Bioavailable Cadmium in Water, Sediment, and Fish, in a Highly Contaminated Area on the Thai-Myanmay Border

O. Krissanakriangkrai[1], W. Supanpaiboon[2], S. Juwa[1], S. Chaiwong[1], W. Swaddiwudhipong[3] and Anderson K. A.[4]
[1] Faculty of Public Health, Naresuan University
[2] Faculty of Medical Science Naresuan University
[3]Department of Community and Social Medicine, Mae Sot General Hospital
[4]Department of Environmental and Molecular Toxicology, Oregon State University
E-mail: koraphin@hotmail.com

Abstract

Mae-Sot District in Tak Province is contaminated with high cadmium levels. Studies have found high concentrations of cadmium in rice fields and grain. People in this area have experienced high cadmium levels in their urine resulting in kidney problems. Cadmium concentrates in fish and shellfish by accumulating in their muscle tissue, and may result in posing a health risk to fish consumers. This study was to determine the magnitude of cadmium pollutants in water, sediment, fish and shellfish that have been found to cause adverse effects to humans. Water and sediment samples were collected from 9 sites along Mae-Toa creek. Six fish species and one shellfish species were caught from 3 sites along Mae-Toa creek. Seasonal variations in the bioavailable cadmium concentrations were observed. Rainy months were found to have higher cadmium concentrations than during dry months. Cadmium levels in the river sediment exceed the allowable standard. The highest concentrations of cadmium were detected in Swamp eel (0.27 mg/kg wet weight). Concentrations of cadmium in pond snail were 0.13 mg/kg-wet weight. According to human health risk assessment the hazard quotient (HQ) from eating Swamp Eel was 1.3 which is higher than one. As a result of this study, adverse health effects may occur and remediation is needed.

Keyword: Bioavailability, Cadmium, Fish/Shellfish, Mae-Sot, Health Risk assessment, Seasonal-variation.

1. Introduction

The toxicity of trace pollutants to aquatic organisms is related to the bioavailable fraction of contaminants available for assimilation. Bioavailability is defined as the fraction of the total amount of a chemical substance that can be taken up by living organisms within a certain time span [1]. The effects of metal contamination in aquatic systems are of particular concern due to their persistence and toxicity. Unlike organic contaminants whose toxicity decreases with biodegradation, metals cannot be degraded further and their toxic effects can be long lasting [2]. Mining sites are especially at risk, with metal concentrations coming in at several orders of magnitude higher than those for uncontaminated sites [3]. Of greatest concern is the potential adverse human health risks associated with the consumption of fish and shellfish from contaminated areas.

Storm water runoff is estimated to be one of the largest contributors of pollutants to coastal areas, oceans and inland waterways [4]. While storm water runoff may only occur during a few days or weeks of the year, it can contribute a pulse of pollutants to the river system [5]. Schiff found that while runoff from urban surfaces accounted for only 9% of the total discharge volume, it accounted for 34-41% of metals entering the Santa Ana River in California [6].

Cadmium is an element that occurs naturally in the earth's crust and is released to the environment from point sources such as industrial discharges and from non-point sources such as agricultural runoff [7]. There is concern over the elevated levels of cadmium entering the environment as a result of improper mining techniques and from the fertilizer applied to agricultural fields, which may contain up to 1500 mg/kg on a dry material base [8].

Mae-Sot District in Tak Province is contaminated with high levels of cadmium. Previous studies have found high concentrations of cadmium in the rice fields and rice grains [9, 10]. People that live in this area have high levels of cadmium in their urine and have experienced kidney problems [11]. Cadmium accumulates in fish and shellfish by accumulating in their muscle tissue. Even extremely low concentrations of bioaccumulating cadmium (detected in water or bottom sediment) may result in fish or shellfish posing a health risk to fish consumers.

The objectives of this study were to develop a better understanding of the spatial and temporal transport and fate of bioavailable cadmium along the Mae-Toa creek and in so doing, evaluate various estuary sampling in the environmental risk assessment process. The evaluation included: 1) surface water; 2) bottom sediment; and 3) aquatic organisms (fish and shellfish) for determining bioaccumulation of toxic metals.

2. Materials and Methods

Study area

The field site is located on the Mae-Toa Creek, Mae-sot District in Tak Province, Thailand. Nine sampling stations were designated in a 2 kilometers portion of the Mae-Toa Creek. This is a rural community segment of the river with significant agricultural and mining uses.

The sample locations were selected to represent various anthropogenic uses. The 2 stations located in Prathart Padang Sub-district were classified as upstream pristine. The next 2 stations in Mea-Ku Sub-district were classified as rural community areas, as shown in Figure 1.

Field sampling

Whole water grab samples and bottom sediment samples were collected at the same location during dry (March) and wet (June) events in 2006. This was done to investigate how seasonal fluctuations affect cadmium levels. All samples were transported on ice and stored at 4ºC until processing and analysis.

Fish were collected from sampling points 6, 8, and 9. Six species of fish and one shellfish were caught including: batrachian walking catfish (*Clarias batrachus*), common climbing perch (*Anabus testudimeus*), Swamp eel (*Fluta alba*), striped snake head fish (*Channa stiatus*), red-tailed snake head (*Channa gachua*), temminck's kissing (*Helostoma temmicki*), and pond snail (*Sinotaia ingallsiana*). Fish were collected by hook line and sacrificed by a quick blow to the head. Shellfish were collected from the sediment in the river.

Pond snails were chosen as a test species because of their importance in the human diet and aquatic food web. Each individual fish and shellfish was immediately wrapped in aluminum foil and placed in a zip lock bag and kept at 4°C for transport to the laboratory.

Sample processing and analysis

Sample processing and analysis of trace metals were performed under a laminar flow hood using clean techniques. Whole water grab samples were filtered thru 0.45 μm filter prior to amalysis in order to quantify dissolved cadmium. Water samples were analyzed using the EPA method 200.5 [12]. Bottom sediment samples were dried and ground prior to analysis. Sediment samples were analyzed using the EPA method 3050B [13]. To avoid metal contamination, all equipment was rinsed with 10% HNO_3.

Each of the fish and shellfish samples was prepared within 24 hrs of delivery to the laboratory. For fish, sex, weight, and length were recorded. Individual whole fish were homogenized in a high-speed blender (Robot Coup ® Bixer FSI BX 6) using liquid nitrogen. Samples were maintained frozen at -20°C until analysis. Approximately 1 g wet weight of fish and pond snail were digested with 3 ml of 66% HNO_3. Samples were digested overnight at ambient temperature, for 1 hr at 70°C, followed by 1 hr at 100°C, then 130°C, until the tissue was completely digested. Trace elements in water, bottom sediment, and fish tissues were quantified by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Varian ICP-AES Liberty 150). The analysis method of heavy metals in animal tissues using ICP-AES has been previously detailed [1].

Quality control

Quality control (QC) samples represented 40% of all samples analyzed. QC samples included: trip blank, field blank, fortified samples, certified reference material (CRM), laboratory duplicates, laboratory blanks, and check standards; each QC type was included in all batches. The average percent recoveries of fortified grab water at 20 μg/L of cadmium was 87%. The average recovery of CRM TORT-2 (National Research Council Canada) Lobster hepatopancreas of cadmium was 111%. The average percent recovery of NIST (National Institution Standard and Technology) 1640 Trace Elements in Natural Water CRM for cadmium was 72%.

The duplicates relative percentage difference (RPD) for all laboratory duplicates was $\leq$ 25%. Calibration curves were composed of at least three standard concentrations. The instrument linearity was determined from 3 standard concentrations. The instrument detection limits were determined from 3 standard deviations of 7 blanks. Instrument detection limits were determined to be 0.5 μg/L.

3. Statistical analyses

Wilcoxon Sign Rank Test, Mann-Whitney U Test, and Tukey Kramer were used to determine differences in cadmium concentrations collected from surface water and sediment between collection events and between downstream and up-river sampling locations. All the statistical analyses were performed using SPSS 11.5 software.

4. Results and Discussion

Spatial and temporal distribution of cadmium in surface water

Figure 2 shows the distribution of cadmium levels in surface water collected during the summer and rainy seasons in 2006 from the Mea-Toa Creek. There was statistical evidence that the seasonal temporal distribution of cadmium concentrations in surface water between the two seasons of sampling was significantly higher for the rainy season than for the dry season (p-value 0.001, using Wilcoxon Sign Rank Test, α=0.05). This may be due to the increase in storm water and agricultural and industrial runoff occurring in these months. In general, during the summer months, the spatial distribution of cadmium was not significantly different for the sampling locations in the Mea-Toa Creek. However, during the rainy season, the concentration of cadmium varied from site 3 to site 7. The highest concentration of cadmium was at site 7 (5.0 μg/l), located in the community areas. This may be explained by the pH of the water at this area site being slightly lower than for other sites as shown in Table 1. The pH of the water impacts metal solubility and bioavailability [15]. The lower the pH, the higher the solubility of metal, and thus an increase in metal bioavailability. Human activities can affect the pH of soil and water; for instance, agricultural activities such as using chemical fertilizer can decrease pH. In addition, mining activities using acid in their processes will increase the solubility of cadmium into surface water. However, cadmium levels in surface water in the Mae-Toa Creek did not exceed the standard of 5μg/l [16].

Spatial and temporal distribution of cadmium in river sediment

Figure 3 shows the distribution of cadmium levels in river sediment sampled during the summer and rainy seasons in 2006 from the Mea-Toa Creek. During this same time, surface water samples were collected. There was no statistical difference between the cadmium levels in the sediment between the two seasons of sampling (p-value 0.131, using Wilcoxon Sign Rank Test, α=0.05). Results suggest that concentrations of cadmium in the sediment were much higher than concentrations in the surface water. Cadmium levels in the sediment were found to exceed the UK Health Protection Agency standard of soil and sediment of 2 mg/kg, at pH 7 [17]. However, they did not exceed the Thai standard of 37 mg/kg [18]. This may be explained by the sediment acting as a sink of most pollutants in the river [19]. The spatial distribution of cadmium was significantly different for the sampling locations within the Mea-Toa Creek. The concentrations of cadmium at sites downstream (site 3 to site 9) of the mining site were significantly higher than those found upstream (site 1 and site 2) (p-value 0.002, using Mann-Whitney U Test, α=0.05).

Health risk assessment of cadmium bioavailability in fish and shellfish

Cadmium is a target analyte in fish due to its relationship to proteinuria in humans [20]. Concentrations of cadmium in 6 species of fish and one shellfish collected from Mae Toa creek are shown in Figure 4. The average concentration of cadmium in all fish species ranged from 0.03 to 0.27 mg/kg, wet weight. The highest average concentration of cadmium was found in swamp eel (0.27 mg/kg), follow by pond snail, batrachian walking catfish, common climbing perch, and striped snake head fish (0.13 mg/kg, 0.11 mg/kg, and 0.06 mg/kg, respectively). The average concentration of cadmium found in swamp eel exceeded the allowable contamination level of FAO/ WHO standard of 0.2 mg/kg [19]. This study found no relationship between sex, weight, and length of fish to the cadmium concentration. This might be due to small sample size.

Using US Environmental Protection Agency guidelines [18] human health risk assessment, the hazard quotient (HQ) from eating Swamp Eel was 1.3, which is higher than one. Hazard quotients of Pond Snail, Batrachian Walking Catfish, and Common Climbing Perch were 0.593, 0.522, and 0.475, respectively. As a result of this study, adverse health effects may occur and remediation is needed. According to ADI calculation, Swamp Eel could be eaten fewer than 8 meals per month while Batrachian Walking Catfish, Common Climbing Perch, and Pond Snail could be taken fewer than 16 meals per month.

Many factors can affect chemical contaminants in fish and shellfish sampling, such as human activities, storm events, spilled chemical incidence, etc. The type of species analyzed can also contribute to the difference in cadmium concentrations. Swamp eel is one of the most popular fish consumed by people in this community. The swamp eel is a predator and scavenger in the fresh water ecosystem. The location of the swamp eel at the top level of the food chain puts it in a position where it can accumulate more contaminants [22]. In addition, the swamp eel has no scales and has thinner skin than other fish tested in this study. This may give the swamp eel a higher ability to absorb more contaminants, thus having a higher bioavailability than other fish [23]. High levels of cadmium found in ponds snail may be explained by their habitat in the river sediment and their limited mobility.

5. Conclusion

Concentrations of cadmium in surface water along the sampling sites in the Mae Toa Creek change seasonally, giving higher concentrations in wet events due to storm water runoff. Elevated concentrations of cadmium in the rainy season may be due to agricultural and mining run off. Cadmium levels in river sediment were higher than those found in river water and exceed the allowable standard. This study found elevated concentrations of cadmium contaminants in swamp eel; therefore, a health risk to humans can occur if consumption of a few large meals occurs over a very short period of time.

Future monitoring is warranted to verify other contaminant levels in the agricultural products grown and consumed in this area. The monitoring of sediment, water, and other aquatic biota should be continued given that mining activities are on-going in this area. Health risk assessment and risk management should be performed. The environmental standard of Thailand should be revised since the soil standard for cadmium is far higher than that found in other countries.

6. Acknowledgement

We acknowledge the National of Research Funding of Thailand for research financing. We would also like to thank all the public health officers in Mae Sot District for their helpful information. Our appreciation goes to Dr. Rufus L. Chaney, a Senior Research Agronomist with the USDA for his constant help in providing technical resources.

7. Reference

[1] Wang Z, Huang S, Liu Q. Use of Anodic Stripping Voltammetry in Predicting Toxicity of Cu in River Water, Environ Toxocol Chem Vol. 21, pp.1788-1795, 2002.

[2] Clark, R.B. *Marine Pollution*, Oxford, U.K: Clarendon Press, pp. 61-79, 1992.

[3] U.S. Environmental Protection Agency, Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1-fish Sampling and Analysis 3rd ed. EPA 826-B-00-007, Washington, D.C., USA, 2000.

[4] Bay S, Jones BH, Schiff K, *Study of the* Impact of Storm Water D*ischarge on Santa Monica bay*, Executive Summary November 1, 1999.

[5] Snymann RG, Reinecke AJ, Nel JAJ, Uptake and Distribution of Copper in the Freshwater Crab *Potamonautes perlatus* (Crustacea) in the Eerste River, South Africa, *African Zoology*, Vol. 37 No.1, pp. 81-89, 2001.

[6] Shiff KC, Tiefenthaler LL., Anthropogenic Versus Natural Mass Emissions from an Urban Watershed,

Southern California Coastal Water Research Project, Annual Report, Long Beach California USA, 2001.

[7] Goyer, R.A.,Toxic Effects of Metals in Klaassen C.D., eds, *Casarett & Doull's* Toxicology the Basic Science of Poisons, 5thed, New York, USA: McGraw-Hill, pp. 696-721, 1996.

[8] Anderson, A., and Hahlin, M., Cadmium Effects from Phosphorus Fertilization in Field Experiments, *Swedish J Agric Res*, pp. 11-12, 1981.

[9] Simmons R.W., Pongsakul P., Saiyasitpanich D. and Klinphoklap S. Elevated levels of cadmium and zinc in paddy soils and elevated levels of cadmium in rice grain downstream of a zinc mineralized area in Thailand. Environ Geochem and Health Vol. 27, pp. 501-511, 2005.

[10] International Water Management Institute, Briefing note: Cadmium contamination in soil and crops of Tambon Phathat Padaeng and Tambo Mae Tao, Amphur Mae Sot, Tak Province, Thailand: Implications for public health. 2003.

[11] Swaddiwudhipong W., Limpatanachote P., Mahasakpan P., Krintratun S., Padungtod C., Cadmium-Exposed Population in Mae Sot District, Tak Province: Prevalence of High Urinary Cadmium Levels in the Adults, Journal of Medical Association Thailand; Vol. 90, No. 1 pp. 143-148, 2007.

[12] US Environmental Protection Agency. Determination of trace elements in drinking water by axially viewed inductively coupled plasma atomic emission spectrometry: Method 200. 5. EPA/600/-06/115. Ohio:, USA. 2003.

[13] US Environmental Protection Agency Acid digestion of sediment sludge and soil: Method 3050B, Revision 2. Ohio:, USA. 1996.

[14] Anderson K.A., *Analytical Techniques for Inorganic Contaminants*, Maryland: AOAC International, pp. 9, 10, 73, 1999.

[15] Waite T.D., and Moral FMM. Photoreductive Dissolution of Colloidal Iron Oxices in Natural Waters, Environmental Sciences Technology, Vol. 18, pp. 860-868, 1984.

[16] Thai Pollution Control Department, Surface Water Quality Standards, Notification of the National Environmental Board, No. 8, B.E. 2537 (1994), the Royal Government Gazette, Bangkok, Thailand, Vol. 111, Part 16, Dated February 24, B.E. 2537, 1994.

[17] U.K. Health Protection Agency, Cadmium Exposure Standards, Guidelines or Regulations. Online Cite 15th April 2007, Available from http://www.hpa.org.uk/chemicals/compendium/cadmium/exposure.htm.

[18] Thai Pollution Control Department, Soil Quality Standard for Habitat and Agriculture, Notification of the National Environmental Board, No. 25, B.E. 2547 (2004), the Royal Government Gazette Bangkok, Thailand: No. 121 Special Part 119 D Dated October 20, B.E. 2547, 2004.

[19] U.S. Environmental Protection Agency, National Study of Chemical Residues in Fish. Volume I EPA 823-R-92-008a, Washington, D.C., USA: Office of Science and Technology 1992.

[20] U.S. Environmental Protection Agency, Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1-fish Sampling and Analysis 3rded., EPA 826-B-00-007, Washington, D.C., USA: 2000.

[21] Joint FAO/WHO Food Standard Program, CODEX Alimentarius Commission, Twenty-ninth Session International Conference Centre, Geneva, Switzerland, 3-7 July 2006.

[22] Wiwattanachaiseth Y. How to Raise Swamp eel, Thai Fishery Gazette, Vol. 57, No. 2, pp. 167-175, 2004.

[23] Chumdawong S., Accumulation of Heavy Metals in Aquatic Animals, Thailand Fishery Seminar, Khonkan University, Thailand, 1995.

Table 1. Physical conditions and cadmium concentrations in the Mae-Tao Creek sampling period (March to June 2006)

Sampling Site	Position		Temperature (°C)		pH		Cadmium in water samples (µg/l)		Cadmium in sediment samples (mg/kg-dry)	
	E	N	Summer	Rainy	Summer	Rainy	Summer season	Rainy season	Summer season	Rainy season
							Mean ±SD	Mean ±SD	Mean ±SD	Mean ±SD
1	98 40 32.8	16 40 40.2	31.0	29.5	8.0	8.0	ND	ND	1.03±0.32	0.50±0.07
2	98 40 32.0	16 40 37.5	31.0	29.5	8.0	8.0	ND	ND	3.62±0.11	3.53±0.04
3	98 37 33.4	16 40 25.3	32.0	29.0	7.0	6.5	ND	3.33±0.25	27.86±0.65	28.26±0.57
4	98 37 37.9	16 40 35.5	31.5	29.5	7.0	6.5	ND	3.10±0.15	8.10±0.20	4.46±0.32
5	98 35 37.7	16 40 30.2	32.5	29.0	7.0	6.5	ND	1.42±0.06	16.63±0.67	4.50±0.30
6	98 34 38.8	16 40 31.3	32.5	29.5	7.0	7.0	ND	3.10±0.31	20.56±0.35	31.67±0.61
7	98 34 56.9	16 40 29.7	32.5	29.5	7.0	7.0	ND	5.00±0.20	27.13±0.21	23.67±1.07
8	98 34 42.8	16 40 37.4	32.5	30.0	8.0	7.0	ND	1.37±0.15	25.46±0.49	23.86±0.65
9	98 33 45.3	16 41 07.1	32.0	29.5	8.0	8.0	ND	1.20±0.17	24.70±0.96	7.07±0.51

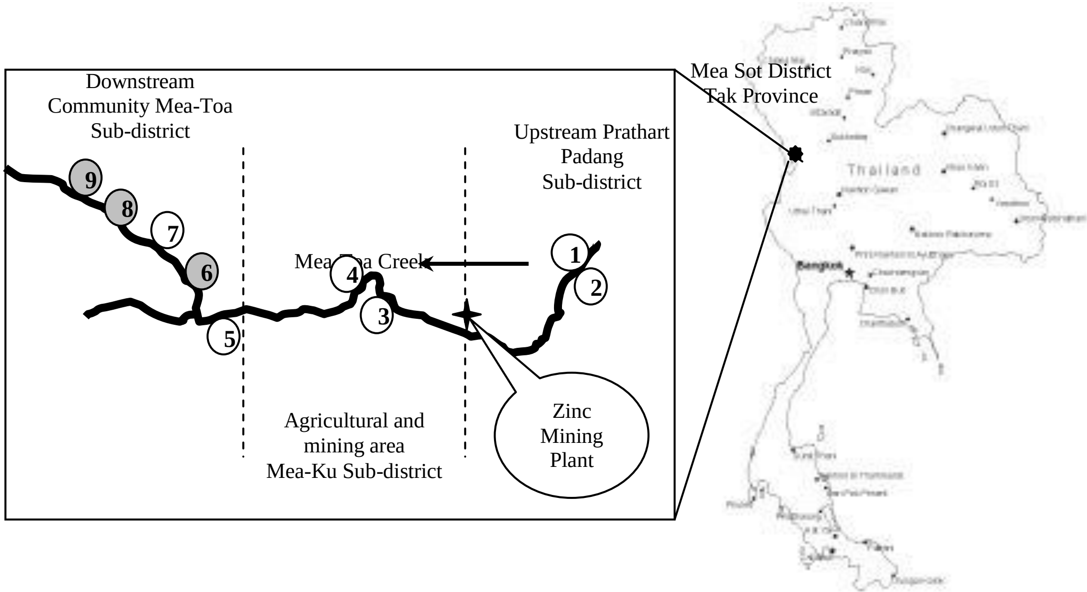

Figure 1. Study area in 3 Sub-district (Mea-Toa, Mea-Ku, and Prathart Padang) of Mea-Sot District, Tak Province, Thailand.

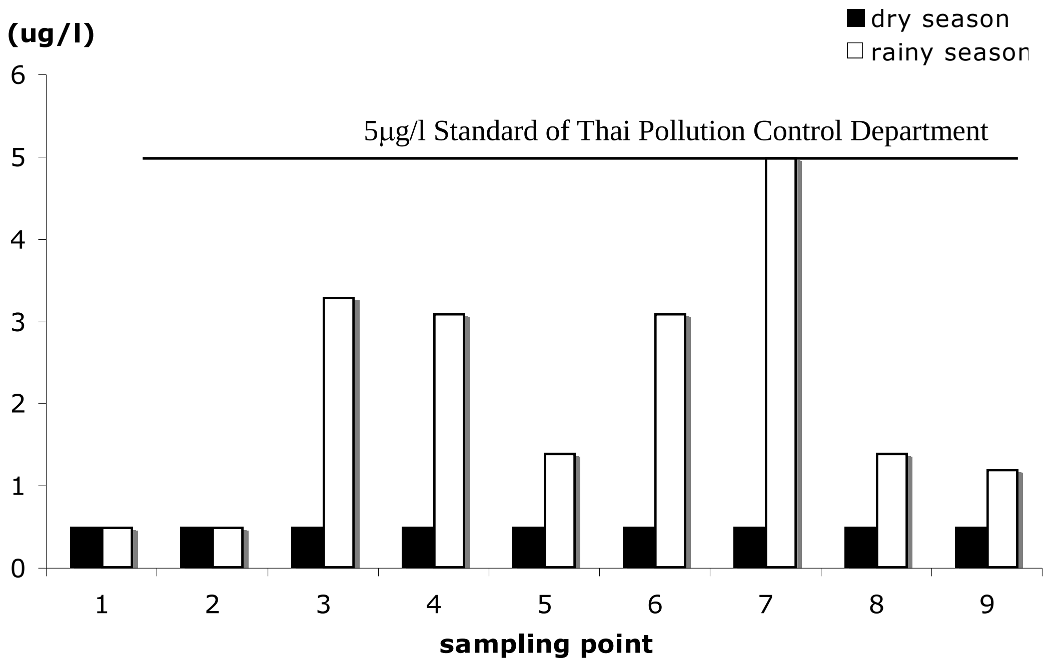

Figure 2. Concentrations of cadmium in water samples collected from Mea-Toa Creek, Mea Sot District, Tak Province, Thailand during the dry and rainy season 2006.

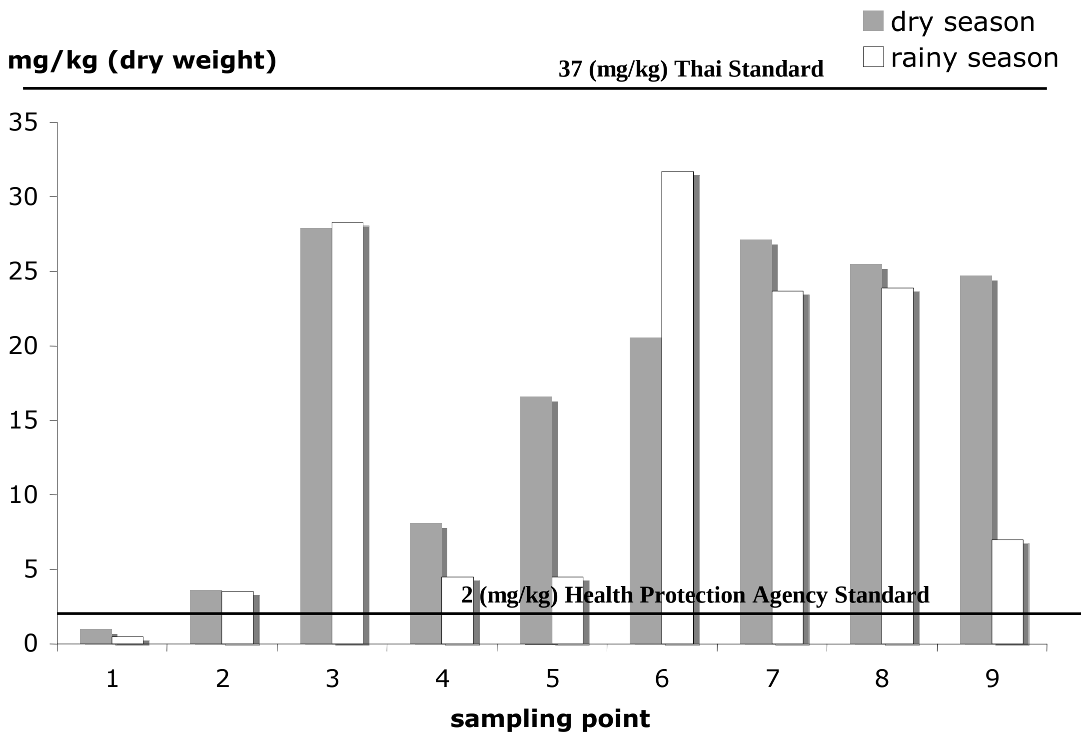

Figure 3. Concentrations of cadmium in sediment samples collected from Mea-Toa Creek, Mea Sot District, Tak Province, Thailand during the dry and rainy season 2006.

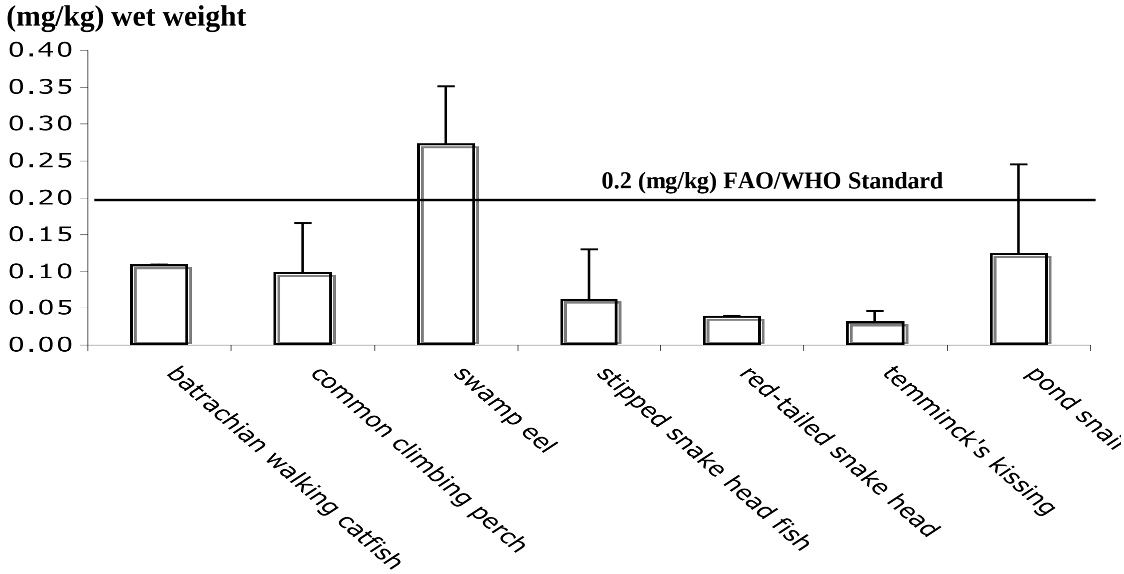

Figure 4. Concentrations of cadmium in fish and shellfish samples (n = 8 in each species) collected from Mea-Toa Creek, Mea Sot District, Tak Province, Thailand during the dry and rainy season 2006.