular emission and low concentrations of residual pesticide in water, PS will be used instead of the traditional

grab water sampling method. Pesticides assessment using passive samplers will also be conducted in Can Tho River, Vietnam, Mekong Delta³³.

2 Materials and methods

2.1 Location

The research was conducted in Northern Mindanao, Philippines, where the major source of economy is agriculture. One of the major water resource is Mt. Kitanglad Mountain Range which is approximately 3,000 meter above sea level. The area of research was limited only to the two river systems, (1) Bubunawan River in Libona and (2) Cagayan de Oro River in Maasin with head-tail from Mt. Kitanglad watershed. These rivers transverse towards Cagayan de Oro River in Cagayan de Oro City in the downstream.

The three sampling sites were in Lapinigan Creek, Bubunawan River Junction designated as S1; Maasin, Cagayan de Oro River midstream designated as S2 and Taguanaw-Lumbia Diversion; Cagayan de Oro River downstream designated as S3. Detailed location of the sampling sites are shown in Figure 1. S1 and S2 are along agricultural areas (mostly annual crops), while S3 is located along wooden grassland and near the residential areas.

Figure 1 Sampling sites for the pesticide assessment. These were conducted in the following rivers: S1 Bubunawan River, Libona; S2 Cagayan de Oro River (midstream), Maasin and S3 Cagayan de Oro River (downstream), Taguanaw.

2.2 Preparation and deployment of passive samplers

Before water sampling, SR were pre-cleaned for 100 hours using ethylacetate solvent in a soxhlet apparatus. The ethylacetate was removed by soaking the SR in methanol twice for eight (8) hours of approximately 4mL of methanol per sheet. The SRs were then spiked with PRC. SD as an adsorption sampler was not pre-spiked with PRC. Samplers SR and SD were stored in glass containers until the actual sampling.

In the deployment, PS were composed of six (6) sheets of SR and three (3) pieces of SD. These were attached firmly in an iron post and submerged below the water surface at approximately 1.5 to 2.0 meters below the surface for uninterrupted 34 days. After sampling, the PS were dismantled. These are shown in Figure 2. The set of PS were kept in its original glass containers and stored at -20⁰ C before actual analyses.

Figure 2 Passive samplers' installation, monitoring and dismantling.

Passive samplers were installed in three sampling sites (a). The sites were in Bubunawan River, Libona (a1), Cagayan de Oro River, Maasin (a2) and Cagayan de Oro River, Taguanaw (a3). For the installation (b), the samplers (b1) were composed of 6 silicon rubbers (SR) and 3 speedisks (SD) arranged in an iron stand and submerged in river water (b2). After 34 days, the iron stand with the samplers were removed for pesticide analyses (c).

The deployment of PS started approximately two months after the raining season starts and completed almost at the end of the raining season.

2.3 Extraction and Analysis

The preparations, extraction and chemical analysis were performed in the laboratory of the Department of Environmental Modelling, Sensing and Analysis (EMSA) of TNO in Utrecht, the Netherlands. Both samplers, SR and SD, were extracted by acetonitrile by dialysis, and successively, after mild evaporation, transferred into hexane for GC-MS MS analysis or re-dissolved in a defined volume of acetonitrile. Hydrophobic organic compounds and pre-spiked PRC on SR were analysed by GC-MS MS. Hydrophilic compounds were analysed by LC-MS MS.

The release model of Rusina (25) on the pre-spiked PRC on SR before deployment was used to calculate the freely dissolved concentrations in water and estimate the sampled volume. The freely dissolved concentrations and respective sampled volumes were calculated by integrating the freely dissolved concentrations of fluoranthene and pyrene from SR with the measured concentration in SD. These two compounds exhibits comparable behaviour in both samplers.

2.4 Calculation

The calculation for the aqueous concentrations of analytes used the formulas developed by Smedes and Booij (4). The water sampling rates were necessary and were calculated by the retained PRC fractions, which were ratios of the amount of PRC at the beginning and end of exposure. The PRC data were pre-screened before calculating the sampling rates. The detection limits from the extract may depend on the amount of other compounds present. PRC were carefully scrutinised for possible interferences. It can only be processed further if PRC peak showed no interferences.

The PRC fractions (f) can be calculated by the equation:

$$f = \frac{N_t}{N_0} = \text{exponent} \left(-\frac{R_s t}{K_{pw} m} \right) \quad (1)$$

Where N_t and N_0 were respectively the dosed amount in the reference SR and the amount after exposure; R_s is the equivalent water sampling rate (1/d), t was the exposure time (d), m was the mass of the SR (kg) and K_{pw} (1/kg) was SR-water partition coefficient. The K_{pw} can be obtained from Smedes (34). The degree of R_s can be controlled by the passage of the water boundary layer as proven by Rusina (25) that R_s decreases with increasing molar mass (M).

$$R_s = \frac{B}{M^{0.47}} \quad (2)$$

250 where B was a proportionality constant that was proportional to the sampler's surface area.

251 Thus equation 1 becomes:

$$f = \text{exponent} \left(-\frac{B t}{K_{pw} M^{0.47} m} \right) \quad (3)$$

252 The absorbed organic compounds were calculated by the following equations given by Booi
253 (35):

$$N_t = K_{pw} m C_w \left(1 - \text{exponent} \left(-\frac{R_s t}{K_{pw} m} \right) \right) \quad (4)$$

$$C_w = \frac{N_t}{K_{pw} m \left(1 - \text{exponent} \left(-\frac{R_s t}{K_{pw} m} \right) \right)} \quad (5)$$

254 Then to use the proportionality constant B, C_w can be calculated by combining equations 2 and 5
255 to have a general equation 6 that incorporates the linear uptake, transition and equilibrium stages.

$$C_w = \frac{N_t}{K_{pw} m \left(1 - \text{exponent} \left(-\frac{B t}{K_{pw} M^{0.47} m} \right) \right)} \quad (6)$$

256 The K_{pw} values were necessary to PRCs and target organic compounds that approach
257 equilibrium. K_{pw} values can be obtained from Smedes (34).

258 **3 Results and discussion**

259 The study sites, Bubunawan and Cagayan de Oro Rivers are classified under Class A by the
260 Department of Environment of Natural Resources. Class A means a Public Water Supply Class
261 II, which is intended as sources of water supply requiring conventional treatments, like
262 coagulation, sedimentation, filtration and disinfection, to meet the Philippines National Standards
263 for Drinking Water of 2017 ³⁶. These PNSDW standards were obtained using grab water sampling
264 method with various standardised analytical instruments. This study used different methodology,
265 passive samplers (SR and SD), and analytical instruments GC-MS MS and LC-MS MS. Thus,
266 instead of the set PNSDW standards, this study applied the 10 ng/L threshold level.

267 SR samplers spiked with PRC were capable of detecting 163 organic compounds, were able to
268 measure 105 emerging organic pollutants in this study. These were composed of 56 organic
269 pesticides, 7 polychlorinated biphenyls (PCB), 16 polycyclic aromatic hydrocarbons (PAH), 22
270 OCP and 4 antibiotics/pharmaceuticals. This paper is only limited to the 11 prevalent organic and
271 organochlorine pesticides measured. For the complete list of emerging pollutants measured,
272 please refer to the paper of Salingay (37).

3.1 Prevalent Organic Pesticides

Of the 56 pesticides measured, 11 were beyond the applied threshold level of 10 ng/L as shown in Table 1. The chemical structure of these prevalent pesticides are shown in Figure 3. These organic pesticides are composed of one or more ring/s that is polysubstituted, except dichlorvos. These are further categorise into its mode of action, as fungicides, herbicides, and insecticides.

Table 1 Concentration of prevalent pesticides measured in ng/L per sampling site.

Pesticides	S 1		S 2		S 3	
	SR	SD	SR	SD	SR	SD
Fungicides						
Boscalid	45	5	6	<1	13	5
Carbendazim	11	>0.1	5	nd	nd	>0.1
Dimethomorph E&Z	24	>0.1	>1	nd	4	nd
Metalaxyl	10	nd	20	>1	17	>1
Propiconazole	12	>1	3	nd	4	>1
Pyrimethanil	203	<1	>1	nd	23	>1
Herbicides						
Diuron	368	13	81	2	101	5
Monuron	15	>1	nd	nd	nd	nd
Simazine	158	nd	121	nd	125	nd
Insecticides						
Dichlorvos	11	nd	nd	nd	nd	nd
Phenamiphos	40	2	6	<0.1	13	<1

nd = not detected

Source: National Center for Biotechnology Informations, PubChem Database.

Figure 3 Structures of pesticides measured above the applied threshold level of 10ng/L.

3.1.1 Fungicides

To eradicate or prevent the growth of fungi and its spores that damage plants, fungicides are used. These fungal diseases in plants can easily be spread and contaminate other plants when moist. Before applying fungicides, identification of these fungal diseases are important. In some cases, fungicides were created to prevent plant diseases and become ineffective if symptoms already developed ³⁸. Fungicides measure were boscalid, carbendazim, dimethomorph, metalaxyl, propiconazole and pyrimethanil.

Boscalid is a fungicide used against *Alternaria spp.*, *Botrytis spp.* and *Schlerotinia spp.* that acts as enzyme succinate dehydrogenase inhibitor. Boscalid has solubility in water (H_2O_{sol}) of 4.6 mg/L at 20°C, has a half-life (DT_{50}) in soil of 104-224 days, non-volatile in water surfaces and dry soil ³⁹. Boscalid was measured in all sampling sites and both samplers (SR and SD). Higher concentrations were measured in SR, which means hydrophobic. This can also be seen in its chemical structure in Figure 3, which shows three rings and polysubstituted.

Boscalid was measured in decreasing concentration of: S1 (50 ng/L) > S3 (18ng/L) > S2 (7 ng/L). Considering H_2O_{sol} and DT_{50} in soil, the measured concentrations were most probably from soil absorption. Pesticides are usually applied during the dry season. During the wet season, constant raining in high lands enhanced soil erosion to loosely-held-soil crops.

Carbendazim is used to control diseases that include *Fusarium* and *Septoria*. At below 50°C, it can be stable for 2 years or more and in acidic medium it will form water-soluble salts. As shown in its chemical structure, it is a benzimidazole, with methoxycarbonyl group attached to it. It was measured in all sampling sites with concentrations in decreasing order of: S1 (11 ng/L) > S2 (5 ng/L) > S3 (0.2 ng/L). It was measured higher in SR, except in S3 where it was only detected in SD. It is necessary to monitor carbendazim as when combined with sodium nitrite it is carcinogenic ⁴⁰. Carbendazim is classified by USEPA (41) as “possible human carcinogen,” and banned for food uses in the US. It is also not approved for use in the EU ⁴².

Dimethomorph is mixture of E and Z isomers in an unspecified ratio, where only the Z isomer has fungicidal activity. It was measured in SR, except in S1, in a decreasing order of S1 (24 ng/L) > S3 (4 ng/L) > S2 (>1 ng/L). S3 value was greatly influenced by the agricultural runoff from S1 than by S2. In case of photolysis, it would happened more in S3. As S1 and S2 are located in a much higher elevation and sunlight is limited only to 5-7 hours in a day or even less during the rainy season. Dimethomorph has limited information on its breakdown in surface water. Dimethomorph has three rings and polysubstituted in its structure, It is non-volatile in water, low soil mobility and leaching potential ⁴³.

Metalaxyl has moderate to high mobility in soil and undergoes fast aerobic degradation in soil. It showed higher concentration in S2 with the decreasing order of S2 (21 ng/L) > S1 (18 ng/L) > S3

(10 ng/L). This shows that farms along and above S2 used metalaxyl more than farms in S1. Metalaxyl in water, will not readily be adsorbed by sediments or suspended solids. Under environmental conditions, it resists chemical hydrolysis. This can be seen in the complexity of its chemical structure as shown in Figure 3. It has DT_{50} of approximately 40 days, H_2O_{sol} of 8.4×10^3 mg/L at $22^\circ C$ and degrades in the presence of humic acid with more than 60 hours of irradiation⁴⁴. Knowing its rate of degradation, most of metalaxyl in farms above S1 and S2 degraded before it was measured.

Propiconazole was measured in all sampling sites and both samplers, except in S2. The concentration in decreasing order is S1 (12ng/L) > S3 (4ng/L) > S2 (3ng/L). Propiconazole has H_2O_{sol} of 100 mg/L at $25^\circ C$. Propiconazole has been proven to be stable in water and soil environments as it does not readily reacts with water and air. The stability can be readily seen in its chemical structure in Figure 3. It got three rings and polysubstituted. It undergoes degradation of 40-70 days in aerobic soil, 25-85 days in water and 60-96 days in typical soils⁴⁵. If applied on the dry season, the degradation process of propiconazole coincides, more or less, with the sampling period of this study.

Pyrimethanil was measured in all sampling sites and both samplers, except in S2. The highest concentration was obtained in S1 (204 ng/L) and a very low concentration in the other river system S2 (>1 ng/L). The concentration of S3 (24 ng/L) is obviously, mostly contributed by S1. Pyrimethanil as shown in Figure 3, is an aminopyrimidine. An aryl hydrocarbon receptor agonist with H_2O_{sol} of 121 mg/L at $25^\circ C$. Pyrimethanil degrades with a DT_{50} of 27-82 days in soil experiments but degrades faster in field experiments of DT_{50} 7-54 days⁴⁶. Considering the DT_{50} of pyrimethanil, the concentrations measured by samplers were just a small fraction of the original amount.

3.1.2 Herbicides

Herbicides are used to eliminate unwanted weeds. Its mode of action can be selective or non-selective. To safeguard the desired agricultural crops unaffected and only eliminate unwanted plants, selective herbicide should be used. After harvest when clearing lands is necessary, non-selective herbicide will be used as it kills almost any plant type. Herbicides can either act immediately or may take longer, like a week or more. Some even persist for a certain period of time in plants, soil, water or other organisms⁴⁷. Herbicides measured were diuron, monuron, and simazine.

Diuron was measured in both samplers in all sampling sites. The concentrations obtained in decreasing order is; S1 (381ng/L) > S3 (106 ng/L) > S2 (83 ng/L). Higher concentrations in SR would mean hydrophobic, which is also shown in Figure 3 as a polysubstituted one ring compound. Diuron and its derivatives has DT_{50} of 1-12 months and 1-5 months, respectively. It

has H_2O_{sol} of 42 mg/L at 25°C, But in pineapple farms, diuron residues stay three years after the application⁴⁸. Considering the DT_{50} of diuron, the concentrations measured could be the sum of the recently applied or from the previous year/s.

Monuron was only measured in S1 and in both samplers with an obtained concentration of 15 ng/L. The no detection (nd) in S2 does not mean that farms along and above S2 were not using monuron. DT_{50} in soil ranges from less than 30 to 166 days, in surface water with natural sunlight is approximately 15 days and accelerated by surfactants⁴⁹. Considering DT_{50} of monuron, the concentration of monuron must be too small to be detected or probable diluted by the volume of water in the various river systems above S2. This holds true in S3 as well.

Simazine was measured only in SR. Which means hydrophobic as readily seen its structure in Figure 3, which is a polysubstituted triazine. The concentration obtained in decreasing order is; S1 (158 ng/L) > S3 (125 ng/L) > S2 (121 ng/L). It does not readily absorb by soil but has the ability to leach and mostly likely to contaminate groundwater. DT_{50} on sandy loam soil is 36-234 days, 16-25 weeks on loamy sand and 75 days in other soil type. Residual simazine stays for 60-210 days after application since it absorbs to clays and wastes⁵⁰. Simazine measured must be applied on the fields in the last two months or more due to the DT_{50} in clayish soil, the sampling time, H_2O_{sol} of 6.2 mg/L at 20°C.

3.1.3 Insecticides

In farms, to eliminate or control one or more insect species, insecticides are used. Insecticides mode of action can either be systemic, contact or ingested. Systemic insecticide can be applied through soil drenching, contact is used in aiming at target insects and ingested is when insecticide is placed on locations where insects can ingest it. Insecticides acts on the nervous system that disrupt the exoskeletons. But this mode of action can also pose risk to other non-target organisms, including humans⁵¹. Insecticides measured were dichlorvos, and phenamiphos.

Dichlorvos it was only measured in SR of S1 of concentration 11 ng/L. The values obtained can be explained by the H_2O_{sol} of 8.00×10^3 mg/L at 20°C and the rapid DT_{50} in soil of 7 days in both extreme pH. Dichlorvos has the ability to leach into the ground within 5 days to a depth of 30 cm. The rate of breakdown is fast in alkaline environment of DT_{50} 4.5 hours at pH 9.1 as compared to acidic environment of DT_{50} of 50 hours at pH 1.0⁵². As shown in its structure in Figure 3, it is an aliphatic organophosphate compound. Unlike the other pesticides, it has no ring and highly volatile. Most of the dichlorvos applied on the field biodegraded or hydrolysed before it reach the sampling sites.

Phenamiphos was measured in all sampling sites and in both samplers. Concentration in decreasing order is; S1 (42 ng/L) > S3 (14 ng/L) > S2 (6 ng/L). It has H_2O_{sol} of 329 mg/L at 20°C and a DT_{50} range of 4-11 days in four types of soils. If repeated application of phenamiphos were

done, the degradation increases by 10 to 20 times higher compared to untreated soil⁵³. Based on short DT₅₀ ranges, phenamiphos measured must be from the repeated application.

In the Philippines, phenamiphos is a restricted pesticide since 1989, but can be used for banana and pineapple plantations⁵⁴. It is restricted because some studies showed it is an acetylcholinesterase inhibitor but it is classified by USEPA as not carcinogenic for humans^{41, 53}.

In this study, the general trend of concentrations per sampling site of the 11 prevalent pesticides is in decreasing order of S1>S3>S2, except in metalaxyl, where S2 had higher concentrations. The eleven prevalent pesticides were all measured in S1, while monuron and dichlorvos were not detected in S2 and S3. It is also important to highlight the high values of pesticides boscalid, dimethomorph E & Z, diuron, pyrimethanil, phenamiphos and simazine in S1. Pesticides diuron and simazine were measured high in SR samplers in all three sampling sites.

Residual organic pesticides measured in S1 and S2 are expected as these areas are surrounded with agricultural farms or plantations. The whole river basin has eight sub watersheds and covers the local government units of Baungon, Cagayan de Oro, Libona, and Talakag. With a land area for annual and perennial crops of almost 6,000 and 3,030 square km, respectively.

There are important notes that should be considered in the 11 prevalent pesticides measured. Pyrimethanil was classified as possible human carcinogen⁴⁶; diuron is known/likely to be human carcinogen⁵⁵; carbendazim is banned in the US and EU, monuron is no longer registered in the US but manufactured for export⁴⁹; simazine classified in 1989 as carcinogen but reclassified as not genotoxic in 2005⁵⁶; dichlorvos was proposed by EPA in 1995 to cancel its usage but now classified by USEPA as probable human carcinogen⁵⁷ and lastly, phenamiphos was declared restricted in the Philippines.

3.2 Persistent Organic Pollutants POPs

Organochlorine pesticides, OCP, are compounds classified under POPs. OCP were either banned or restricted for almost two decades in the Philippines⁵⁴ in compliance with the Stockholm Convention agreement. OCP measured in this study in nano-traces are shown in Table 2. Looking closely on some of OCP chemical structures of some OCP shown in Figure 4, these are polychlorinated alicyclic or cyclodienes. OCP measured were aldrin, dieldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), endosulfan, hexachlorocyclohexane (HCH), heptachlor, heptachlor epoxide, hexachlorobenzene, hexachloro-1,3-butadiene and pentachlorobenzene.

Aldrin, in the presence of sunlight and bacteria will be converted to dieldrin. The H₂O_{sol} of aldrin and dieldrin at 25°C are respectively 2.7x10⁻² mg/L and 1.95x10⁻¹ mg/L⁵⁸. So often, these two compounds are treated as one. Aldrin was measured in decreasing order of S3 (<0.01 ng/L) > S1 and S2 (>0.01 ng/L). Dieldrin on the other hand has the decreasing order of S1 (<0.1 ng/L) > S3

(<0.01 ng/L) >S2 (nd). In both cases, sources of residual aldrin and dieldrin were high in S1 than in S2. Both compounds were measured only in SR samplers. Aldrin and dieldrin were banned in the Philippines since 1989 because of its adverse effect to human. Dieldrin has DT₅₀ of approximately five (5) years. But in tropical conditions, oxidation is faster as well as the disappearance of dieldrin through evaporation occurs within 30 days⁵⁹.

Table 2 Concentration of organochlorine measured in ng/L per sampling site.

Organochlorine Pesticides	S 1		S 2		S 3	
	SR	SD	SR	SD	SR	SD
Aldrin	>0.01	nd	>0.01	nd	<0.01	nd
Dieldrin	<0.1	nd	n.d.	nd	<0.01	nd
Chlordane-cis (α)	<0.01	nd	> 0.01	nd	>0.01	nd
Chlordane-trans (γ)	<0.01	nd	n.d.	nd	>0.01	nd
DDD-o,p'	>0.001	nd	>0.001	nd	>0.001	nd
DDD-p,p'	<0.001	nd	<0.001	nd	<0.001	nd
DDE-o,p'	<0.0001	nd	<0.0001	nd	<0.0001	nd
DDE-p,p'	>0.01	<0.001	<0.001	nd	<0.001	nd
DDT-o,p'	<0.0001	nd	<0.0001	<0.001	<0.0001	nd
DDT-p,p'	<0.001	<0.01	<0.001	<0.01	>0.001	<0.01
Endosulfan-α	<0.01	nd	<0.01	nd	<0.01	nd
Endosulfan-β	<0.1	nd	>0.1	nd	< 0.1	nd
Endosulfan sulphate	>1	nd	>1	nd	>1	nd
HCH-α	>0.01	nd	>0.01	nd	<0.001	nd
HCH-β	nd	<0.001	>0.1	nd	n.d.	nd
HCH-δ	n.d.	nd	>0.001	<0.001	<0.001	nd
HCH-γ (lindane)	<0.01	nd	>0.01	nd	>0.01	nd
Heptachlor	<0.001	nd	n.d.	nd	<0.0001	nd
Heptachlor exo-epoxide	<0.1	<0.01	<0.001	nd	<0.01	nd
Hexachlorobenzene	<0.001	nd	<0.001	nd	<0.001	nd
Hexachloro-1,3-butadiene	<0.0001	nd	0.0001	nd	<0.0001	>0.01
Pentachlorobenzene	>0.001	nd	>0.001	nd	>0.001	nd

nd = not detected

Source: National Center for Biotechnology Information, PubChem Database.

Figure 4 Structures of some organochlorine pesticides measured in traces of pg-ng/L

Chlordane has H_2O_{sol} of 5.6×10^{-2} mg/L at $25^{\circ}C$ and approximately half of it evaporates within 2-3 days. DT_{50} in soil of 350 days but can stay until 3500 days and if absorbed by organisms, is stored in the body fats⁶⁰. Chlordane were measured only in SD with decreasing order of S1 (<0.01 ng/L) $>$ S3 (0.01 ng/L) $>$ S2 (>0.01 ng/L). Chlordane was banned by the government in 1999⁵⁴. Even after two decades, traces were still measured. It showed its persistence to stay in the environment.

DDT and metabolites DDE and DDE can exist in two forms, -p,p' or -o,p'. DDT has H_2O_{sol} of 5.5×10^3 mg/L at $25^{\circ}C$ ^{61, 62}. DDT-p,p' was measured in all samplers while DDT-o,p' was detected in all SR and only in the SD of S2. Higher values were obtained at SD samplers for DDT-p,p' of <0.01 ng/L. Aside from DDT, metabolites DDE-o,p', DDE-p,p', DDD-o,p', and DDD-p,p' were also measured. DDE and DDD in both forms were measured in SR, except DDE-p,p' in S1. The concentrations of DDT and metabolites DDD and DDE were higher in the -p,p' forms. DDT was banned in the Philippines in 2005⁵⁴. But pico to nano traces of DDT and its metabolites in both -o,p' and -p,p' forms were still measured.

Endosulfan - α and - β have DT_{50} of 60 and 800 days, respectively. While the oxidised form endosulfan sulfate has lower DT_{50} of approximately 40 days. Endosulfan can also hydrolysed at varying rates depending on the pH of the environment and much faster with the presence of ferric hydroxide⁶³⁻⁶⁵. Endosulfan stereoisomers, - α , - β and the oxidized form endosulfan sulphate were measured only in SR samplers in all sampling sites. The concentrations of endosulfan - α , - β and endosulfan sulphate summed up per sampling sites were all > 1.1 ng/L. The approximate values is in the decreasing order of: S1 $>$ S3 $>$ S2. The oxidized form, endosulfan sulphate have higher concentrations in all sites. Endosulfan was a restricted pesticide for pineapple plantations in the Philippines until eventually banned in 2015 by the government⁵⁴.

Hexachlorocyclohexane (HCH) has eight isomers of which only four have commercial significance. These four isomers HCH- α , HCH- β , HCH- δ and HCH- γ (lindane) has H_2O_{sol} at $25^{\circ}C$ of 2.0 mg/L, 2.4×10^{-1} mg/L, 31.4 mg/L and 7.3 mg/L, respectively. The DT_{50} of HCH- α and HCH- β is 7-8 years, while HCH- γ has only 65 hours⁶⁶. These four isomers HCH- α , HCH- β , HCH- δ and HCH- γ (lindane) were measured either in SR or SD or both. The concentrations of HCH (sum) per sampling sites is in decreasing order of: S2 (>0.1 ng/L) $>$ S1 (<0.01 ng/L) $>$ S3 (>0.01 ng/L). HCH was banned in the Philippines in 1989, except HCH- γ (lindane). HCH- γ is restricted for soil pre-plant application on pineapple plantations⁵⁴. The two river systems transverse along pineapple plantations, measuring HCH- γ was expected.

Heptachlor oxidized by plants and animals forms heptachlor epoxide. Heptachlor has a DT_{50} of six months to 3.5 years. But trace levels were detected even 14-16 years after application⁶⁷. Heptachlor and heptachlor epoxide (sum) concentrations in decreasing order is: S1 (<0.1 ng/L) $>$ S3 (<0.01 ng/L) $>$ S2 (<0.001 ng/L). Heptachlor epoxide was detected in S2 but not heptachlor.

Heptachlor and heptachlor epoxide were measured in SR samplers, except heptachlor in S2 and heptachlor epoxide was measured in SD in S1. Heptachlor was banned by the government in 1989⁵⁴. Few years ahead of the worldwide prohibition.

Hexachlorobenzene was used as fungicide with H_2O_{sol} of 4.7×10^{-3} mg/L at 25°C. It is very stable even if exposed to acidic and basic conditions. Trace concentrations of hexachlorobenzene is necessary to be monitored as chronic exposure will result to liver disease associated with skin lesions and human carcinogen associated with thyroid, kidney and liver cancer⁶⁸. It was measured in SR of all sites of concentration of $<1.0 \times 10^{-3}$ ng/L.

Hexachloro-1,3-butadiene was commonly used as solvent in making lubricants. H_2O_{sol} is 3.20 mg/L at 25°C. DT_{50} is approximately 117 days⁶⁹. The concentrations of hexachloro-1,3-butadiene in SR in all sampling sites were approximately 1.0×10^{-4} ng/L and 1.0×10^{-2} ng/L in SD in S3. Considering the DT_{50} of hexachloro-1,3-butadiene and being banned for more than a decade, measuring in trace amounts show its persistence to stay in the environment. More importantly, this compound is considered potentially occupational carcinogenic⁷⁰.

Pentachlorobenzene was used as fungicide and flame retardant. Incompatible with strong reducing and oxidizing agents and relatively unreactive with H_2O_{sol} of 8.3×10^{-1} mg/L at 25°C and DT_{50} of 74 days. In animal studies, it show that long term exposure have effects on liver and possible effect to human reproduction or development⁷¹. It was measured in SR of all sites of $>1.0 \times 10^{-3}$ ng/L. It is necessary to monitor pentachlorobenzene due to its chronic effect to human liver and reproduction after years of constant exposure to it.

In this study, the general trend of concentrations per sampling site of OCP is in decreasing order of $S1 > S3 > S2$, except HCH, where S2 had higher trace concentrations. OCP were measured in one organic form or another and measured in either SR or SD or both samplers, with some exceptions. HCH- δ was not detected in S1, dieldrin, chlordane- γ and heptachlor were not detected in S2 and HCH- β was not detected in S3. Nano-pico traces of OCP that were banned or restricted for almost two decades shows its persistence to stay in the environment for years or probably some farmers were still using it after the government prohibition.

Generally, the concentrations of prevalent organic pesticides in ng/L and traces of banned OCP in ng-pg/L are within the controllable level of river water contaminations. The results showed a good soil absorption capacity of the region. Aside from pesticides, the farmers apply also fertilizers to condition the soil to yield quality crops. It should be considered that this region, where the study was conducted is mostly run by large and medium size land owners, where good agricultural practices are in place, necessary to produce crops for international market³⁷.

4 Conclusion and recommendation

The passive samplers, SR and SD, developed by Deltares and analysed with highly sensitive analytical instruments, GC-MS MS and LC-MS MS, were able to measure 56 organic pesticide contaminants in ng/L (10^{-9} g/L) and traces of 22 banned OCP in ng/L to pg/L (10^{-9} g/L to 10^{-12} g/L). The methodology used in this study showed the effectiveness in measuring irregular and very low concentrations of pollutants in river water.

Results show that agricultural expansion and intensification of the farms above and along the two river systems produced agricultural runoff contaminated with multiple residual pesticides. Although within a controllable level, it is still necessary to have regular pesticide monitoring and evaluation. As these residual pesticides were also measured on Cagayan de Oro River (downstream), where these pesticides were not even applied.

Since the country experiences pesticide-related disputes with farm owners and workers in the past and recent past, baseline data is necessary to avoid conflict in the future. The data obtained in this study can be used as basis to establish baseline data by concerned government agencies for the amendments or implementation of existing environmental laws.

It is recommended that in environmental monitoring of pesticides, PS should be used instead of the traditional grab sampling method and analyzed with sensitive analytical instruments of low detection limits like GC-MS MS and LC-MS MS. Monitoring the concentrations of residual pesticides is necessary not only to assess the acute and chronic effects to farmers and communities within the vicinities of the farms but also the chronic effect on the communities along the river systems that have been constantly exposed to small quantities for years.

It is further recommended to conduct further study on the health impact assessment and implications of the measured pesticides on the communities that are dependent and continuously exposed by these constituents by these river waters using software like Physiologically Based Pharmacokinetic (PBPK) or NORMTOX.

Declaration

Availability of data and materials. The necessary datasets are already presented in this paper.

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Figures

Figure 1

Sampling sites for the pesticide assessment. These were conducted in the following rivers: S1 Bubunawan River, Libona; S2 Cagayan de Oro River (midstream), Maasin and S3 Cagayan de Oro River (downstream), Taguanaw. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Passive samplers' installation, monitoring and dismantling. Passive samplers were installed in three sampling sites (a). The sites were in Bubunawan River, Libona (a1), Cagayan de Oro River, Maasin (a2) and Cagayan de Oro River, Taguanaw (a3). For the installation (b), the samplers (b1) were composed of 6 silicon rubbers (SR) and 3 speedisks (SD) arranged in an iron stand and submerged in river water (b2). After 34 days, the iron stand with the samplers were removed for pesticide analyses (c).

Fungicides

Boscalid

2-chloro-N-[2-(4-chlorophenyl)phenyl]pyridine-3-carboxamide

Z-Dimethomorph

(Z)-3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-1-morpholin-4-ylprop-2-en-1-one

Propiconazole

1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole

Carbendazim

methyl N-(1H-benzimidazol-2-yl) carbamate

Metalaxyl

methyl 2-(N-(2-methoxyacetyl)-2,6-dimethylanilino)propanoate

Pyrimethanil

4,6-dimethyl-N-phenylpyrimidin-2-amine

Herbicides

Diuron

3-(3,4-Dichlorophenyl)-1,1-dimethylurea

Monuron

3-(4-Chlorophenyl)-1,1-dimethylurea

Simazine

6-chloro-2-N,4-N-diethyl-1,3,5-triazine-2,4-diamine

Insecticides

Dichlorvos

2,2-dichloroethyl dimethyl phosphate

Fenamiphos

N-[ethoxy-(3-methyl-4-methylsulfanylphenoxy)phosphoryl]propan-2-amine

Source: National Center for Biotechnology Informations, PubChem Database.

Figure 3

Structures of pesticides measured above the applied threshold level of 10ng/L.

Source: National Center for Biotechnology Information, PubChem Database.

Figure 4

Structures of some organochlorine pesticides measured in traces of pg-ng/L

Supplementary Files

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