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RESEARCH ARTICLE

Chlorpyrifos contamination of fresh water in a commercial vegetable cultivation area in Sri Lanka and factors affecting contamination

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Abstract: The study investigated the interrelationships among chlorpyrifos (CPF) concentrations in water resources, CPF application and rainfall during peak pesticide application period with usual rainfall pattern. Water samples were collected at three day intervals from groundwater and surface water resources at Marassana, a commercial vegetable cultivation area in the Kandy District, Sri Lanka, during a 5-month period. CPF application and rainfall data were also collected simultaneously. High performance liquid chromatography analyses revealed that the average CPF concentration in groundwater and surface water samples were 0.63 and 0.52 μg/L, respectively. The respective corresponding maximum values were 7.1 and 3.7 μg/L. Multiple linear regression analysis of the data established that 1 L of CPF 40 % (= 400 g/L concentration) applied in the catchments increased the CPF concentration in the groundwater and surface water by 0.65 μg/L and 0.120 μg/L, respectively; 1 mm of cumulative rainfall received increased the CPF concentration of surface water by 0.021 μg/L but did not affect the groundwater concentration significantly. Uncertainties in the model parameters analysed using Monte Carlo stochastic simulation established that there was an 88 % probability for the CPF concentration to remain positive in the surface water.

Keywords: Chlorpyrifos, pesticide, pollution, uncertainty groundwater, surface water.

INTRODUCTION

Chlorpyrifos (CPF) is the common name used for *O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl)-phosphorothioate, which is a broad-spectrum chlorinated organophosphate insecticide. CPF accounts for nearly 50 % of all the organophosphate insecticides imported, and about 20 to 25 % of all insecticides imported to Sri Lanka (Registrar of Pesticides, 2007). CPF and other pesticides applied in the field are likely to be transported from field to surface water mainly by surface runoffs and to groundwater by leaching through soil. The objective of this study was to estimate the CPF concentrations in surface water and groundwater in a commercial vegetable cultivation area in the central hills of Sri Lanka, and to determine the factors affecting the contamination. The factors considered were, quantities of CPF applied, rainfall in the study area, soil properties and the CPF mobility in soil.

CPF is a pesticide having a non-polar nature and it does not easily ionize in solution. Therefore, solubility of CPF in water varies within a low range, between 0.44 - 1.12 mg/L at a temperature range of 25 – 20 ^{o}C (Gebremariam, 2011). CPF is stable for several weeks in neutral or slightly acidic conditions when stored at room temperature (WHO, 2002). It is moderately toxic and classified in Toxicity Category II for all exposure routes (Smegal, 2000). According to the United States Environmental Protection Agency (USEPA, 1999), exposure to CPF could result in neurotoxicity in animals and humans and decreased birth weight of babies (Zhao *et al*., 2004 ; Tian *et al*., 2005), and increased risk of lung cancer (Dinham, 2005). The maximum permissible level for CPF in fresh water is 0.041 μg/L according to the USEPA (2009) water quality criteria. The 2008 amendment (NER, 2008) to the Sri Lankan National Environmental Regulations (NER) has increased the tolerance limit of total pesticides for the discharge of

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effluent into inland surface waters from "undetectable" (NER, 1990) to a maximum of 5 µg/L. The regulation stipulates that such discharged effluent should be diluted by at least eight volumes of clean receiving water, which amounts to 0.55 µg/L, the maximum permissible tolerance limit for pesticides in surface water. The permissible levels of CPF for ground water resources are not yet defined.

CPF has been found at concentrations bound by a maximum of 0.109 µg/L in four out of the 544 water samples collected from irrigation tanks and drinking water sources in the Dry Zone of Sri Lanka (Aponso *et al*., 2002). Water samples collected from a small stream running through a commercially cultivated area in Sri Lanka have been positive for CPF with the maximum of 2.48 µg/L (Menike *et al*., 2007; 2008), which is a many- fold increase above the tolerance limits stated by the Sri Lankan standard (NER, 2008). A number of international research studies have also reported detection of CPF residues in surface water, groundwater and soil (Fenelon & Moore, 1998; Troiano *et al*., 2001; Jergentz *et al*., 2005; Menon *et al*., 2005; Claver *et al*., 2006; Ntow *et al*., 2008; Muhamad *et al*., 2010).

Although numerous factors affect the pesticide concentrations in ground and surface water bodies, many of these factors such as soil type, stream channel network, land use, and landscape remain almost unchanged over time for a given geographical system. In such cases, changes of pesticide concentrations in surface water and groundwater are primarily dependent on factors such as rainfall, quantities of pesticide application in the catchments, soil properties and pesticide mobility in soil. Rainfall can be used as a proxy for the total amount of surface runoffs and pesticide application represents the source of contamination.

Mathematical models to predict pesticide occurrence at surface water bodies have been developed based on detailed descriptions of transport processes (Nakano *et al*., 2004; Leu *et al*., 2005). Uncertainties in modelling the complexity of natural systems have been observed to limit the predictive capacity of such models (Leiguo *et al*., 2004). Variations in pesticide concentrations in surface and ground waters with respect to parameters such as rainfall, transport and the amount of pesticide applied, have been established using multiple linear regression analysis (MLR) (Kreuger & Törnqvist, 2008; Sprague & Nowell, 2008).

A Sri Lankan commercial vegetable cultivation area where CPF is the most widely applied insecticide was chosen for this case study. Water samples were collected from selected surface water and groundwater locations in the study area. CPF concentrations of the water samples were determined using a high performance liquid chromatograph (HPLC). Statistical methodologies like, mean equality test and MLR were then used to analyse the interrelationship among CPF concentration, CPF application and rainfall, and to develop a linear regression model. The model was found to be statistically significant in the case of CPF contamination of surface water. Uncertainties surrounding the developed model were accounted for in the predictions made by a stochastic model developed using the Monte Carlo stochastic simulation procedure (Smith, 2002). In the case of groundwater, no significant statistical relationships were found. The hypothesized cause of groundwater contamination as CPF moving through the soil to reach groundwater was justified by the results (Menike *et al*., 2011).

METHODS AND MATERIALS

Study area

Figure 1 shows the schematic of the study area, which is a cultivated field of 35 acres in the catchments of a small stream, called Kiwullinda Oya running through Marassana in the Central Sri Lanka. The geographical coordinates of Marassana are 7° 13' 0" North, 80° 44' 0" East. The area belongs to the mid country Intermediate Zone, which receives an average annual rainfall of 1100 mm, of which, about 65 % is received from the north-east monsoon and the rest from the south-west monsoon (Punyawardhana, 2008).

The study area was divided into catchments A and B. Catchment A shown in Figure 1, was about 19 acres belonging to 41 farmers. About 65 % of the total land area was cultivated with tomato, 20 % with bitter gourd, snake gourd and loofah, and the other 15 % with cabbage, green chilli and root vegetables. Catchment B, as shown in Figure 1, was about 16 acres belonging to 27 farmers. About 70 % of this area was cultivated with tomato, 15 % with bitter gourd, snake gourd, green chilli and root vegetables, and the other 15 % with cabbage**.**

Properties of the soil at the area studied (Menike *et al*., 2011) were as follows: the soil structure was sandy clay loam; organic matter content (OM) was 3−3.2 %; P content was 60 – 150 ppm; K content was 160 – 400 ppm and the soil pH was in the acidic range, the maximum reported value being 6.4.

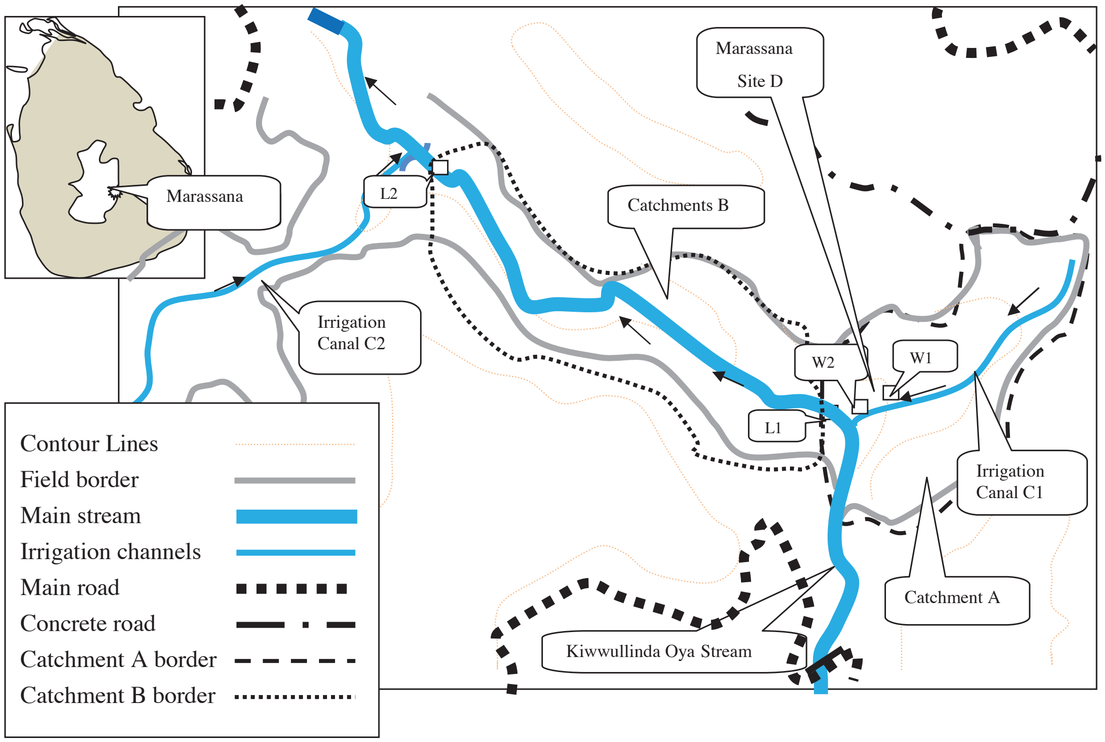

Figure 1: Schematic showing the sampling locations in relation to the site selected (not drawn to scale)

Water resources

Kiwullinda Oya stream was where the surface water resource studied. Water samples were collected at locations L_1 and L_2 in the stream (Figure 1). An irrigation canal (labelled C_1) receiving surface runoffs from catchment A merged with the stream just upstream of L_1. Irrigation canal (labelled C_2) situated outside the study area merged with the stream just downstream of L_2. Even though no irrigation canal merged with the stream in between L_1 and L_2, there was no hindrance for the surface runoffs from catchment B to reach the stream between L_1 and L_2 (as shown in Figure 1).

There were two community wells in the study area (W_1 and W_2) situated at the lowest elevation in catchment A. Those two wells were selected as the groundwater sources for the study. The irrigation canal C_1 ran adjacent to the walls of the wells (Figure 1). The depth and cross sectional area of well W_1 measured with 0.05 m accuracy, were 3 m and 2.5 m x 3 m, respectively, and those of W_2 were 2.5 m and 2 m x 3 m, respectively. Both wells were protected with 0.5 m of freeboard to prevent surface runoff water mixing with well water. Water level of the wells reached up to ground level during rainy season and decreased by 1.5 m from ground level in the drought season.

Sample collection and preparation

Water sample collection: The water samples were collected from L_1, L_2, W_1 and W_2 at a frequency of once in three days as described by Leiguo *et al*. (2004) during the vegetable cultivation period spanning five months. Water samples were collected in 500 mL amber glass bottles with glass lids, which were cleaned according to the procedure provided by Korth and Foster (1998). Sample collection from all four locations were carried out at about 7.00 am to minimize the mixing of sediments due to farmers' activities.

The water samples from the stream were collected manually by holding the immersed bottle open at a position within 3 cm deep from the top surface of the water flow. The samples from the wells were collected in bottles using a galvanized bucket. All the water samples were transported to the laboratory situated 40 km away from the research site, within 3 h of sample collection. The samples were stored below 4 ^{o}C temperature until the time of extraction.

Preparation of water samples: Sample preparation and analysis of CPF were carried out based on the methodology described by Korth and Foster (1998) and CIPAC Handbook 1C (1985). In this method, water samples from cold storage were equilibrated at room temperature and filtered using a standard code H20261 filter paper into a 1000 mL separating funnels, and 20 mL of HPLC grade dichloromethane (DCM) was added to each separating funnel. Funnels were shaken by inverting 180^0 while releasing the stopper from time to time to release the built up pressure. Shaking was repeated 50 times and the funnels were kept in a rack for 45 min for separation. Once the separation occurred the DCM with CPF at the bottom of the separating funnel was allowed to run into a 50 mL labelled round flask by opening the stopper at the bottom and the whole extraction procedure was repeated thrice. The solvent collected was concentrated and evaporated to dryness. The residue was dissolved in acetonitrile prior to the analysis using HPLC.

Analysis of samples

HPLC analysis for CPF: The sample residues were analysed for the presence of CPF using a HPLC (Agilent HP 1100 series, Chemstation). In this method, a C_8 column (ZORBAX Eclipse XDB-C8; 4.6 × 150 mm, 5 µm) was used for analysis under 62 bar pressure of at a wavelength of 285 nm in variable wavelength detector (VWD). The composition of the mobile phase was 60 % v/v HPLC grade acetonitrile, 39.5 % v/v deionised water and 0.5 % v/v HPLC grade acetic acid at a constant flow rate of 1 mL/min. A 20 µL aliquot of the sample was manually injected at a temperature of 25 ^oC. The HPLC run time was 20 min and the peak due to CPF on the chromatogram was identified at a retention time of 15.25 ± 0.30 min.

Quality control: Quantification of CPF was carried out using a calibration curve that was developed by injecting triplicates of 13 different concentration levels of CPF standards ranging between 0.0 and 700 μgL^{-1}. Linear relationships between the ratios of the peak area and the corresponding concentrations were observed with a correlation coefficient of 0.99, and a slope of 0.024. These values agree with the guidelines provided by Bassett *et al*. (2000). Coefficients of the linear regression were used in the respective conversion. The minimum level of detection of CPF was 0.001 µg/L, established according to the method described by Bassett *et al*. (2000). The repeatability (precision) is usually expressed as the relative standard deviation (RSD). The precision in terms of repeatability was obtained by carrying out the extraction and analysis of 12 different fortified samples. Each extract was injected three times. The RSD obtained for these values were shown to be < 20 % and was acceptable according to the recommendations of Bassett *et al*. (2000).

Data collection

CPF application data collection: Names of the farmers at the research site and the area cultivated by each of them were collected from the Cultivation Officer at Marassana. The type of crop cultivated, the cultivation period and the usage of pesticides were collected from the farmers themselves by meeting on a regular basis. Names of the pesticides applied, amounts of each pesticide applied and the reason for the application were meticulously collected from the farmers on an individual basis.

From the pesticide information collected, CPF (at 40 %) (commercially available formulation, 40 % w/v of CPF) application data were summed up separately in each catchment. The farmers used 10 L of water to dilute 28 mL or more of CPF (at 40 %), and hence the minimum spraying concentration of CPF was found to be 1.12 g/L. It was observed that those who selected CPF for insect control applied CPF at regular time intervals, and these intervals may change according to the crop cultivated on each land.

Rainfall data collection: Rainfall data were collected *in-situ* using a rain gauge prepared according to Wrage *et al.* (1994). The least count of the rain gauge was 1 mm. The total rainfall received at Marassana area during the study period was 350 mm, which is a relatively low value.

Auxiliary data collection: During the interviews with the farmers, information on safety precautions taken during pesticide application, modes of equipment handling, any related health hazards and chronic illnesses experienced by them were gathered. Atmospheric and wet bulb temperatures (^{o}C) and stream water flow rates (m^3/s) up to three decimal figures (using a current meter, ATOT Pro.No. 03) were measured on a regular basis.

Statistical analysis

CPF concentration in the surface water was assessed by examining the summary statistics of the data collected at the two locations in the stream, L_1 and L_2. Similarly, CPF concentration in the groundwater was assessed by examining the summary statistics of the data collected at the two wells, W_1 and W_2. The eqality of means of CPF concentration at the two locations of surface water as well as at the two wells were tested using analysis of variance (ANOVA).

The pesticide concentration in water has been modelled as a function of a variety of explanatory variables using MLR by several researchers (Törnqvist, 1998; Barbash *et al*., 2001; Muller *et al*., 2002; Kreuger & Sprague *et al*., 2007). A similar procedure was followed in this study and the following MLR model was used:

$$C_i = \beta_0 + \beta_1 R_i + \beta_2 P_i + \varepsilon_i \quad ...(1)$$

where $i=1..N$ (N= sample size), C denotes the CPF concentration (µg/L) in surface water (or in groundwater), R denotes the cumulative rainfall between sampling (mm), P_t denotes the cumulative CPF application between sampling (L), and $\beta_{0,}$ β_1 and β_2 are parameters to be estimated. Random error term ε is assumed to be normally distributed with a zero mean and a constant variance σ^2 $(\varepsilon \sim N(0, \sigma^2))$.

Applicability of the above model should be restricted to the peak pesticide application period with usual rainfall pattern, since the data used to estimate the parameters of the model were collected under such conditions. During the peak pesticide application period, it is highly probable that P is non zero for a prolonged period of time.

Uncertainty analysis

In view of the limited number of data used in the statistical analysis, it was highly likely that the estimates of the parameters $\beta_{0,}$ β_1 and β_2 of equation 1 be different from the true parameters. Therefore, CPF concentrations predicted using the estimated regression equation would be subjected to uncertainties. Moreover, rainfall and pesticide applications in the field could vary in different situations. Uncertainties in the estimated parameters and the input variables of the model were transformed as a probability distribution of the CPF concentration using a Monte Carlo stochastic simulation procedure (Smith, 2002) as follows:

Step 1: Normal distribution having the estimated mean (µ) and the estimated standard deviation (σ) of a chosen parameter was used to describe the uncertainty in the said parameter, and was denoted by N(µ, σ).

Step 2: Input variables were described by normal distributions having respective mean and standard deviation (σ) tabulated in Table 1.

Step 3: Numerical values of the parameters and variables were generated randomly from the chosen normal distributions. In this study, 10,000 possible values were generated for each parameter.

Step 4: Randomly generated parameters and input variables were used in the model to simulate CPF concentration.

Step 5: The simulated CPF concentration would describe a probability distribution, from which the degree of confidence in the CPF concentration in the surface water (or groundwater) was assessed.

RESULTS AND DISCUSSION

Table 1 provides summary statistics of the CPF concentration data, CPF applications and rainfall. There were 38 observations for each variable listed in Table 1, with minimum values being zeroes in all cases, except in one case where the value is almost close to zero.

In case of surface water contamination, maximum CPF concentrations were recorded as 3.71 µg/L and 2.154 µg/L at L_1 and L_2 respectively. It is of interest that these maximum concentrations were recorded on the same day [22nd of May, see Figure 2 (a)]. The corresponding cumulative rainfall between two consecutive samplings was 70 mm (the second largest rainfall recorded during the study period). The corresponding cumulative CPF applications between samplings were 0.896 L and 0.140 L at catchments A and B, respectively.

In case of groundwater contamination, maximum CPF concentrations were recorded as 7.089 µg/L and 3.250 µg/L at W_1 and W_2 respectively, which were recorded on the same day [18th June, see Figure 2(b)]. The corresponding cumulative CPF application between two consecutive samplings in catchment A was 3.584 L, which was the maximum recorded CPF application (Table 1). It must be noted that there was no rain at the catchments since the 10th of June. It was therefore probable that the CPF applied could not have been washed off into the surface water sources, and may have leached through the soil from irrigated water to the groundwater.

The lower bound of the mean and median of the CPF concentrations tabulated in Table 1 being 0.205 µg/L (corresponding to W_2) clearly demonstrated that the surface water and groundwater were indeed contaminated by CPF during the period of sample collection. Moreover, it could be said with 75 % confidence that CPF concentrations lay in the range bounded by the values corresponding to 12.5 and 87.5 percentiles (tabulated in Table 1). Thus, it could be concluded with 75 % confidence that, during the period of the study, CPF concentration varied in the range 0.111–1.023 µg/L at L_1,

Table 1: Summary statistics of CPF concentrations, CPF applications and rainfall data

Statistic	CPF concentration in water (µg/L)				CPF application in catchments (L)		Rain fall (mm)
	L_1	L_2	W_1	W_2	A	B	
Observations	38	38	38	38	38	38	38
Minimum	0.020	0.000	0.000	0.000	0.000	0.000	0
Maximum	3.710	2.154	7.089	3.250	3.584	1.484	86
Mean	0.588	0.453	0.695	0.565	0.908	0.404	10
Std. dev.	0.668	0.486	1.180	0.783	0.884	0.359	20
Median	0.390	0.212	0.412	0.205	0.560	0.338	0
Sum					34.5	15.4	377
12.5th percentile	0.111	0.095	0.035	0.030	0.000	0.000	0
87.5th percentile	1.023	0.959	1.252	1.170	2.016	0.812	31
25th percentile	0.191	0.124	0.102	0.090	0.224	0.084	0
75th percentile	0.691	0.702	0.723	0.690	1.512	0.616	12

Note: Symbols L_1 and L_2 stand for fresh water sampling locations, W_1 and W_2 for groundwater sampling locations. Symbols A and B represent catchments A and B, respectively.

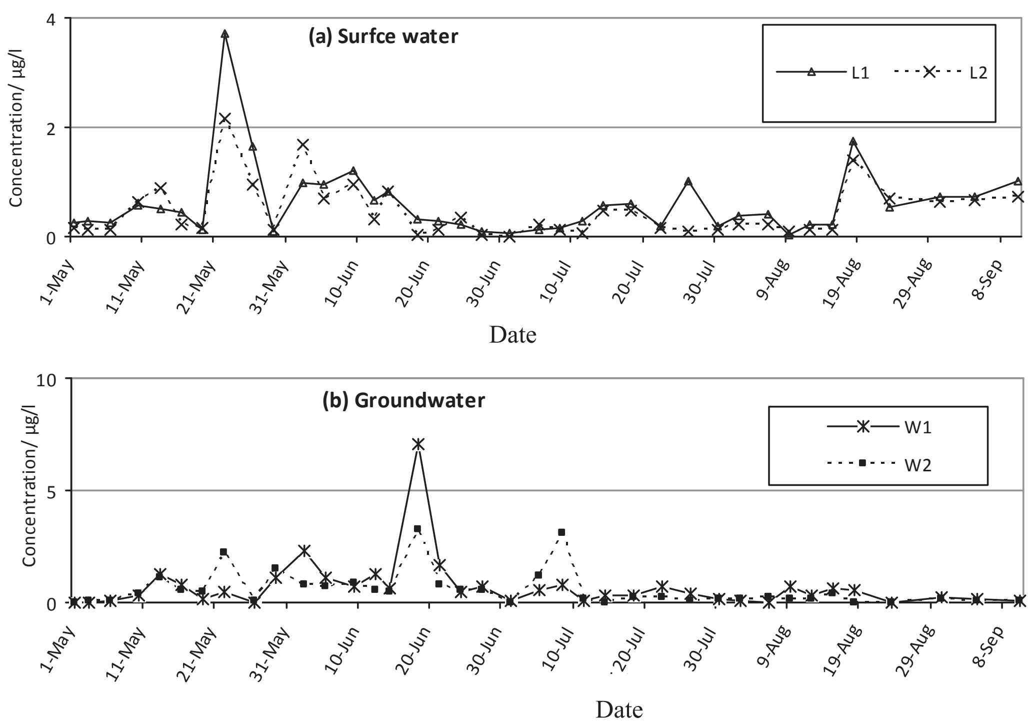

Figure 2: Variations of CPF concentrations (a) surface water and (b) ground water

0.095 – 0.959 µg/L at L_2, 0.035 − 1.252 µg/L at W_1 and 0.030 − 1.170 µg/L at W_2. The respective ranges at 50 % confidence were 0.191 − 0.691, 0.124 – 0.702, 0.102 – 0.723 and 0.090 – 0.690. CPF contamination of the surface water and groundwater during the study period was therefore established.

Summary statistics of CPF application (Table 1) shows that the CPF application in catchment A was nearly as twice as that of catchment B. Total application weight of CPF in catchment A was 14 kg, and in catchment B was 6.5 kg, applied at concentration of 1.12 g/L. Mean and median values of CPF applications provided evidence to the steadiness of CPF applications during the period of study. The maximum cumulative rainfall in the catchments between samplings was recorded as 86 mm, and the total rainfall during the study period was 377 mm. The mean rainfall was 10 mm, modal value of rainfall was zero, and rainfall was below 31 mm even at a 75 % confidence level. All these observations indicate the period of study was a relatively dry one.

Table 2: Test results for equality of means between CPF concentration series

Data series compared	ANOVA F-test statistics	Probability
CPF concentrations at L_1 and L_2	1.01	0.319
CPF concentrations at W_1 and W_2	0.32	0.574

Note: Symbols used are same as in Table 1

Table 2 shows the results of the tests for equality of means between CPF concentration series, obtained using the package StatTools™. In the case of CPF concentrations of surface water and groundwater, ANOVA statistics were 1.01 and 0.32, respectively, and the corresponding probability values were above 0.3. Therefore, there was no statistical evidence to conclude that CPF concentrations differ across the two locations of the surface water (or of the groundwater). Therefore, the CPF concentrations at the two locations of surface water were considered together in the regression analysis reported below. The same procedure was followed with the CPF concentrations at the two locations of groundwater.

CPF in surface water

Regression model: In the tabular data used for estimating the parameters of equation 1, CPF concentrations at L_1 were listed against corresponding cumulative rainfall and CPF application in catchment A. CPF concentrations at L_2 were listed against corresponding cumulative rainfall and CPF application in catchment B. Regression result obtained with StatTools™ is given below:

$$C_s = \underset{[0.0742]}{0.2299^{**}} + \underset{[0.0025]}{0.0213^{****}}\, R + \underset{[0.0694]}{0.1202}\, P_t^{*} \qquad ...(2)$$

where C_s represents CPF concentration in surface water, standard errors are given within the square brackets below the respective parameters, and symbols ****, ** and * denote p value being less than 0.0001, 0.01 and 0.1, respectively.

Regression statistics corresponding to equation 2 were $R^2 = 0.50$, adjusted $R^2 = 0.49$, standard error of estimate = 0.4184, and F-ratio = 36.6 and probability (F-statistic) < 0.0001, hence the above model could be considered statistically significant in an overall sense. Adjusted R^2 being 0.49 revealed that 49 % of the variability in the CPF concentration in surface water was explained by rainfall and CPF application. It was noteworthy that the multiple R value, the correlation between the actual and fitted CPF concentrations was 71 %. The estimated parameters of equation 2 revealed that 1 mm of cumulative rainfall received in the catchments could cause a 0.021 μg/L increase of CPF concentration in the surface water by holding the other variables constant. The P variable measures the cumulative amount of CPF applications. The results indicate that 1 L of CPF (40 %) applied (400g of CPF) in the catchments (cultivation area) during previous three days could cause 0.120 μg/L increase of CPF concentration in the surface water, when the other variables are held constant, provided CPF applications and rainfall followed similar patterns as the one reported in this study.

As the pesticide application variable in equation 2 was significant only at 90 % confidence and the rainfall variable is highly significant at 99.99 %, this result appears a little uncharacteristic since CPF application is the main variable, which initiates the contamination. P_t is the current cumulative pesticide application (i.e., pesticides applied during previous 2nd day to 4th day). The base model was modified by adding the first lag value of P_t; pesticides applied during previous 5th day to 7thday (P_{t-1}) and second lag value of P_t; pesticides applied during previous 8th day to 10th day (P_{t-2}), while keeping Pt in the model. The comparison of the regression statistics of the base model and modified model are shown in Table 3.

The F-ratio of the modified model is 23 with a probability (F-statistic) < 0.0001; hence the model is statistically significant in an overall sense and therefore the model may be accepted. The R^2 value and the adjusted R^2 value have increased up to 0.57 and 0.55, respectively. Accordingly a 55 % of variability of CPF in surface water is described by the variables included in the model. Schwarz criterion is less than that of the base model as shown in Table 3. The multiple R value, the correlation between actual value and the fitted value of the modified model is 74 %, higher than the said value of the base model.

Table 3: Comparison of regression statistics of the base model and the modified model of surface water

Model parameters	Base model	Modified model
P_t	0.12* (p = 0.08)	0.055 (p = 0.42)
P_{t-1}	-	0.098 (p = 0.14)
P_{t-2}	-	0.183*** (p = 0.0089)
R	0.021**** (p = 0.0000)	0.021**** (p = 0.0000)
β_0	0.229*** (p = 0.002)	0.082 (p = 0.3313)
R^2 value	0.5	0.57
Adjusted R^2 value	0.49	0.55
F-statistic	36.629	23.109
Prob. (F-statistic)	0.00000	0.00000
Schwarz criterion	1.238	1.212
Standard error	0.4184	0.3972

**** p-value< 0.0001 *** p-value< 0.01 * p-value <0.1

The second lag value of cumulative pesticide application (P_{t-2}) is significant at $p < 0.001$. This (P_{t-2}) shows an effect on CPF concentration of surface water at 99 % confidence level, while holding the other parameters constant. The rainfall (R) variable is highly significant at $p < 0.0001$ and shows an effect on CPF concentration of surface water at 99.99 % confidence level when the other variables are held constant. According to the above criteria, it is clear that the modified model provides better prediction of CPF concentration of water in an overall sense.

The modified regression model shows that even when there is no current cumulative application of CPF, the CPF levels at the catchment will not become zero. The rainfall, provides a transport medium to the leftover CPF at the catchment to reach water resources thus becoming the most significant variable explaining the CPF contamination of surface water. Moreover, it is interesting to see that the intercept β_o is significant at 99 % confidence level in the base model and has become insignificant in modified model with a diminished value. This implies that in the base model, β_o might be representing omitted variables in the model. In the modified model, β_o is insignificant and the SIC value is lower, which indicates that it is a better fit than the base model.

It must be noted that the rainfall variable was associated with a p value < 0.0001, which means that the said parameter was statistically significant at 99.99 % level of confidence. The second lag value of CPF application was also significant at 99 % level of confidence. A number of previous studies (Leiguo *et al*., 2004; Ntow *et al.*, 2008) also have established that rainfall and pesticides application has an impact on the pesticides concentration in surface water. This study demonstrated that the quantities of pesticides used in the catchment area and rainfall were the most important estimators of the level and amount of pesticides occurring in the stream. High confidence level of the rainfall parameter was to be expected since rainfall could have a direct impact on CPF concentration in surface water. The following mechanism is suggested: Part of the CPF applied to the vegetable crops could fall directly on the soil surface, and in the absence of rainfall, it would remain in the soil for a period of time as the half-life of CPF is about 10 to 120 days (Singh, 2003). Since the soil at the site was sandy clay loam, having 45 to 80 % sand, and the organic matter content of the soil was as low as 3.0-3.2 % affinity of CPF to soil is poor at the studied site (Chai *et al*., 2009; Menike *et al*., 2011). Therefore, in the event of rainfall, CPF could easily be carried over to the stream, either *via* the runoff or through leaching despite the low solubility for CPF in water. Even in the case of CPF adsorbed in soil, presence of water after a rainfall could cause desorption of CPF, and the runoffs may take CPF to the nearest surface water source. Further, the soil itself may be carried to the surface water sources by the surface runoffs at high rainfall intensities.

CPF application variable in the 2 models described above were statistically significant only at a low level of confidence compared to rainfall. This is to be expected since CPF applied on the field needed a carrier, such as rainfall, to take the CPF to the surface water. The period of study was relatively dry and the results of MLR are acceptable according to the CPF transport mechanism described above.

Uncertainty analysis: Even though the regression model given by equation 2 could be considered reasonable in describing the interrelationship among CPF concentration in the surface water, CPF application and rainfall, it was probable that the estimated parameters were different from the true parameters. Moreover, the input parameters could also be considered to possess uncertainty. Thus the said model was subjected to the uncertainty analysis outlined previously.

Equation 2 provided the mean and the standard deviation of the rainfall parameter as 0.0213 and 0.0025, respectively, and those of the CPF application parameter as 0.1202 and 0.0694, respectively. The mean and standard deviation of the intercept were given by 0.2299 and 0.0742, respectively. In the uncertainty analysis carried out, rainfall parameter, CPF application parameter and the intercept were therefore considered being described by the random distributions N(0.0213, 0.0025), N(0.1202, 0.0694) and N(0.2299, 0.0742), respectively. The input data on rainfall and CPF applications were described by the random distributions N(10, 20) and N(0.6559, 0.7164), respectively.

Using the said normal distributions, 10,000 possible values were randomly generated for each parameter, intercept and input variables, which were then used in the linear model (similar to equation 2) to simulate CPF concentrations. Results of the Monte Carlo stochastic simulation obtained using @RISK are shown in Figure 3.

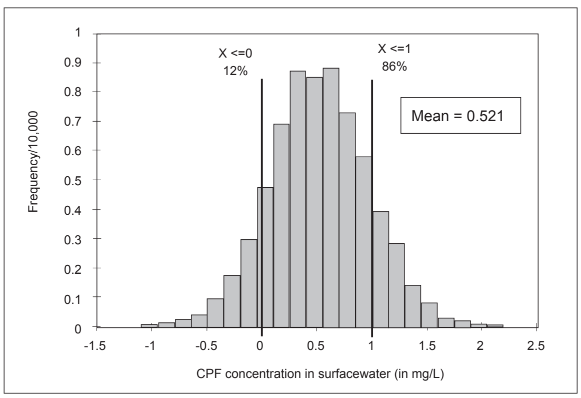

Figure 3: Probability distribution of the simulated CPF concentration in the surface water

The left most delimiter (or grey vertical line overlaying the histogram) was at the 12th percentile (marked by 12 %) having the *x* value less than or equal to zero. This means that there is a 12 % probability that the CPF concentration in the surface water was zero (since it cannot be negative). The rightmost delimiter was at the 86th percentile (marked by 86 %) having the *x* value less than or equal to unity, hence there was a 14 % probability that the CPF concentration in the surface water was above 1 µg/L. Therefore, the probability of CPF concentration of surface water lying between 0 and 1 µg/L was 74 %.

The analysis carried out above with @RISK showed that there was a 50 % probability for CPF concentration in the surface water to be between 0.221 and 0.822 µg/L, with the mean CPF concentration being 0.522 µg/L. Therefore, the mean value of CPF concentration of surface water did not exceed the maximum permissible level of (0.55 µg/L) total pesticides (NER, 2008) at a 50 % probability. The mean value of CPF concentration of surface water was higher than the maximum permissible level (0.041 µg/L) for CPF in fresh water according to the USEPA (2009) water quality criteria.

CPF in groundwater

Regression model: Since the results of Table 2 showed that CPF concentrations in the groundwater did not have a statistically significant difference across the two locations, they were considered together in estimating the parameters in equation 1. The rainfall remained the same for the two locations. Since both wells were situated in catchment A (see Figure 1), CPF application data also remained the same as that of catchment A. Regression result obtained with StatTools™ is given below:

$$C_g = \underset{[0.1567]}{0.0226} + \underset{[0.0050]}{0.0016}\,R + \underset{[0.1130]}{0.6508}\,P_A^{****} \qquad ...(3)$$

where C_g represents CPF concentration in groundwater, subscript $_A$ represents catchment A, standard errors are given within the square brackets below the respective parameters, and symbol **** denotes p value being less than 0.0001.

Regression statistics corresponding to equation 3 were $R^2 = 0.32$, adjusted $R^2 = 0.30$, standard error of estimate = 0.8330, and F-ratio = 17.2 with p value < 0.0001. Even though the overall model was statistically significant, judging by the p value of F-ratio, rainfall parameter and intercept were not statistically significant. CPF application parameter, on the other hand, was statistically significant at 99 % level of confidence. Explanation of this observation may be that in the presence of irrigated water, CPF residues on the soil surface are carried downwards through soil (Huggenberger *et al*., 1973). In the event of such continuous movement, it is probable for CPF to reach the water table (which is never below 1.5 m depth close to the wells) and contaminate groundwater. However, since adjusted R^2 was as low as 0.30, only 30 % of the variability in the CPF concentration in groundwater could be explained by CPF application. Correlation between the actual and fitted CPF concentrations being 57 % pointed to the fact that equation 3 could only poorly describe the CPF concentrations in groundwater. Therefore, equation 3 was abandoned as a model incapable of explaining CPF concentration in groundwater.

CPF mobility in soil: As indicated in the preceding section, CPF contamination of groundwater may be explained by CPF applied in the field being transported through the soil to groundwater. In order to test the above hypothesis, the selected soil characteristics and the downward movement of CPF through soil at Site D (shown in Figure1) has been analysed up to 60 cm depth in soil, at 15 cm intervals (Menike *et al*., 2011). They demonstrated that CPF moves downward through soil up to 60 cm depth in about two days. According to the physical and chemical properties reported, the soil in the study area was acidic and the major part of the soil was identified as sand. The soil in the area being seriously deprived of organic fertilizers such as compost and/or manure, the organic matter content was low. These properties of the soil account for the low value (1.875 L/kg) of the sorption coefficient (K_d) of CPF in soil (Menike *et al*., 2011). Thus it was concluded that the above mentioned coherent features support the weak adsorption affinity of CPF to soil and may cause CPF to move downwards through the soil with relative ease, resulting in groundwater contamination.

Since the pesticide application data were collected once in three days, regression analysis reported in the preceding section was repeated with the current and previous pesticide application data. The result obtained using StatTools™ is given below:

$$C_{gt} = \underset{[0.2059]}{-0.1207} + \underset{[0.0049]}{0.0019}\, R_t + \underset{[0.1149]}{0.6378}\, P_{At}^{****} + \underset{[0.1122]}{0.2208}\, P_{A,t-1}^{**} - \underset{[0.1128]}{0.0333}\, P_{A,t-2} \quad ...(4)$$

where C_{gt} represents CPF concentration in groundwater, subscript $_A$ represents catchment A, standard errors are given within the square brackets below the respective parameters, and symbol **** denotes p value being less than 0.0001.

Where P_{At}, current cumulative pesticides application was the pesticides applied during the three days (previous 2nd day to 4th day) prior to sampling and $P_{A,\ t-1}$ and $P_{A,\ t-2}$ are first lag value and second lag value of $P_{At,}$ as explained earlier in this paper.

R^2, adjusted R^2, standard error of estimate and F-ratio values were 0.37, 0.33, 0.8237, and 12.9, respectively with p value < 0.0001. The correlation between the actual CPF concentration and the predicted CPF concentration was also increased to 60 %.

The parameters and statistics of equation 4 were the same as equation 3, with the parameter of P_A being highly significant as in equation 3. The added characteristic in equation 4 was that the coefficient of the first lag value of P_A and this was also statistically significant at 95 % level of confidence, whereas the second lag value was not statistically significant. This implies that CPF applied to the field within the last three days and six days can have a statistically significant effect on the C_g, but the latter is not affected by CPF applied nine days prior to sampling. These results corroborated the results of CPF mobility studies reported above.

CONCLUSION

CPF was a widely used insecticide in the selected commercial grade vegetable cultivation area in Marassana. One of the objectives of this study was to estimate the CPF contamination of surface water and groundwater in the said area. Throughout the vegetable cultivation period from May - September, the selected surface water resource, Kiwullinda Oya stream and ground water resources were found to be positive for CPF, demonstrating that the surface water and groundwater were indeed contaminated with CPF.

It is concluded that the CPF concentration across the two locations was not statistically significantly different. The proposed linear regression model was statistically accepted and demonstrated that the CPF concentration in the stream water varied with rainfall (99 % confidence limits) and with CPF application (90 % confidence limits). These findings established that the CPF applied on the field needed a carrier, such as rainfall, to take the CPF in to the surface water. This occurrence could be explained in the following way; when the CPF application is heavy, low adsorption affinity to soil leads to lingering free CPF within the soil that can be easily carried into the stream either *via* runoff or through leaching despite the low solubility of CPF in water. CPF may also enter the stream with soil that is carried by surface runoff at high rainfall intensities.

A 1 mm of cumulative rainfall received in the catchments result in an increase of CPF concentration in surface water by 0.021 μg/L when the CPF application variable is held constant, and a 1 L of CPF (40 %) applied in the catchments cause an increase of CPF concentration in the surface water by 0.120 μg/L when the rainfall variable is held constant, provided similar geographical and climatic factors as the one reported in this study prevails.

The probable uncertainty between the estimated parameters and true parameters was estimated using a suitable tool, the Monte Carlo stochastic simulation. The results of the simulation show an 88 % probability that the CPF concentration in the surface water is more than 0 µg/L. It also shows that there was a 14 % probability that the CPF concentration in the surface water is above 1 µg/L. The probability of CPF concentration of stream water exceeding the maximum permissible level for total pesticides in freshwater (NER, 2008) was less than 50 %. The mean value was fairly larger than the maximum permissible level (0.041 µg/L) for CPF in fresh water according to the USEPA (2009) water quality criteria.

CPF is transported through soil within a maximum of 6 days into ground water, as a result of low organic matter content and the sandy base soil structure. These results corroborated the results of regression analysis carried out with current and previous pesticide application data. The current cumulative application of CPF was highly significant at 99 % confidence level and the first lag value of the current cumulative pesticides application (which included the CPF applied from previous 4^{th} day to 7^{th} day) was significant at 95 % confidence level demonstrating the effect of these two factors on the CPF concentration of ground water.

Results of this study demonstrated that for a given watershed, rainfall and CPF use are the two major factors controlling the dynamics of CPF transport into surface water, whereas CPF application, the soil structure, and soil organic matter content are the major factors controlling CPF transport into groundwater.

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