The Residues of Atrazine Herbicide in Stream Water and Stream Sediment in Huay Kapo Watershed, Phetchabun Province, Thailand

On-Anong Phewnil[1]*, Nipon Tungkananurak[1], Supamard Panichsakpatana[2], Bongotrat Pitiyont[3], Namyen Siripat[4], and Hirozumi Watanabe[5]

[1]*College of Environment, Kasetsart University, Bangkok 10900, Thailand.*
[2]*Faculty of Agriculture, Kasetsart University, Bangkok 10900,Thailand*
[3]*Faculty of Science, Kasetsart University, Bangkok 10900, Thailand*
[4]*Department of Agriculture, Ministry of Agriculture and Cooperatives, Bangkok 10900,*
[5] *Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan.*

Abstract

The Huay Kapo watershed is located in Phetchabun Province in northern Thailand. The area has always been used to cultivate maize (*Zea mays* L.) by the application of atrazine at 1.25-1.56 kg/ ha. The Objective of this study is to monitor atrazine concentrations in stream water and stream sediment in the Huay Kapo watershed. Based on the data monitored from 15 sample sites each month during the wet season (August-November 2008), the average atrazine concentrations in stream water and sediment samples were 4.7 µg/L and 27.42 µg/ kg, respectively. The content of atrazine in stream sediment was 5.87-fold significantly higher than that in the stream water.

Key words: atrazine/ residues/ maize/ stream sediment/ stream water/watershed

1. Introduction

Thailand has been importing great amounts of herbicides. In 2007, atrazine, at an amount of 3,686,650 kg was ranked the seventh of the imported pesticides to Thailand. It has been widely used to control narrow-leaf and broad-leaf annual weeds amongmaize, sorghum, pine apple, and sugarcane plantations in several areas of cultivation. Impact on the aquatic ecosystems is likely to occur if atrazine is transported from cultivated areas by runoff or leaching. The Huay Kapo watershed, located in Lakdan Sub-District, Nam Nao District, Phetchabun Province in northern Thailand, is mostly mountainous (elevation between 400-920 m). Atrazine has been used intensively for weed control in the maize cultivation area in the watershed. The watershed is reported to suffer from a high rate of soil loss (120.15 ton/ha/yr) (Royal Thai Army, 2008). The average slope is approximately 18%. Maize has always been cultivated in the area (*Zea may* L.) by the application of atrazine in concentrations of 1.25-1.56 kg/ha, which has caused atrazine contamination of the stream water and the stream sediment. The atrazine absorption in the field soil and the transportation by means of soil erosion are probably the major processes which attribute to the atrazine contamination of the aquatic environment of the watershed. Atrazine losses by runoff water and soil erosion were reported previously to be 0.00-31.3 g/ha/yr and 0.09-9.82 g/ha/yr, respectively (Attanandana and Chanchareonsook, 1999) as reported in literature. In order to determine the fate of atrazine and its distribution in the aquatic environment of the Huay Kapo watershed, the atrazine residues in stream water and stream sediment in the watershed called for investigation. Moreover, the consequent results of such a study are useful to formulate the impact of atrazine on the water quality standard in stream

*Corresponding author
E-mail: fgraonp@ku.ac.th

waterways in Thailand and to reduce pesticide residues in the aquatic environment in the future. Aims of this study are to monitor the atrazine concentrations in both stream water, and the stream sediment on the riverbed in the Huay Kapo watershed.

2. Methodology

2.1 Study area

The study of residues of atrazine herbicide in stream water and stream sediment was performed in the Huay Kapo watershed, Lakdan Sub-District, Nam Nao District, Phetchabun Province, Thailand. The secondary data such as land use, topography, and community area was compiled from the 1:50,000 geographic map of the area. The expected data collected from the community in the study and surrounding areas was pertinent to pesticide use, application date of pesticide, amount of pesticide applied, and the agricultural calendar. Thirty-six of the totals of 323 sample interviews were with farmers from the Huay Kapo community. The remaining interviews were done with farmers within 5 km of the study area.

2.2 Stream sediment and water sampling

The samples of stream sediment and stream water were collected from 15 study sites distributed in Huay Kapo watershed, Lakdan Sub-District, Nam Nao District, in Phetchabun Province (Figure 1). Sampling stations A1-A7 were located on the main stream "A" of the watershed. Stations B1-B4 and D1 were on the first order of streams "B" and "D", respectively in the west of the watershed. Stations C1-C3 was on the first order of stream "C" in the north of the watershed. The monitoring of atrazine concentration in stream water and sediment was conducted during the wet period from August through November 2008, which coincided with the application period of atrazine by the farmers. The sampling periods comprised of 19-20 August 2008, 19-20 September 2008, 19-20 October 2008, and 19-20 November 2008.

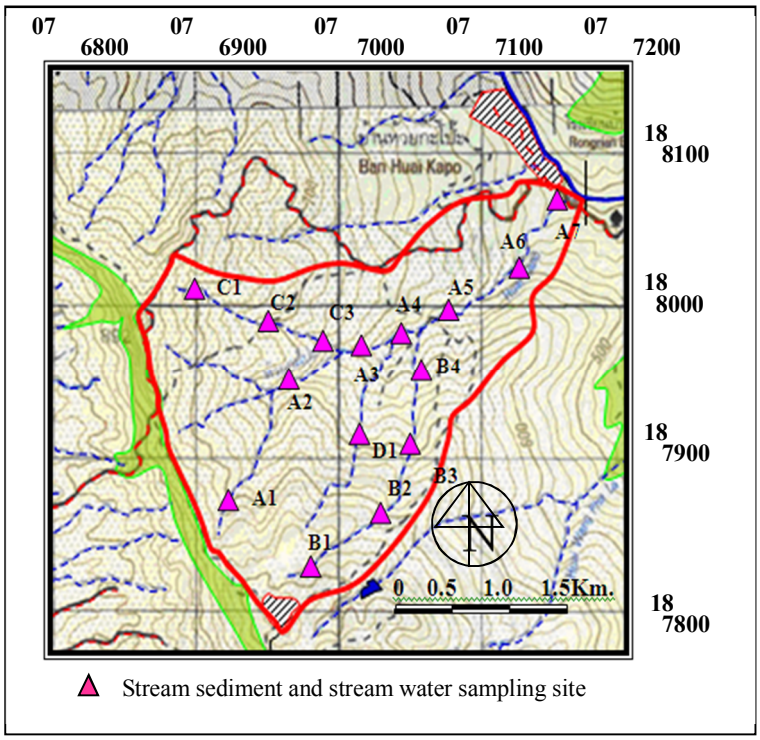

Figure 1 Sampling stations of stream sediment and stream water in the Huay Kapo watershed, Lakdan Sub-District, Nam Nao District, Phetchabun Province.

The stream sediments on the river bed were collected with a stainless spade with a depth of approximately 15 cm. to obtain composite samples from each station. Such a practice resulted in a total of 60 stream sediment samples. All samples were kept in black bags to prevent photodecomposition and subsequently stored in at 4°C in an ice storage tank prior to transfer to the laboratory (Gao et al., 1998). The stream sediment samples were dried, ground and sieved (diameter of 2.0 mm and 0.5 mm) for determining the physical and chemical properties (Attanandana and Chanchareonsook, 1999).

Four liters of stream water were collected monthly from 15 stations during the monitoring period. The stream water was sampled one liter at a time by means of a glass bottle for the atrazine determination at a depth of 30 cm from the water surface. A total of sixty stream water samples were taken. All samples were stored at 4°C in and ice storage tank and transferred to the laboratory within 48 hours (APHA, AWWA and WEF, 1992).

2.3 Chemical analysis

The atrazine concentration was determined by means HPLC (Ministry of Public Health Welfare and Sport, 1996; Zweig and Sherma, 1972). The method used to measure the atrazine concentrations in both the stream sediment and the stream water (Baiadul, 2001; Thurman and Mills, 1998) were as follows:

2.3.1 Atrazine in stream sediment: atrazine was extracted with a solid phase extraction cartridge, SCX-Verti Pak cartridge (Vertical, USA). Approximately 100 g of soil was briefly suspended in 99 ml. of acetronitrile/water (9:1, v/v), prior to the addition of one milliliter (0.2 mg/ml. atrazine) of the standard

solution and subsequent vigorous agitation for five minutes. The samples were then filtered through a paper filter (Whatman GF/C), with the first 5 ml. of filtrate discarded with the remaining 10 ml. used for the analysis. The cartridges were then flushed with one column volume of acetic acid (1%), prior to the addition of 2 ml. of acetic acid (1%). 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, followed by one column volume of water, and finally 1 ml. of 0.1 M dipotassium hydrogen phosphate. Between the individual rinses, the cartridge was briefly dried for approximately 15 seconds in a vacuum. The cartridges were then eluted with 2 ml. acetonitrile/0.1 M dipotassium hydrogen phosphate (1:1). Finally, the samples were filtered with a nylon sieve and 2 µL of each sample was injected into the HPLC.

2.3.2 Atrazine in stream water: atrazine was solid phase extracted with the application of a C18-VertiPak cartridge (Vertical, USA). The cartridges were conditioned with 5 ml of methanol and 5 ml of distilled water prior to use. A 1,000 ml sample of surface water was briefly passed through a suitable glass fiber filter and acidified with 2 ml of the concentrated hydrochloric acid. 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 subsequently dried in a vacuum for the duration of 20 minutes. The cartridges were then eluted with 15 ml. of acetronitrile concentrate and eluted in a vacuum with nitrogen gas. Finally, the samples were sieved through a nylon filter and a 2 µl of each sample was injected into the HPLC.

2.3.3 HPLC analysis: 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 was used. 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. The detection limits of atrazine for water and sediment samples were set at 0.01 µg/L and 0.01 µg/kg, respectively. The recovery ratio of atrazine in water and sediment were 97.0±0.2% (n=3) and 98.0±0.2% (n=3), respectively.

3. Results and Discussion

3.1 Atrazine application and hydrological condition in watershed

The analysis of the data revealed that most farmers (93.7%) perform rain-fed agriculture. Most of the interviewed farmers (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 three maize crops a year. Most of the farmers (85.7%) use agricultural chemicals, whereas atrazine was applied in an approximate concentration of 1.25-1.56 kg/ha in granule twice per crop for pre planting in August and November and mixed with other herbicides such as paraquat, glyphosate, ametryn, and alachlor for spraying during the cultivated crop periods.

Daily rainfall measured at the Lom Sak weather station, located approximately 20 km. from the Huay Kapo watershed for August, September, October and November, respectively. The corresponding area enjoyed frequent

rainfall in August and September. Approximately 34.1 mm and 14.5 mm. of rainfall were observed at the weather station on a sampling day in August. The rainfall became less significant during September and with the start of the dry season in October (Figure 2).

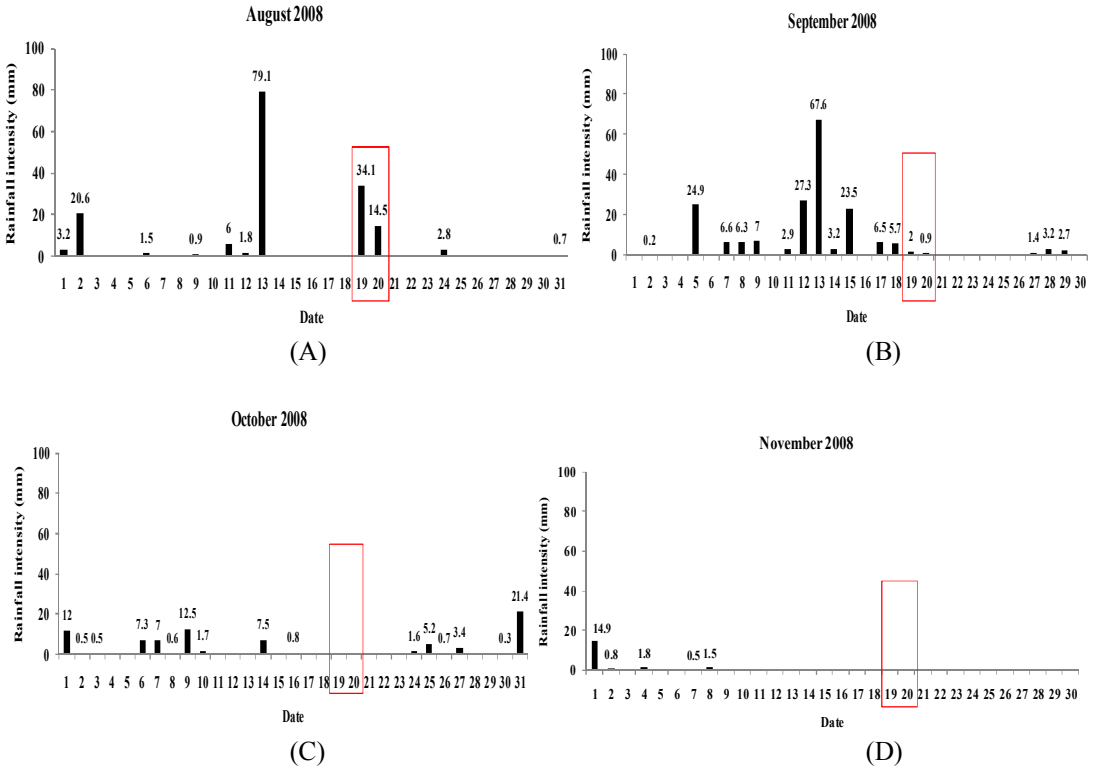

Figure 2 Rainfall intensity in the sampling site during the wet season from August (A) to November 2008 (B), during the wet season from October (C) to November 2008 (D)

3.2 Atrazine residues in stream water

The highest detected concentration was 33.80 µg/L at station B2 in November, and the detected average concentration for stream water samples were 6.13, 0.28, 0.24, 12.09 µg/L, respectively for August, September, October, and November (Figure 3). The 38 samples of stream water, or 63.3% of total stream water samples, were atrazine contaminated with an average concentration of 4.7 µg/L. Due to the villagers in Huay Kapo community using water from the stream for domestic consumption, there is a risk to their health. Such a concentration exceeded the standard limit for atrazine concentration in potable water set forth by US.EPA (2003) and WHO (1973) at 3 µg/L.

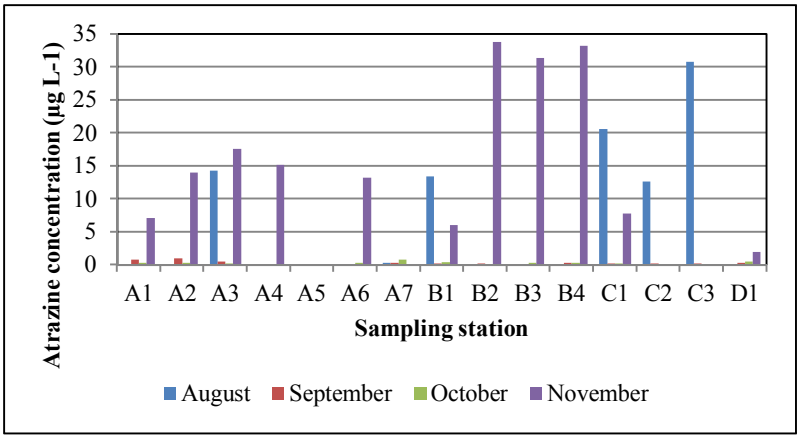

Figure 3 Average of atrazine concentrations in stream water in the Huay Kapo watershed between August to November 2008.

The noticeably high levels of concentration of atrazine in stream water above 3 µg/L was found in 15 samples, or 39.5% of the 38 samples, collected in August and November, while only 61.13% of the samples collected in September and October had detectable concentration levels with a maximum of 1.0 µg/L. These findings coincide with the pattern of atrazine usage by the farmers. The agriculturalists generally apply larger amounts of atrazine in the months of August to November, whereas less atrazine is usually applied in September and October, This pattern of usage is reflected by the levels of atrazine concentrations in the stream water during the monitored period. Detected atrazine concentrations in the Huay Kapo watershed are in line with previous studies. The report on atrazine concentrations in stream water and stream sediment in the Klong E Tao Sub watershed, Nakorn Ratchasima Province, Thailand, revealed a range of approximately 0.03 µg/L to 4.45 µg/L (Saenpan, 2005). In Kansas, USA, atrazine concentrations were previously reported to be detectable throughout the year with a maximum concentration of 22.0 µg/L in early June. This measurement coincided with maximum runoff and erosion (Kansas Department of Health and Environment, 1998). Among the stations, atrazine concentrations were different, this is potentially due to the diverse local topography, occurrence of rainfall, rainfall intensity and atrazine application in the sub basin (Figure 3). In August, atrazine was mainly detected in stream water of the C tributary with concentration levels in the range of up to approximately 30.8 µg/L, which corresponds to the reported atrazine concentrations in a local stream in Kansas USA (Kansas Department of Health and Environment, 1998). However, the highest atrazine concentration (time-weighted) from the field runoff over a period of 60 minutes of rainfall event was reported as 449 µg/L. The decrease in Atrazine concentrations in the tributary water along main stream A becomes lower further downstream due to the probable dilution with the watershed discharge which correlates with the significant precipitation on the day of sampling. This also corresponds to the reported atrazine concentration in the aforementioned local stream in Kansas USA (Kansas Department of Health and Environment, 1998). Data points such as A3 and B1 potentially reflect the use of insignificant amounts of atrazine locally.

Whereas in November, the majority of atrazine in the watershed was detected in main stream A and tributary B. The elevated concentration level exceeded 30 µg/L in tributary B. The rainfall data illustrated in Figure 2 suggests the watershed discharge consists mainly of base flow, whereas no field runoff is expected. Possible sources of atrazine load in this stream water are the irrigation return flow and point source discharge of locally used atrazine. The field observation revealed that some farmers directly washed atrazine containers in the stream B in November.

3.3 Atrazine residues in stream sediment

Elevated atrazine concentration in stream sediments were detected in most parts of the watershed except in downstream main river A in August. The average concentration of atrazine for 43 detected stream sediment samples (equivalent to 71.7% of total stream water samples) was 27.4 µg/kg with the highest over 100 µg/kg. Atrazine residues in each station varied differently probably due to its application in each station and stream characteristics as in the concentration of stream water. Atrazine residues in the stream sediments in each month also related to atrazine application periods when it was used in granule form for pre planting in August and November. Detected average concentrations in the stream sediments were 44.74, 24.97, 8.35, 30.62 µg/kg, respectively for August, September, October, and November (Figure 4).

Since the parent material of the soils in the assessed areas consisted of sandstone, most of the stream sediments were found to be sand with low contents of organic matter (0.45%) and low levels of clay content (4.02%). The soil erosion process and sediment transport in the stream are responsible for the coarse texture of the sample of stream sediments in the river bed (Chunkao and Tungtham, 1993). The stream sediments were slightly acid with a pH 6.5. Since the atrazine adsorption is an exothermic reaction and the equilibrium of the reaction of solids and liquids occurred at a pH level of 6.1, the adsorption of atrazine in the suspended solids is potentially due to the main process of atrazine contamination in the aquatic environment (Meakins et al, 1994; Kovaios et al., 2006). Furthermore, atrazine is likely to be absorbed by algae or biofilm at the bottom of the stream (Alvord and Kadlec, 1996). Reported atrazine concentration in the stream sediment in China and Western Mediterranean Sea in the estuary sediment were found to be in range from 0.008 µg/kg (Gfrerer et al., 2002) to 82.0 µg/kg (Gómez-Gutiérrez et al., 2006). In Thailand, the reported atrazine concentration in the stream sediment was in an approximate range of 1.00 µg/kg to 179 µg/kg (Saenpan, 2005).

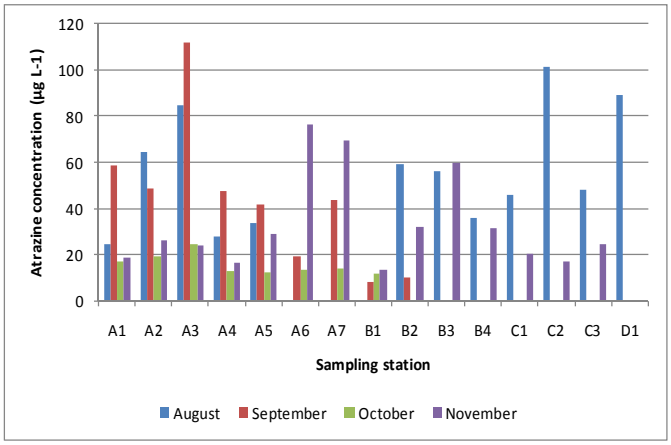

Figure 4 Average concentration of atrazine in soil sediment in Huay Kapo watershed between August to November 2008

3.4 Relation of atrazine residues in stream sediment and stream water

The results from these observations revealed the concentration of atrazine in the stream sediments to be 5.87 fold of that in the stream water. Based on these results, the levels atrazine residues present in stream sediments for each month were determined in respect of concentrations as follows: The highest concentrations were established in November, followed by August and September with the lowest concentrations in the month of October. The concentration levels of atrazine residues in stream water were found as follows: the highest concentrations levels in August, followed by the months of November and September, while October revealed the lowest concentration levels. However, atrazine residues both in the stream sediments and in the surface water were quite evident in August and in November (Figure 5) 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, 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 at the bottom of streams.

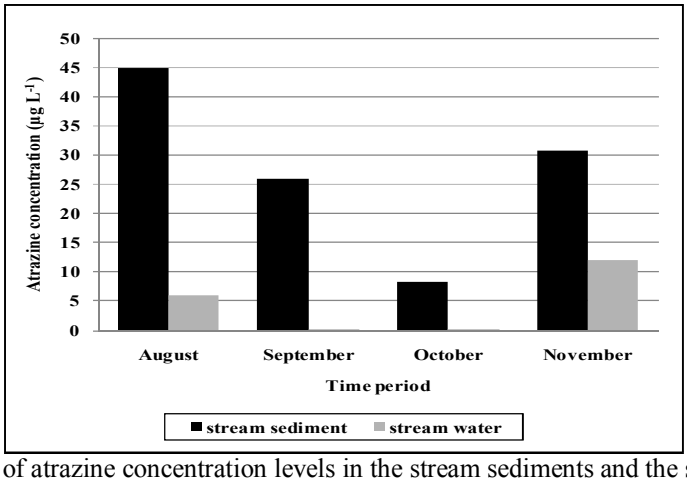

Figure 5 Average of atrazine concentration levels in the stream sediments and the stream water in the in Huay Kapo watershed.

The concentration of atrazine in the stream water does not largely reflect the absorption of atrazine in the stream sediments. Such an absence of correlation is likely to be due to the divergence of in the time scale between the atrazine transport in stream water and the sorption kinetics in the water sediment system. Atrazine transport in stream water is influenced by the field conditions such as tillage practice, pesticide application method, amounts of precipitation, the timing of the atrazine application (Watanabe et al., 2007), as well as the stream characteristics at each station. Pesticides concentrations found in stream sediments were approximately 1-100 folds of those of the surface water (Pimpan, 1989). Conversely, the atrazine sorption process occurs in a relatively short period such as 24 hours (Apiwatkaroon, 2005). Upon the fresh application, levels of atrazine contamination were established in both the sediments and the stream waters. The residues determined in the sediments subsequently decreased over a period of a fortnight (Figure 5). However, levels of atrazine residues in the surface water were only marginally reduced during the identical time frame (Figure 3). These findings correlate with the decrease of pesticide concentration present in both the stream sediment and the stream water (Rice et al., 2004).

4. Conclusions

The average atrazine concentration in the stream sediment and the surface water in the Huay Kapo watershed were determined to be 27.4 µg/kg and 4.7 µg/L, respectively. As many as 15 samples (39.5%) of the surface water contained atrazine contamination levels in excess of the maximum limit permissible for potable water (3 µg/L). The atrazine residue levels established in the stream sediment was 5.87 fold of that found in the surface water. Subsequently, after its application, atrazine was adsorbed in upland soils and rapidly transported from the elevations into the aquatic environment. Atrazine residue in the sediments was degraded by 50% within a month, this significant decrease helped attain minimal levels of residue in stream water l within an identical time period. Further studies of conditions which favor atrazine desorption from the stream sediment to the surface water are called for in order to analyze the toxicity of atrazine in aquatic plants, since atrazine has the potential to inhibit the photosynthesis process of aquatic plants, which negatively impacts the aquatic ecology.

5. Acknowledgements

The authors would like to acknowledge the King's Royally Initiated Laem Phak Bia Environmental Research and Development Project for cooperation. This study was funded by the Environmental Impact Assessment Project, College of Environment, Kasetsart University.

6. References

Alvord, H.H. and Kadlec, R.H. 1996. Atrazine fate and transport in the Des Plains Wetlands. **Ecological Modeling** 90(1): 97-107.

American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). 1992. **Standard Methods for the Examination of Water and Wastewater**. 18th ed. Washington, DC: American Public Health Association.

Apiwatkaroon, D. 2005. **Adsorption Isotherm of Atrazine**. Bangkok: Kasetsart University.

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

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

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

Chunkao K. and Tungtham N. 1993. **Principles of Watershed Management**. Bangkok: Kasetsart University.

Gao, J.P., Maguhn, J., Spitzauer, P., and Kettrup, A. 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 Research** 32: 2089-2094.

Gfrerer, M., Martens, D., Gawlik,B.M., Wenzl, T., Zhang, A., Quan, X., and Kettrup, A. 2002. Triazines in the aquatic systems of the Eastern Chinese River Liao-He and Yangtse. **Chemosphere** 47: 455-466.

Gómez-Gutiérrez, A.I., Jover, E., Bodineau, L., Albaigés, J., and Bayona, J.M. 2006. Organic contaminant loads into the Western Mediterranean Sea: estimate of Ebro River inputs. **Chemosphere** 65: 224-236.

Kansas Department of Health and Environment 1989. **Atrazine in Kansas, Water Quality Assessment Section**. Manhattan, Kansas: Bureau of Water Protection, Department of Health and Environment.

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

Meakins, N.C., Bubb, J.M., and Lester, J.N. 1994. The behavior 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**. Netherlands.

Pimpan, P. 1989. Toxic elements in aquatic and management. **Toxic Substance Bulletin** 16: 130-137.

Rice, P.J., Anderson, T.A., and Coats, J.R. 2004. Effect of sediment on the fate of metolachlor and atrazine in surface water. **Environmental Toxicology and Chemistry** 23 (5): 1145-1155.

Royal Thai Army. 2008. **Quality of Life Development Project in Upstream Nam Nao Watershed, Phetchabun Province (Year 2006-2008).** Phetchabun, Thailand.

Saenpan,S. 2005. **Effect of land use practices on atrazine in stream flow and sediment of Klong E Tao sub watershed, Wang Nam Khieo district, Nakhon Ratchasima province**. Bangkok: Kasetsart University.

Thurman, E.M. and Mills, M.S. 1998. Solid-phase Extraction Principles and Practice. In: Windfordner, J.D. (ed.)**: Chemical Analysis: a series of Monographs on Analytical Chemistry and its Applications**

(Vol. 147). New York: Wiley-Interscience.

United State Environmental Protection Agency (USEPA). 2003. **Edition of the Drinking Water Standards and Health Advisories**. USA.

Watanabe, H., Watermeier, N.L., Steichen, J.M., Barnes, P., and Phong, T.K. 2007. Impacts of tillage and application methods on atrazine and alachlor losses from upland fields. **Weed Biology and Management** 7: 44-54.

World Health Organization (WHO). 1973. **Guideline for Drinking Water Quality**. USA.

Zweig, G. and Sherma, J. 1972. **Analytical Methods for Pesticides and Plant Growth Regulators**. New York: Academic Press.