Atrazine Transport from The Maize (*Zea mays* L.) Cultivated Upland Soil in Huay Kapo Watershed, Nam Nao District, Phetchabun Province, Thailand

O. Phewnil[1], S. Panichsakpatana[2,*], N. Tungkananuruk[1] and B. Pitiyont[3]

[1]College of Environment, Kasetsart University, Bangkok, Thailand
[2]Department of Soil Science, Faculty of Agriculture, Kasetsart University, Bangkok, Thailand
[3]Department of Environmental Science, Faculty of Science, Kasetsart University, Bangkok, Thailand

**Corresponding author. Email: agrsmp@ku.ac.th*

Abstract

Huay Kapo Watershed is located in Lakdan Sub-District, Nam Nao District, Phetchabun Province, Thailand**.** The watershed is located at approximately 400-920 m MSL, has a slope of approximately 18%, high erodibility, and a high soil loss rate (120.15 t ha^{-1} yr^{-1}). This area is used to cultivate maize (*Zea mays* L.) year round and receives atrazine at a rate 1.25-1.56 kg ha^{-1}. Topsoil (0-15 cm), subsoil (15-30 cm), soil sediment and stream water were collected from 15 stations during the rainy season (August-November 2008). The analytical results revealed that topsoil and subsoil of the upland soils were mostly sandy clay loam, with pH 5.0, low CEC (average 13.30 and 9.75 cmol kg^{-1}, respectively), low clay content (23.60 and 25.10%, respectively) and low organic matter (1.78 and 1.45%, respectively). Topsoil at the amount of 80% of the total 48 samples contained atrazine, with the 133.59 µg kg^{-1} average concentration, while 83.33% of the total 50 samples of subsoil was contaminated with atrazine at the average concentration of 183.23 µg kg^{-1}. Furthermore, 71.76% of the sediment samples were found to contain atrazine at the average concentration of 27.42 µg kg^{-1}. The soil sediment samples were mostly sand and had a low clay content (4.02%), low organic matter (0.45%), low CEC (4.36 $cmolkg^{-1}$) and pH of 6.5. Stream water samples at the amount of 63.33% of all samples were contaminated with atrazine from the cultivated area with the average atrazine concentration of 4.7 µg L^{-1}. The stream water as many as 15 samples (39.47% of the total samples) contained atrazine in levels higher than the standard limit of atrazine concentration in drinking water set by USEPA at 3 µg L^{-1}. Atrazine in the upland soil was 4.87-fold higher than that in the soil sediment and 39-fold higher than that in the stream water. Additionally, the content of atrazine in the soil sediment was 5.87-fold higher than that in the stream water. Overall, the contents of atrazine could be ranked in the following order: subsoil > topsoil > soil sediment > stream water. The results revealed that atrazine was transported from upland soils into the aquatic environment by adsorption, run-off and leaching processes.

Keywords: atrazine, herbicide, soil, maize, soil sediment, stream water, transport, watershed

Introduction

Thailand has imported large amounts of herbicides to control and eliminate pests. These compounds have been applied directly to the soil and sprayed over cultivated areas, which has led to residues in the environment. In 2007, approximately 3,686,650 kg of atrazine (s-triazine) were imported into Thailand, making it the 7th most imported pesticide. Atrazine has been widely

applied in several cultivated areas for the control of broad-leaf annual weeds in maize, sorghum, pine apple, and sugarcane fields. Atrazine functions by inhibiting photosynthesis in weeds; however, it may cause similar inhibition effects in aquatic ecosystems that receive atrazine via runoff or leaching. Huay Kapo watershed is located on a high mountain range that contains many maize farms that are treated with atrazine. As a result, there are atrazine residues in the upland soils that may be transported into aquatic ecosystems in this watershed. Accordingly, it is important to study atrazine transport and residues in maize cultivated area, soil sediments and stream water in the region to identify a mechanism by which atrazine distribution to the aquatic environment occurs. The results obtained in this study may then be used to develop atrazine standards for the stream water of Thailand and to reduce pesticide residues in the environment in the future. Accordingly, this study was conducted to determine atrazine residues in maize cultivated areas, soil sediments and stream water to evaluate the mechanism of atrazine transportation from upland soils into aquatic environments.

Materials and Methods

Study Area

The Huay Kapo watershed is located approximately 400-920 m MSL. The watershed has a slope of approximately 18%, high erodibility, and a high soil loss rate (120.15 t ha^{-1} yr^{-1}). The secondary data such as land use, topography, and community area were compiled from the 1:50,000 geographic map. The interviews were made with 323 farmers. Specifically, 36 farmers in Huay Kapo, Lakdan Sub-District, Nam Nao District, Phetchabun Province were selected together with 287 farmers who lived within 5 km of the study area.

Sample Collection Setting

Samples of upland soil, soil sediment and stream water were collected at 15 stations in Huay Kapo Watershed, Lakdan Sub-Distrcit, Namnao District, Phetchabun Province (Figure 1) from August to November 2008, which is the rainy season and the time at which atrazine is generally applied.

Soil Sampling

Soil samples were collected with augers and v-shaped dig with a stainless steel spade and composit sampling and random sampling methods were applied. Topsoil (0-15 cm) and subsoil (15-30 cm) were collected from 15 stations during the 4 months period. One kilogram of soil was collected from each soil layer. After sampling, the soil samples were kept in black bags to prevent photodecomposition and stored at 4^{o}C in a cooler during transport to the laboratory.

Soil Sediment Sampling

The soil sediment samples were collected with a stainless steel spade by composite sampling (Gao et al., 1998) from 15 stations each month, which gave a total of 60 samples. The samples were kept in black bag to prevent photodecomposition and stored at 4^{o}C in a cooler during transport to the laboratory.

Stream Water Sampling

The 4 liter of stream water samples were collected from 15 stations during 4 months of data collection. Each sample consisted of 3 liter-sample for water quality determination. The stream water was collected 1 liter at a time by 1 liter-polyethylene bottle at the level of 30 cm from the top of stream water layer (APHA, AWWA and WEF, 1992). The rest 1 liter of the stream water sample was collected separately with 1litter-chacoal glass bottle for atrazine determination. Therefore, total stream water samples were 60 samples. All of the samples were stored in 4 ^{o}C in ice storage tank and transferred directly to the laboratory.

Soil and soil Sediment Preparation

The soil samples and soil sediment samples were dried, ground, passed through a sieve (Ø2 mm and 0.5 mm) and analyzed physical and chemical properties of soil as follow: soil texture, organic matter content, moisture, bulk density, pH, cation exchange capacity (Attanandana and Chanchareon-sook, 1999).

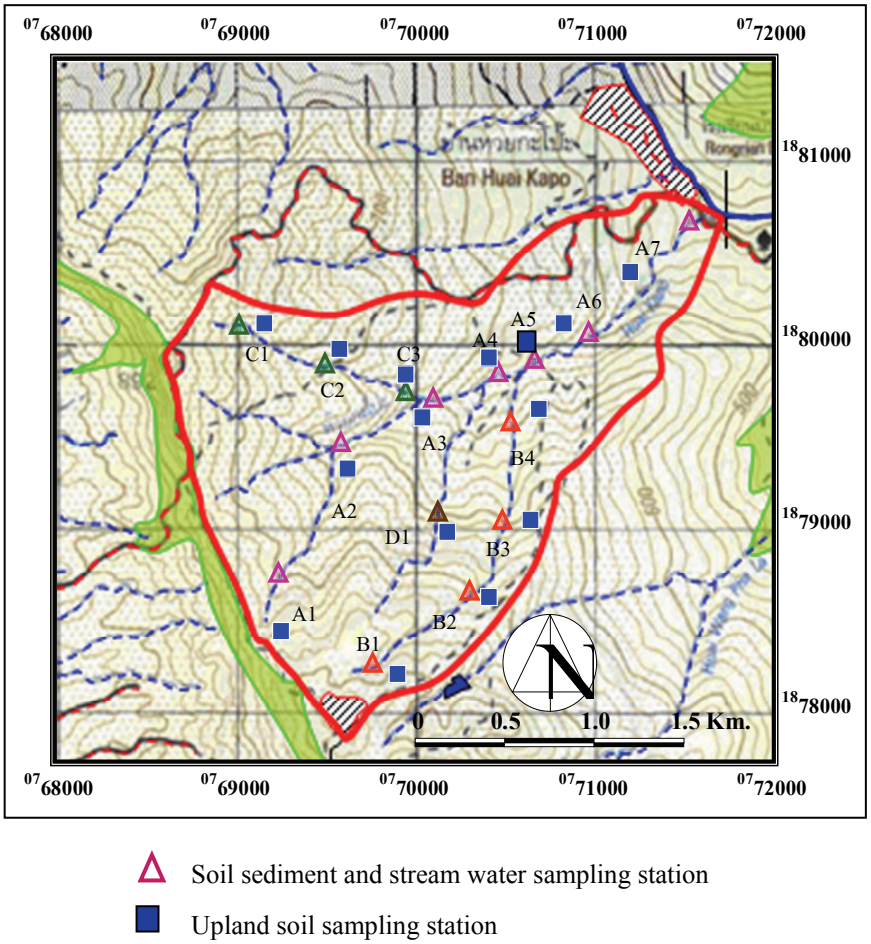


Figure 1 Sampling station in upland soil, soil sediment and stream water of Huay Kapo watershed, Lakdan Sub-District, Nam Nao District, Phetchabun Province.

Atrazine Determination

The samples were determined the atrazine concentration by HPLC (Ministry of Public Welfare and Sport 1996; Zweig, 1972). The method used to measure the atrazine concentration in soil, soil sediment and stream water was adapted from Baiadul (2001) and Thurman and Mill (1998) as follows:

Atrazine in soil and soil sediment

Atrazine was extracted using a solid phase extraction cartridge SCX-VertiPak (Vertical, USA). Briefly, an approximately 100 g of soil was suspended in 99 mL of acetronitrile/water (9:1, v/v), then the standard solution at the amount of 1 mL (0.2 mg mL^{-1} atrazine) was added and the sample was shaken vigorously for 5 min. The samples were then filtered through a paper filter (Whatman GF/C), with the first 5 mL of filtrate being discarded and the following 10 mL being used for analysis. The cartridges were then flushed with 1 column volume of acetic acid (1%), after which 2 mL of acetic acid (1%) were added. A reservoir was placed onto the cartridge with the adaptor prior to use. Next, 5 mL of each sample were then mixed with 25 mL of acetic acid (1%) and poured into the reservoir, stirred and slowly aspirated through the cartridge. The reservoir was then washed with 2 mL of acetic acid (1%), after which the cartridge was washed with 1 mL of acetonitrile, then 1 column volume of water and finally 1 mL of 0.1 M dipotassium hydrogen phosphate. Between the washing steps, the cartridge was dried briefly for about 15 seconds under vacuum. The cartridges were then eluted with 2 mL acetonitrile/0.1 M dipotassium hydrogen phosphate (1:1). Finally, the samples were filtered with nylon filter and 2 µL of each sample was injected into the HPLC.

Atrazine in stream water

Atrazine was extracted using a solid phase extraction cartridge C18-VertiPak (Vertical, USA). Briefly, a 1,000 mL sample of stream water was passed through a suitable glass fiber filter and acidified by 2 mL of concentrated hydrochloric acid. The cartridges were conditioned with 5 mL of methanol and 5 mL of distilled water prior to use. The samples were slowly forced or aspirated through the cartridges, after which they were washed with 2 mL of acetronitrile/water (3:7, v/v) and then dried under vacuum for 20 minutes. The cartridges were then eluted with 15 mL of acetronitrile concentrate and eluted under vacuum with nitrogen gas. Finally, the samples were filtered through a nylon filter and a 2 µL sample was subjected to HPLC.

HPLC was used with a HPLC Young Lin Instrument (type lumene; series Acme 9000,) equipped with a C18-4.6×50 mm x 3 µm column and a UV detector with a wave length of 220 nm. The mobile phase was acetonitrile/water at a ratio of 60:40 v/v, which was applied at a flow rate of 1 mL min^{-1}.

Results and Discussion

Atrazine Application in the Watershed

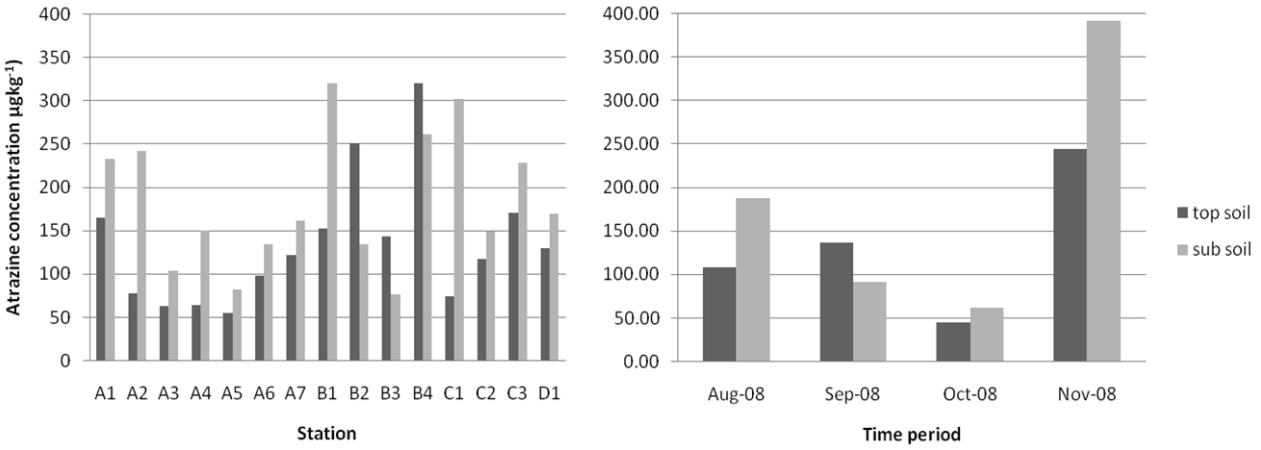
Overall, 93.7% of farmers in Huay Kapo watershed grew maize under rain-fed condition. Most of them (95.7 %) cultivated maize once a year between August and November, while 3.5% grew maize twice a year between April and November. The rest of the farmers planted maize three crops a year. Approximately 85.7% of the farmers reported that they used agricultural chemicals whereas atrazine was applied at the rate 1.25-1.56 kg ha^{-1} during pre planting and mixed with other herbicide such as paraquat, glyphosate, ametryn and alachlor during cultivation.

Atrazine Residues in Maize Cultivated Area

The topsoil and the subsoil in the study area were sandy clay loam (approximately 50.0% and 53.3% of the total samples, respectively). Both soil layers showed average pH of 5.0 and contained low organic matter and low clay contents. The average hydraulic conductivity of saturated soil in the topsoil and the subsoil were 4.608 and 1.19 m d^{-1}, respectively, which were classified as moderate and very low. It was noticeable that the soil loss rate was very high at 120.15 t ha^{-1} yr^{-1}. This amount of loss was classified as very severe soil erosion (Land Development Department, 2002).

Atrazine was found in 48 samples of topsoil (80% of all samples) and 50 samples of subsoil (83.3% of all samples) with average concentrations of 133.59 µg kg^{-1} and 183.23 µg kg^{-1}, respectively. The atrazine concentration was not present in concentrations greater than the standard limit (22 mg kg^{-1}). Though there was no significant difference in the average concentration between the topsoil and the subsoil, the atrazine content tended to be higher in the lower soil samples (Figure 2a). This might be due to the far higher hydraulic conductivity of the topsoil than that of the subsoil together with moderate solubility (~33 mg L^{-1}) of atrazine itself resulted in accumulation of leached atrazine from the topsoil in the subsoil. Additionally, the atrazine concentration varied greatly with time, as indicated by the concentrations occurring in the following order: November > August > September > October (Figure 2b). These differences likely occurred because more atrazine was applied during November and August than September and October.

Since atrazine is slightly alkaline, it is likely to be adsorbed easily by the slightly acidic soil. Adsorption of atrazine is also stronger in clay than in sandy clay loam and loamy sand, and atrazine had high mobility in loamy sand (Suwanketnikom and Sattayanikom, 1992; Oliveira et al., 2001). Additionally, adsorption of atrazine in dry soil is stronger than in moist soil (Panichsakpatana, 1996; Sesthaphakdee, 2001) and the soil with high organic matter content can adsorb atrazine stronger than that contains low organic matter (Bernhard et al., 1994; Konda et al., 2002; Riise and Petterson, 1994; Chefetz et al., 2006). For these reasons, atrazine was well absorbed both in the topsoil and the subsoil. It was gradually accumulated in the subsoil because of higher hydraulic conductivity of the topsoil. Since soil erosion was very severe, atrazine would be washed away with surface runoff (Table 1). This was similar with the cases of Glenn and Angle (1987), Ounok (2003) and Seanpan (2005).



a. Atrazine residues at each station b. Atrazine residues during each month

Figure 2 The average atrazine concentration of topsoil (0-15 cm) and subsoil (15-30 cm) during August-November 2008.

Table 1 Physical and chemical properties of topsoil (0-15 cm) and subsoil (15-30 cm) in maize cultivated area of Huay Kapo watershed.

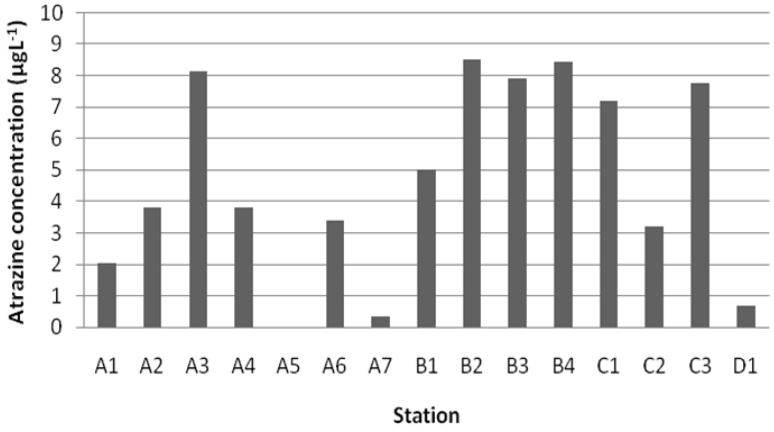
Soil properties	Topsoil	Subsoil
Clay (%)	23.60	25.10
Organic matter (%)	1.78	1.45
Moisture (%)	18.48	18.01
Bulk density (g cm^{-3})	1.56	1.64
Saturated hydraulic conductivity (m d^{-1})	4.608	1.190
Soil loss rate (t rai^{-1} yr^{-1})	19.224	
pH	5.0	5.0
CEC (cmol kg^{-1})	13.30	9.75

Atrazine Residues in Stream Water

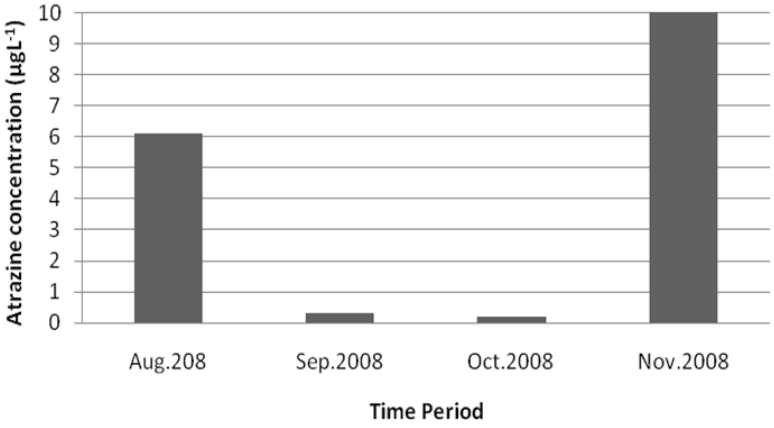
Among 24 out of 38 stream water samples, the average of atrazine concentration was 4.7 µg L^{-1}. This concentration was higher than the standard limit of atrazine concentration in drinking water set by USEPA (2003) and WHO (2003) at 3 µg L^{-1}. The noticeably high concentration of atrazine was found in 15 samples or 39.5 % of the total samples collected in August and November. This is coincide with the application of atrazine by the farmers who normally apply atrazine at the period of August and November higher than those of September and October which resulted in the concentration of atrazine in the stream water during the mentioned periods (Figure 3b). Moreover, field observation revealed that some farmers directly washed atrazine containers in stream in November. Among the stations, atrazine concentrations were different due to the difference of topography and the periods of atrazine application (Figure 3a). It was noticeably found that concentration of atrazine in the stream water of station A5 and A7 were very low. Atrazine concentration in stream water along the main stream A become low towards downstream probably due to dilution with watershed discharge responding to the major rain events on sampling day. Atrazine concentration in station A5 would be diluted by huge volume of water, while less maize cultivated area than other stations in station A7 would be considered as the main underlying factors to control the atrazine concentrations.

Atrazine Residues in Soil Sediment

Since parent materials of the soils in these areas were sandstone, the majority of the soil sediments was sand with low organic matter (0.45 %) and low



a. Atrazine residues at each station



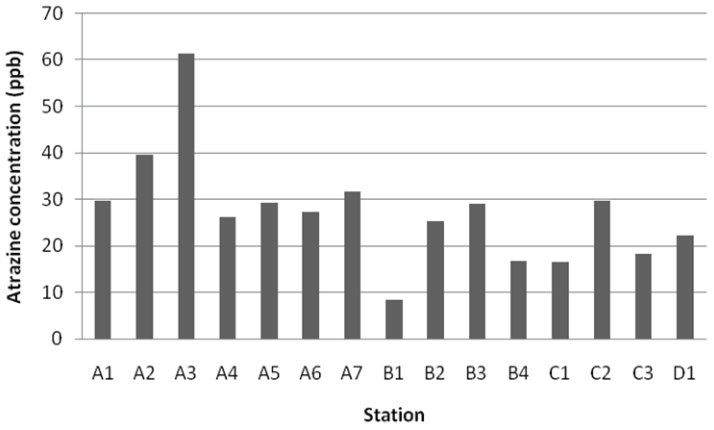
b. Atrazine residues during each month

Figure 3 The average atrazine concentration in the stream water in Huay Kapo Watershed during August-November 2008.

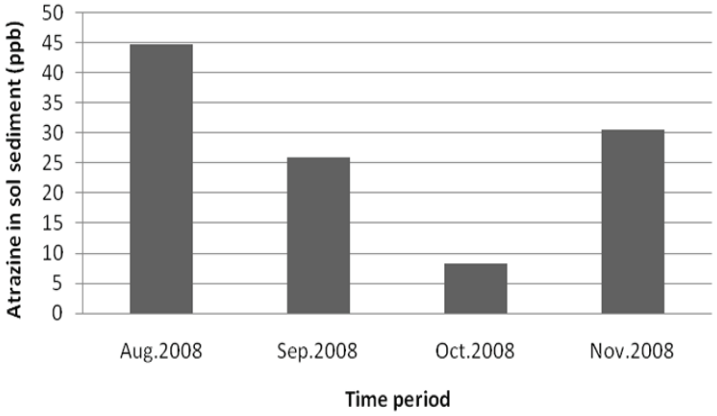
clay content (4.02 %). The soils those were primarily eroded from their origin were transported into aquatic environment and became the soil sediments. By this process the small particles of clay were washed away whereas the bigger particles were deposited beforehand. This resulted in the soil sediments with the coarser texture (Chunkao and Tungtham, 1974). The reaction of the soil sediments was weak acid with pH 6.5. Since adsorption is exothermic reaction and equilibrium of reaction between solid and liquid occurred at pH 6.1, adsorption of atrazine with the suspended solids could be considered as the main process of atrazine contaminated in this aquatic environment (Wild, 1993; Meakins et al., 1994; Kovaios et al., 2006). Furthermore, atrazine might be adsorbed by algae or biofilm present at the bottom of the stream as well (Alvord and Kadlec 1996; Gao et al., 1998). The average concentration of atrazine in 43 soil sediment samples (equivalent to 71.7 % of total sample) was 27.42 μgkg^{-1}. Atrazine residues in each station varied differently (Figure 4a) due to the differences of atrazine application in each station and stream characteristics. Atrazine residues in the soil sediments in each month showed the same tendency as those in the stream water (Figure 4 b).

Atrazine Transport in Upland Soil, Soil Sediment and Stream Water

Concentration of atrazine in upland soil was 4.87-fold greater than that in soil sediment and 39.0-fold greater than the concentration observed in stream water. The level of atrazine in the soil sediment was 5.87-fold greater than that in the stream water. Based on these results, the atrazine residues occurred in the following order: subsoil > topsoil > soil sediment > stream water (Figure 5a.) whereas the atrazine residues during each month were as follows: November > August > September



a. Atrazine residues at each station



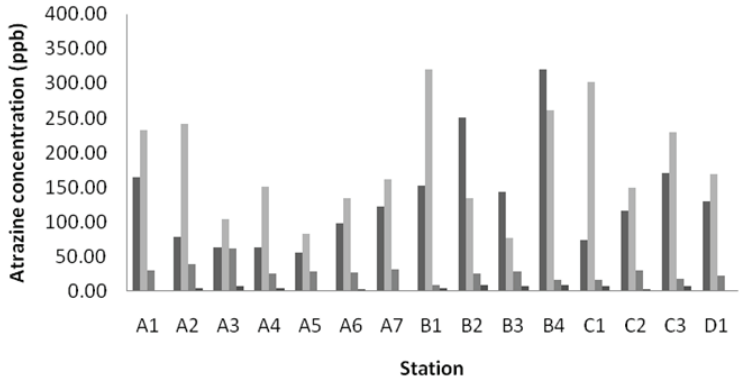
b. Atrazine residues during each month

Figure 4 The average atrazine concentration in soil sediment in Huay Kapo watershed during August-November 2008.

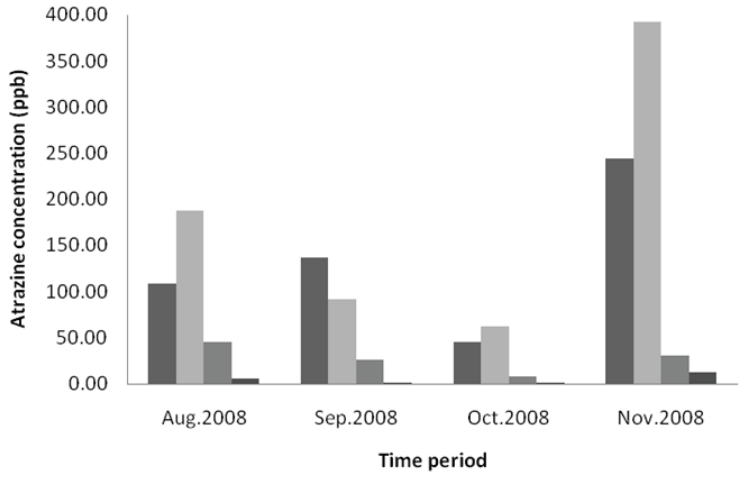
> October (Figure 5b), which likely reflects the application of greater levels during November and August than September and October when atrazine was mixed with other herbicides. Seanpan (2005) found that if there was insufficient rainfall intensity to induce runoff, degradation of atrazine occured more in the upper soil than in the lower together with the leaching of atrazine to the lower soil. When there was high intensity rainfall, more atrazine was lost from the upper soil as a result of surface runoff than leaching. Under this condition, decrease in the levels of atrazine in stream water would occur by dilution effect (Cann, 1995). However, soil particles that adsorbed atrazine were suspended in runoff and deposited into the bottom of stream. These findings are similar to those of a study conducted by Pimpan (1989) and Rice et al. (2004), who reported that pesticides were found in levels approximately 1-100 fold higher in soil sediment than those in stream water.

Conclusions

The average concentrations of atrazine in topsoil, subsoil, soil sediment and stream water were 133.59 μg kg^{-1}, 183.23 μg kg^{-1}, 27.42 μg kg^{-1} and 4.7 μg L^{-1}, respectively. Additionally, 15 stream water samples (39.5%) had atrazine concentrations higher than the maximum allowed in drinking water (3 μg L^{-1}). Atrazine residues in upland soil were found to be present in concentrations 4.87-fold higher than that in soil sediment and 39.0-fold higher than the levels in stream water. The atrazine residues in soil sediment were found to be 5.87-fold higher than that in stream water. In conclusion, atrazine was adsorbed in upland soil and transported from upland soil into the aquatic environment via runoff and leaching processes. Atrazine may inhibit photosynthesis in aquatic plants, thereby leading to a negative effect on aquatic ecology; therefore, the



a. Atrazine residues at each station



b. Atrazine residues during each month

Figure 5 Spatial and temperal variation of average atrazine concentration in upland soil, soil sediment and stream water in Huay Kapo watershed.

mechanisms involved in atrazine desorption from soil sediment to stream water and the toxicity of atrazine toward aquatic plants should be studied to develop methods of reducing pesticide contamination in aquatic environments.

Acknowledgments

The authors would like to express their sincere gratitude to the King's Royally Initiated Laem Phak Bia Environmental Research and Development Project for their cooperation. This study was funded by the Royal Golden Jubilee Ph.D. Scholarship, Thailand Research Fund and the EIA Project, College of Environment, Kasetsart University.

References

Alvord, H.H. and R.H. Kadlec. 1996. Atrazine fate and transport in the Des Plains Wetlands. Ecological Modeling 90: 97-107.

APHA, AWWA, and WEF. 1992. Standard Methods for Examination of Water and Wastewater. American Public Health Association, USA.

Attanandana, T. and J. Chanchareonsook. 1999. Manual of Soil and Plant Analysis Practice. Kasetsart University, Bangkok.

Baiadul, P. 2001. The Development of Pesticide Analytical Technique; Atrazine, Desethyl Atrazine, Desisopropyl Atrazine, Ametryn, and Metribuzin in Water Sample by Gas Chromatography. Department of Agriculture, Bangkok.

Bernhard-Bitaud, M. Schiavon, and F. Andreux. 1994. Environmental Behavior of Pesticides and Regulatory Aspects, European Study Service, Belgium.

Cann, C. 1995. Equation of atrazine transfer from agricultural land to surface water. Phys. Chem. Earth 20: 359-367.

Chefetz,B., K. Stimler, M. Shechter,and Y. Drori. 2006. Interactions of sodium azide with triazine herbicides: effect on sorption to soils. Chemoshere 65: 352-357.

Chunkao, K and N. Tungtham, 1973. Principles of Watershed Management. Kasetsart University, Bangkok.

Gao, J. P., J. Maguhn, P. Spitzauer and A. Kettrup. 1998. Sorption of pesticides in the sediment of the teufelsweiher pond (Southern Germany) II: competitive adsorption, desorption of aged residues and effect of dissolved organic carbon.Water Res. 32: 2089-2094.

Glenn, S. and J.S. Angle. 1987. Atrazine and simazine in runoff from conventional and no-till corn watersheds. Agric. Ecol. Environ. 18: 273-280.

Konda, L. N., Gy. Fuleky, Gy. Morovjan and P. Csokan. 2002. Sorption behavior of acetochlor, atrazine, crabendazim,diazinonimidacloprid and isoproturon on Hungarian agricultural soil. Chemosphere 48: 545-552.

Kovaios, I.D., C.A. Paraskeva, P.G. Koutsoukos and A.Ch. Payatakes. 2006. Adsorption of atrazine on soils: Model study. J. Colloid Interface Sci. 299: 88-94.

Land Development Department. 2002. Soil Loss Assessment in Thailand. Ministry of Agriculture, Bangkok.

Meakins, N.C., J.M. Bubb and J.N. Lester. 1994. The behaviour of the s-triazine herbicides, atrazine and simazine, during primary and secondary biological wastewater treatment. Chemosphere 28: 1611-1622.

Ministry of Public Health Welfare and Sport. 1996. Analytical Methods for Pesticide Residues in Foodstuff. 6th ed. The Netherlands.

Oliveira, R.S.,W.C. Koskinen and F.A. Fereira. 2001. Sorption and leaching potential of herbicides on Brazillian soils. Weed Res. 41: 97-100.

Ounok, K. 2003. Application of modeling of pesticide transportation in environment, cabbage cultivated area in Mae Jam watershed, Chiangmai Province. Thesis. Kasetsart University, Bangkok.

Panichsakpatana, S. 1996. Soil Pollution from Chemical Uses. Kasetsart University,Bangkok.

Pimpan, P. 1989. Toxic elements in aquatic and management. Toxic Subst. Bull. 16: 130-137.

Rice, P.J., T.A. Anderson and J.R. Coats. 2004. Effect of sediment on the fate of metolachlor and atrazine in stream water. Environ. Toxicol. Chem. 23: 1145-1155.

Riise, G. and M. Nandrup Petterson. 1994. Association of Diclorprop and Atrazine with Soil Organic Carbon. European Study Service, Belgium.

Seanpan, S. 2005. Effect of land use to atrazine in stream water and soil sediment in KlongE Tao, Wang Nam Khew District, Nakornratchasrima Province. Thesis. Kasetsart University, Bangkok.

Sesthapakdee, M. 2001. Introduction to Soil Science. 8th Edition. Faculty of Engineering and Agricultural Technology, Rajchamongkol Thanyaburi University, Bangkok.

Suwanketnikom, R. and R. Sattayanikom. 1992. Adsorption, desorption and mobility of s-triazine herbicides in soils. Thai Agri. Res. J. 10: 35-41.

Thurman, E.M. and M.S. Mills. 1998. Solid-Phase Extraction principles and Practice: Chemical analysis: A Series of Monographs on Analytical Chemistry and its Application. USA.

United State Environmental Protection Agency (US.EPA.). 2003. Edition of the drinking water standards and health advisories: EPA 822-R-02-038.

Wild, A. 1993. Soil and The Environment: An Introduction. Cambridge University, New York.

World Health Organization (WHO). 2003. Guideline for Drinking Water Quality.

Zweig, G. 1972. Pesticide and Plant Growth Regulators. Academic Press, USA.

Manuscript received 5 February 2010, accepted 15 December 2010