

Spatial Distribution of Cd, Zn and Hg in Groundwater at Rayong Province, Thailand

T. Makkasap and T. Satapanajaru

Abstract—The objective of this study was to evaluate the distribution patterns of Cd, Zn and Hg in groundwater by geospatial interpolation. The study was performed at Rayong province in the eastern part of Thailand, with high agricultural and industrial activities. Groundwater samples were collected twice a year from 31 tubewells around this area. Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was used to measure the concentrations of Cd, Zn, and Hg in groundwater samples. The results demonstrated that concentrations of Cd, Zn and Hg range from 0.000-0.297 mg/L ($\bar{x} = 0.021 \pm 0.033$ mg/L), 0.022-33.236 mg/L ($\bar{x} = 4.214 \pm 4.766$ mg/L) and 0.000-0.289 mg/L ($\bar{x} = 0.023 \pm 0.034$ mg/L), respectively. Most of the heavy metals concentrations were exceeded groundwater quality standards as specified in the Ministry of Natural Resources and Environment, Thailand. The trend distribution of heavy metals were high concentrations at the southeastern part of the area that especially vulnerable to heavy metals and other contaminants.

Keywords—Groundwater, Heavy metals, Kriging, Rayong, Spatial distribution.

I. INTRODUCTION

GROUNDWATER is one of the major sources of drinking water in the world. The contamination of groundwater is a serious problem to environment and human health. Rayong province, located at the eastern part of Thailand, is an important agriculture and industrial base of the country. Rapid development of Rayong led to increase the potential of pollutants contaminate to groundwater. Heavy metals are priority toxic pollutants that could be released from domestic, agricultural and industrial applications [1]. Generally heavy metal contaminations are often caused by human activities, including mining, wastewater irrigation, leakage of septic tanks, industrial processes that heavy metals residues in their wastes and nonpoint source surface runoff [2], [3]. In addition, another source of heavy metals comes from the nature. For example, erosion and weathering of parent materials [4]. All of activities that can be transport to groundwater with recharged water.

Some metals such as iron (Fe), copper (Cu), manganese (Mn), and zinc (Zn) are essential for living organisms at low concentrations. However toxic effects are observed when concentrations are increase [5], [6]. The trace elements in groundwater are important issue because it affects the use of

water [7]. The accumulation of trace elements in environmental have potential risk to human health and final into the food chain [8].

The objective of this study was to evaluate the distribution patterns of heavy metals, cadmium (Cd), zinc (Zn) and mercury (Hg) in groundwater at Rayong province, an industrial area, at the eastern part of Thailand by spatial interpolation techniques in GIS.

II. MATERIALS AND METHODS

A. The study area

Rayong province covers an area of approximately 3,552 km² at the eastern part of Thailand (12-13 ° N, 101-102 ° E). The topography is plain alternating with mountain and Coastal plain at the southern part, contacts with Gulf of Thailand, with percent slopes high at northeast and center of area along the north to the south. The local economy depend agriculture and industry because Rayong has developing to eastern seaboard project. The region climate is a tropical monsoon. Annual average temperature is 29.30 ° C and precipitation is 1,501.7 mm. Lithology is various units ranges from Precambrian to Cenozoic (Quaternary period) are shown in Fig. 1a. Majority of area are Quaternary-age deposit consists of alluvial deposit and beach sand (Qa) at the southern part and Terrace deposit (Qt) distribute throughout of the area but Carboniferous-age deposit consists of carboniferous granite (Cgr) at the northwestern part [9].

B. Groundwater sampling and analysis

Thirty one samples of groundwater around Rayong province were collected two times over a year in the dry season (March, 2009) and rainy season (September, 2009) from underground wells at the study area the sampling station are shown in Fig. 1b. The samples were selected by using a complete randomization approach from total groundwater wells. Sampling site geo-positions were determined using the global positioning system (GPS). Groundwater samples were pumped out for flushing all retained water in the pipes before sample collection. They were acidified to pH < 2 with nitric acid at collection sites and refrigerated at 4 ° C before chemical analysis. Cd, Zn, and Hg concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY2000). Anion and cation concentrations were analyzed using Ion Chromatography by high performance liquid chromatography (HPLC, SHIMADZU CL-10 ADVP). Other parameters such as pH, conductivities, salinity and TDS were measured on-site by potable meters (YSI 550A and YSI EC 300).

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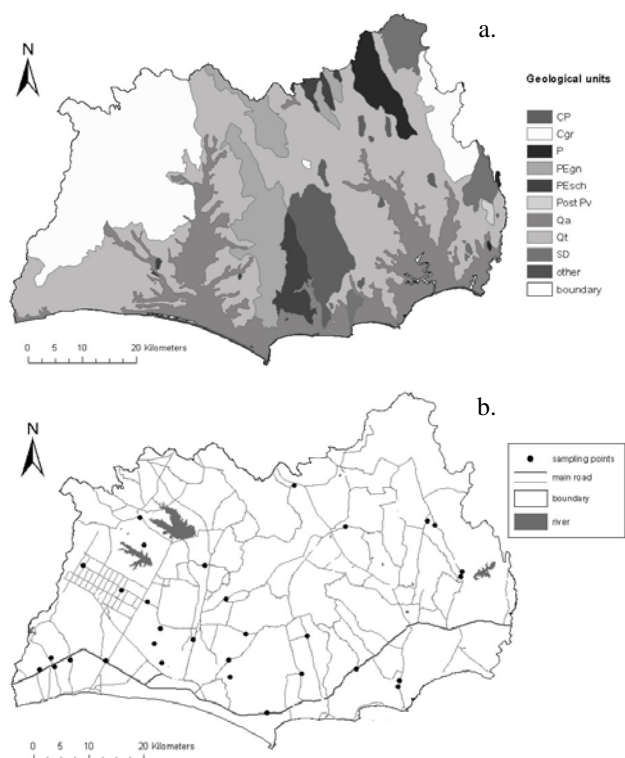


Fig. 1 Geological units (a) and sampling points (b) in study area

C. GIS and spatial analysis

The spatial interpolation of contaminated groundwater is exhibiting some tool to analysis. However, only a small proportion of in-situ data can be analyzed in a field investigation, depended on time and cost. Geostatistics are widely used to estimate the spatial variability and distribution of field data with uncertainty [10]. Kriging is one of the geostatistical tools applied to analyse spatial horizontal distribution of groundwater contaminants [11], [12]. Unsampld location, the values estimated by kriging method are minimizing the error because this method provides statistically optimal and estimates errors of interpolation [13]-[15]. Kriging interpolation was used in this study. The software used for spatial analysis was ArcGIS v.9.3.1. under license of ESRI (Thailand) Co., Ltd.

III. RESULTS AND DISCUSSION

A. Characteristics of groundwater

The chemical characteristics of represented groundwater at Rayong are summarized in Table 1. Generally, groundwater properties in this area were low ion and salinity concentrations. The averages of pH, electrical conductivity (EC), total dissolve solid (TDS), and hardness were 7.08, 324.43 mg/L, 277.60 mg/L and 78.53 mg/L, respectively. Most groundwater quality were below the groundwater quality standards for drinking purposes set by Ministry of Natural Resources and Environment, Thailand (2008) [16].

TABLE I
 CHARACTERISTICS OF GROUNDWATER SAMPLES (N=31)

Parameters	Unit	$\bar{X}\pm SD$	Median	Range
pH		7.08±0.63	7.00	5.92-8.01
Conductivity	µS/cm	324.43±192.72	306.90	60.70-928.00
TDS	mg/L	277.60±193.01	215.40	45.70-829.00
Salinity	ppt	0.14±0.08	0.10	0.00-0.40
Hardness (as CaCO ₃)	mg/L	78.53±72.58	54.40	5.46-270.00
Na	mg/L	19.98±24.98	11.38	2.37-124.28
NH ₄	mg/L	1.02±1.37	0.51	0.09-7.31
K	mg/L	4.64±4.63	2.45	0.19-17.06
Mg	mg/L	4.02±3.84	2.38	0.39-15.14
Ca	mg/L	24.82±24.10	17.87	1.22-83.19
Cl	mg/L	20.24±34.26	10.61	2.51-186.03
NO ₃	mg/L	3.87±8.41	0.16	0.00-29.44
SO ₄	mg/L	4.99±9.87	1.31	0.00-43.91

B. Cd, Zn, and Hg concentrations

The heavy metals concentrations in the study area are shown in Table 2. The averages of Cd, Zn and Hg were 0.021 mg/L, 4.212 mg/L and 0.023 mg/L, respectively. Unfortunately, most heavy metal concentrations were higher than these in groundwater quality standards set by Ministry of Natural Resources and Environment, Thailand [16]. Results show that of anthropogenic activities and natural sources might dominate influence on heavy metals concentrations.

TABLE II
 HEAVY METALS CONTENTS OF GROUNDWATER IN STUDY AREA (N=31)

	Unit	$\bar{X}\pm SD$	Median	Range	Standard ^a
Cd	mg/L	0.021±0.033	0.012	0.000-0.297	0.003
Zn	mg/L	4.214±4.766	2.143	0.022-33.236	5.000
Hg	mg/L	0.023±0.034	0.010	0.000-0.289	0.001

^a Groundwater quality standards (2000).

Ministry of Natural Resources and Environment, Thailand. [16]

C. Spatial distribution analysis

The spatial distribution maps were analysed using kriging methods. Semivariogram analysis for kriging interpolation shows that pH, Cd, Zn and Hg concentrations were best fitted for exponential model, while electrical conductivity was best fitted for gaussian model.

The geospatial trends (Fig. 2) of Cd, Zn and Hg were low concentrations in northwestern part of area, which matched the spatial distribution of conductivity. The same trend was found in distribution of Zn and Hg in southeastern part. The high heavy metals concentrations could be attributed to the low pH due to heavy metals are more easily dissolved in low pH than dissolved in high pH. The geological at the northwestern part is consist of carboniferous granite (Cgr) contained high concentrations of heavy metals [17], [18] whereas there are consist of alluvial deposit and beach sand (Qa) the southeastern part. Groundwater flow direction is downward from the north to the south [9], groundwater can

leach and dissolve heavy metals in the parent rock from the north to the south. Our results also indicated that Zn and Hg were high concentrations at the southeastern part. Conversely, Cd was higher at the eastern part and southwestern part than the other area. Besides, the southeast area is mainly agricultural and residential areas. The major sources of heavy metals may be influence from anthropogenic activities, domestic sewage, or some pesticides [19], [20].

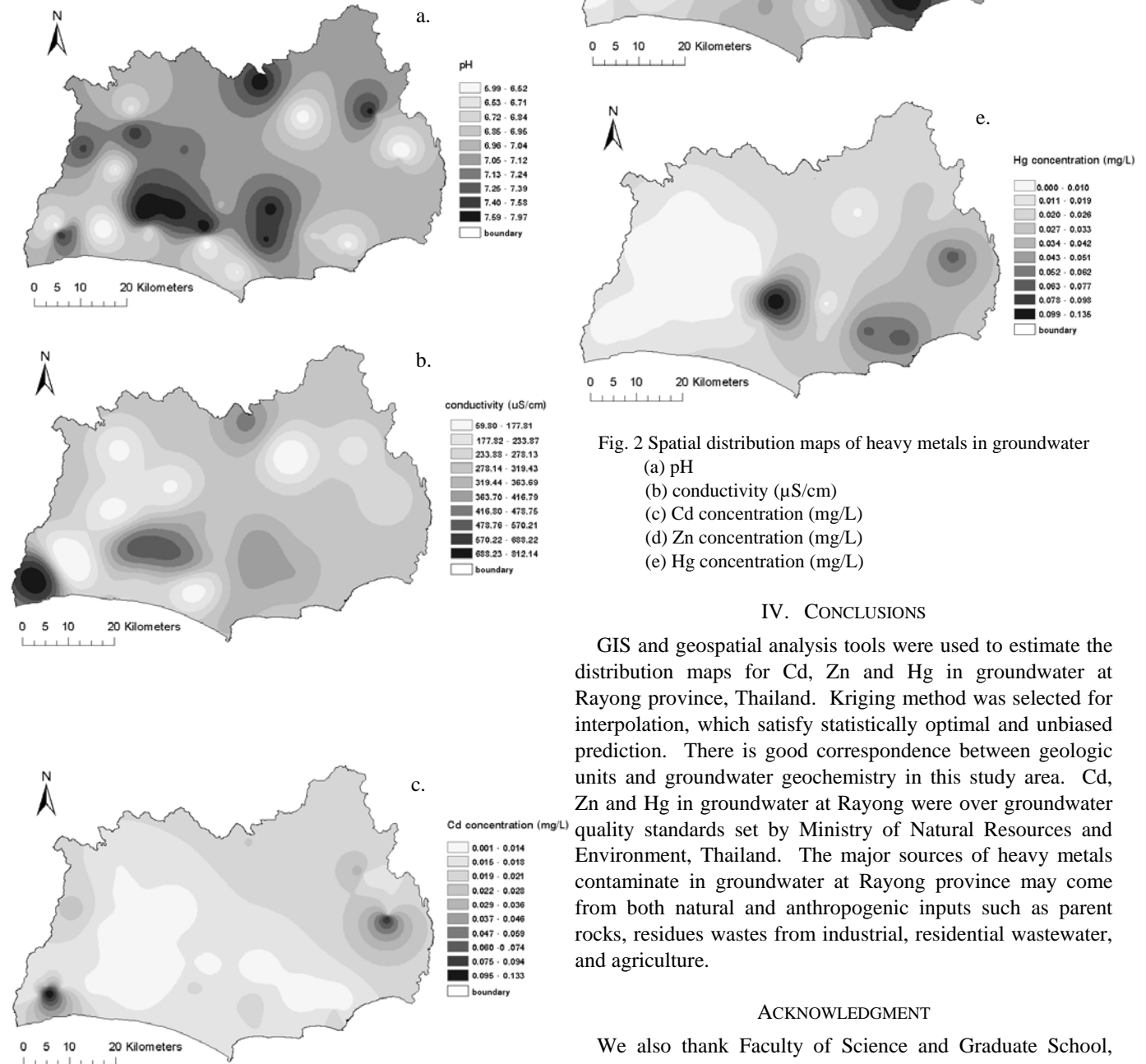


Fig. 2 Spatial distribution maps of heavy metals in groundwater
 (a) pH
 (b) conductivity ($\mu\text{S}/\text{cm}$)
 (c) Cd concentration (mg/L)
 (d) Zn concentration (mg/L)
 (e) Hg concentration (mg/L)

IV. CONCLUSIONS

GIS and geospatial analysis tools were used to estimate the distribution maps for Cd, Zn and Hg in groundwater at Rayong province, Thailand. Kriging method was selected for interpolation, which satisfy statistically optimal and unbiased prediction. There is good correspondence between geologic units and groundwater geochemistry in this study area. Cd, Zn and Hg in groundwater at Rayong were over groundwater quality standards set by Ministry of Natural Resources and Environment, Thailand. The major sources of heavy metals contaminate in groundwater at Rayong province may come from both natural and anthropogenic inputs such as parent rocks, residues wastes from industrial, residential wastewater, and agriculture.

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REFERENCES

- [1] R. Petrus, and J.K. Warchol, "Heavy metal removal by clinoptilolite," *Water Research*, vol. 39, pp. 819-830, Mar. 2005.
- [2] Y. Ouyang, J. Higman, J. Thompson, T. O. Toole, and D. Campbell, "Characterization and spatial distribution of heavy metals in sediment from Cedar and Ortega rivers subbasin," *Journal of Contaminant Hydrology*, vol. 54, pp. 19-35, July 2002.
- [3] A. Navarro, and M. Carbonell, "Evaluation of groundwater contamination beneath an urban environment: The Besos river basin (Barcelona, Spain)," *Journal of Environmental Management*, vol. 85, pp. 259-269, Jan. 2007.
- [4] E. Merian, *Metals and Their Compounds in the Environment*. Germany: VCH Verlagsgesellschaft, 1991, pp. 1438.
- [5] R. L. Calderon, "The epidemiology of chemical contaminants of drinking water," *Food and Chemical Toxicology*, vol. 38, pp. S13-S20, Apr. 2000.
- [6] K. P. Cantor, "Drinking water and cancer," *Cancer Causes and Control*, vol. 8, pp. 292-308, May 1997.
- [7] A. Kouras, I. Katsoyiannis, and D. Voutsas, "Distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece," *Journal of Hazardous Materials*, vol. 147, pp. 890-899, Aug. 2007.
- [8] S. W. Al Rmalli, P. I. Haris, C. F. Harrington, and M. Ayub, "A survey of arsenic in foodstuffs on sale in the United Kingdom and imported from Bangladesh," *Science of The Total Environment*, vol. 337, pp. 23-30, Jan. 2005.
- [9] Department of groundwater resources, *The Eastern Seaboard Groundwater Management Project; to Assess Groundwater Potential, Installation of Groundwater Contamination Monitor, and Development of Remediation Plan in the Area of Rayong and Chonburi Provinces*. Ministry of natural resources and environment, Bangkok, Thailand, 2007.
- [10] N. Cressie, "Fitting variogram models by weighted least squares," *Mathematical Geosciences*, vol. 17, pp. 563-586, July 1985.
- [11] E. H. Isaaks, and R. M. Srivastava, *An Introduction to Applied Geostatistics*. New York: Oxford University Press, 1989, pp. 278-322.
- [12] J. D. Istok, and C. A. Rautman, "Probabilistic Assessment of Groundwater Contamination: 2. Results of Case Study," *Ground Water*, vol. 34, pp. 1051-1064, Nov. 1996.
- [13] A. B. McBratney, and R. Webster, "Optimal interpolation and isarithmic mapping of soil properties. V; Co-regionalization and multiple sampling strategy," *Journal of Soil Science*, vol. 34, pp. 137-162, Mar. 1983.
- [14] S. Tao, "Kriging and mapping of copper, lead, and mercury contents in surface soil in Shenzhen areas," *Water, Air and Soil Pollution*, vol. 83, pp. 161-172, July 1995.
- [15] X. J. Wang, Y. Zheng, R. M. Liu, B. G. Li, J. Cao, and S. Tao, "Kriging and PAH pollution assessment in the topsoil of Tianjin area," *Bulletin of Environmental Contamination and Toxicology*, vol. 71, pp. 189-195, July 2003.
- [16] Pollution control department, *Groundwater Quality Standards*. Ministry of natural resources and environment, Bangkok, Thailand, 2004.
- [17] C. Suthirath, P. Charusiri, and G. Sinclair, "Chemistry and petrology of granitic rocks in Chonburi-Rayong area, eastern Thailand," Chulalongkorn University, Bangkok, Thailand, 2007.
- [18] P. C. Singer, *Trace Metals and Metal-Organic Interactions in Natural Waters*. Michigan: Ann Arbor Science Publishers, Inc., 1974, pp. 89-130.
- [19] R. T. Mehrjardi, M. Z. Jahromi, Sh. Mahmodi, A. Heidari, "Spatial distribution of groundwater quality with geostatistics (case study: Yazd-Ardakan Plain)," *World Applied Sciences Journal*, vol. 4, pp. 09-17, 2008.
- [20] M. Al-Ahmari. *Measuring groundwater contamination in agricultural and urban areas using GIS*. Faculty of the King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, 2006.