รูปที่ 7.5   กราฟแสดงความสัมพันธ์ระหว่างความเข้มข้นของทองแดงและตะกั่ว (mg/L)
กับเวลา (วัน) ที่เปลี่ยนแปลงไป ในชั้นไม่อิ่มตัวด้วยน้ำ ที่ความหนา 2.5 เมตร

        ผลจากการใช้โปรแกรม HYDRUS 1D เพื่อศึกษาการเคลื่อนตัวของโลหะหนักตะกั่ว (Pb) และทองแดง
(Cu) เมื่อพิจารณา ณ เวลาใดเวลาหนึ่ง ค่าความเข้มข้นของโลหะหนัก บริเวณความลึกมากจะพบค่าความเข้มข้น
น้อยกว่าตำแหน่งที่ตื้นกว่า สังเกตจากรูปที่ 7.3 และ 7.4 หลังจากความลึก 50 เมตร ความเข้มข้นของโลหะทั้งสองมี
การลดลงน้อยมาก จากการใช้โปรแกรม HYDRUS 1D ทำการวัดความเข้มข้นของโลหะหนักตะกั่วและทองแดง ณ
ตำแหน่งด้านล่างสุดของชั้นไม่อิ่มตัวด้วยน้ำที่ความลึกต่างๆ   พบว่าปริมาณความเข้มข้นมีการเปลี่ยนแปลงไปตาม
สภาพภูมิอากาศ ดังแสดงในรูปที่ 7.5 กล่าวคือ ขึ้นอยู่กับความชื้นในดินซึ่งมาจากปริมาณน้ำฝนที่ซึมลงมาผ่านชั้น
ไม่อิ่มตัวด้วยน้ำ และค่าการระเหยรายวัน ทำให้ค่าความเข้มข้นของโลหะหนักตะกั่วและทองแดงมีค่าเปลี่ยนแปลง
ตลอดทั้ง 25 ปี ไม่ได้เพิ่มขึ้นเนื่องจากมีเวลาสะสมความเข้มข้นมากขึ้น

        จากกราฟพบว่าค่าความเข้มข้นของโลหะหนักทองแดงจะมีค่ามากกว่าความเข้มข้นของโลหะหนักตะกั่ว
เสมอ สอดคล้องค่าสัมประสิทธิ์การดูดซับ (K_d) ของทองแดงที่มีค่าเท่ากับ 0.069 L/g ซึ่งน้อยกว่าของตะกั่วที่มีค่า
เท่ากับ 0.226 L/g ทำให้การเคลื่อนตัวของทองแดงเคลื่อนตัวได้เร็วกว่าตะกั่วและพบการปนเปื้อนของทองอดงใน
น้ำบาดาลมากกว่าตะกั่ว

7.4 ผลการศึกษาการเคลื่อนตัวของโลหะหนักในชั้นอิ่มตัวด้วยน้ำ

7.4.1 ความเข้มข้นของตะกั่ว (Pb) และทองแดง (Cu)

จากการวิเคราะห์ความเข้มข้นของตะกั่ว (Pb) และทองแดง (Cu) โดยแบบจำลอง Visual Modflow ที่เวลา 25 ปี แล้วนำค่าความเข้มข้นของโลหะหนักแต่ละบ่อจากค่าสูงสุดไปค่าน้อยที่สุดและคำนวณหาค่าที่เปอร์เซ็นต์ไทต์ที่ 25, 50, 75 และ 99 (P_{25} , P_{50}, P_{75} และ P_{99}) โดยแบ่งพิจารณาจากบ่อน้ำบาดาลที่ตั้งอยู่ในบริเวณที่มีอยู่ในไร่พริก ได้แก่ บ่อ 1, 2, 5, 6, 7, 8 และ 10 และบ่อที่อยู่นอกไร่พริก ได้แก่ บ่อ 3, 4, 9, 11 และ 12 ได้ข้อมูลดัง ตารางที่ 7.5 และ 7.6

**ตารางที่ 7.5** ความเข้มข้นของตะกั่ว (Pb) และทองแดง (Cu) จากบ่อที่ตั้งในพื้นที่ไร่พริก

	Type of Analysis	Minimum	P_{25}(µg/L)	P_{50}(µg/L)	P_{75}(µg/L)	P_{99}(µg/L)
	Initial	1.57	10.71	19.65	27.10	32.19
Pb	Model	0.95	18.17	36.65	57.86	264.97
	Monitoring	1.41	11.43	20.80	30.80	111.00
	Initial	2.55	12.33	21.88	29.85	35.29
Cu	Model	1.05	19.57	39.35	61.88	311.49
	Monitoring	4.62	14.80	36.70	85.73	751.00

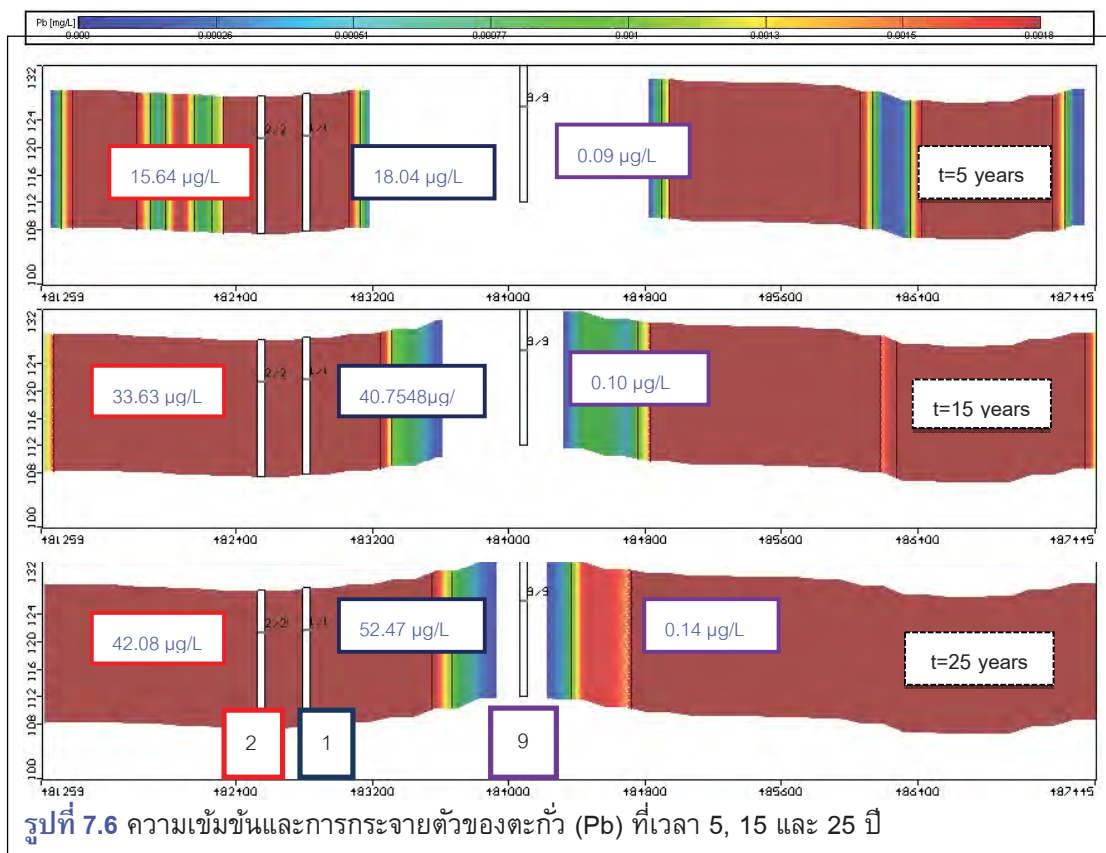**ตารางที่ 7.6** ความเข้มข้นของตะกั่ว (Pb) และทองแดง (Cu) จากบ่อที่ตั้งนอกพื้นที่ไร่พริก

	Type of Analysis	Minimum	P_{25}(µg/L)	P_{50}(µg/L)	P_{75}(µg/L)	P_{99}(µg/L)
	Initial	0.12	0.11	0.13	2.08	3.17
Pb	Model	0.09	0.10	0.10	0.39	7.21
	Monitoring	0.65	0.80	2.11	7.11	11.80
	Initial	0.98	0.98	0.98	2.63	4.26
Cu	Model	0.94	0.97	0.98	1.27	8.47
	Monitoring	0.58	6.63	11.10	23.18	40.60

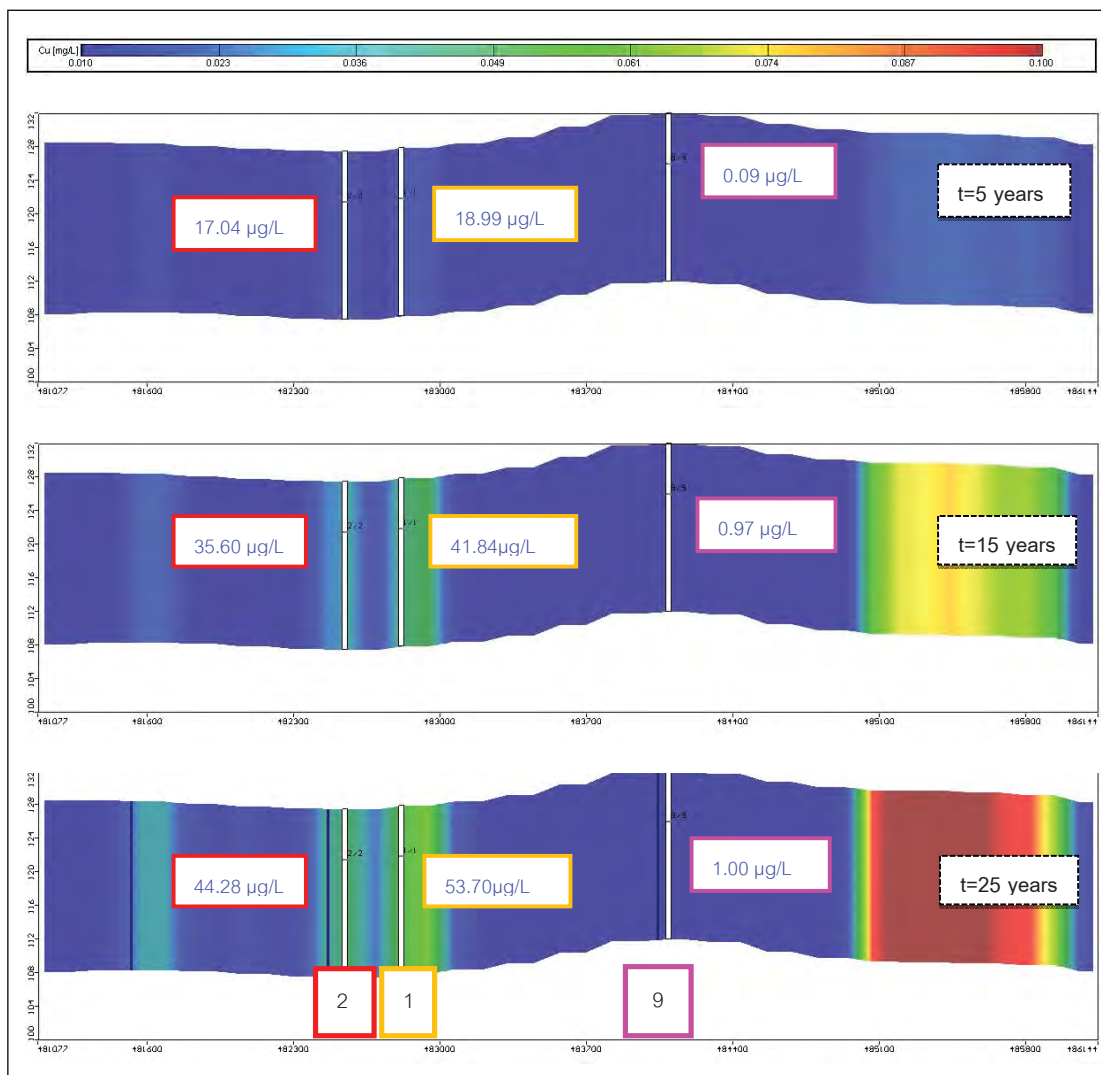### 7.4.2 ความเข้มข้นของตะกั่ว (Pb) และทองแดง (Cu) ณ เวลาต่างๆ

ความเข้มข้นของโลหะหนักเปลี่ยนแปลงไปตามเวลา โดยมีความเข้มข้นของโลหะหนักมีแนวโน้มกระจาย
ตัวไกลออกจากไร่พริกมากขึ้น ดังแสดงในแบบจำลองความเข้มข้นที่เปอร์เซ็นต์ไทด์ที่ 50 (P_{50}) ของบ่อน้ำบาดาล
บ่อ 1 และ 2 ตั้งอยู่ในพื้นที่ไร่พริก ส่วนบ่อบาดาลบ่อ 9 ตั้งอยู่นอกพื้นที่ไร่พริก
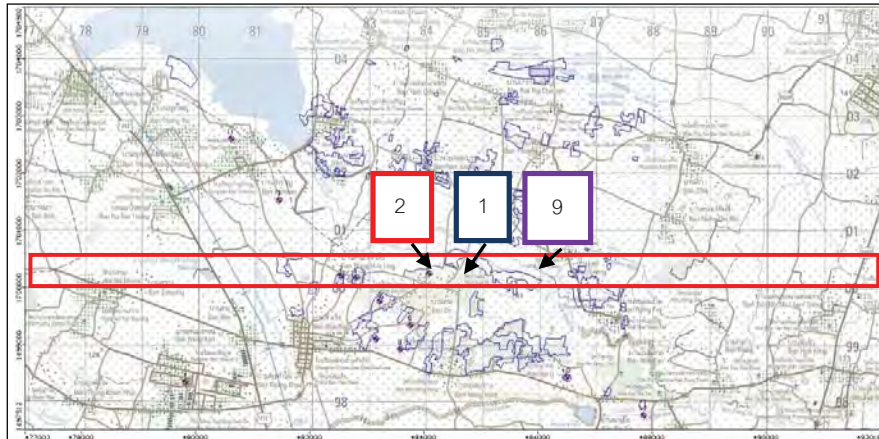
**รูปที่ 7.5** ตำแหน่งของบ่อน้ำบาดาล บ่อที่ 1, 2 และ 9

รูปที่ 7.6 ความเข้มข้นและการกระจายตัวของตะกั่ว (Pb) ที่เวลา 5, 15 และ 25 ปี

รูปที่ 7.7 ความเข้มข้นและการกระจายตัวของทองแดง (Cu) ที่เวลา 5,15 และ 25 ปี

### 7.4.3 ตรวจสอบความน่าเชื่อถือของแบบจำลองด้วย Boxplot

เปรียบเทียบความเข้มข้นของตะกั่ว (Pb) และทองแดง (Cu) เมื่อเวลาผ่านไป 25 ปี เพื่อดูความน่าเชื่อถือ
ของข้อมูลระหว่างการใช้แบบจำลองและค่าที่ตรวจวัดได้จริงจากภาคสนาม ดังแสดงใน รูปที่ 7.8 โดยที่ Box plot ที่
1 เป็นผลที่ได้จากการจำลองโดยใช้แบบจำลอง Modflow สำหรับ Box plot ที่ 2 เป็นผลที่ได้จากผลจากการจำลอง
โดยใช้แบบจำลอง Modflow ร่วมกับแบบจำลอง Hydrus-1D กล่าวคือ นำเข้าผลที่จากการจำลองความเข้มข้นของ
โลหะหนักที่ได้จากการการเคลื่อนตัวของโลหะหนักผ่านชั้นไม่อิ่มตัวด้วยน้ำที่ความหนาต่างๆ   โดยใช้โปรแกรม
HYDRUS 1D เข้าสู่แบบจำลอง Modflow เพื่อจำลองการเคลื่อนตัวในชั้นน้ำ
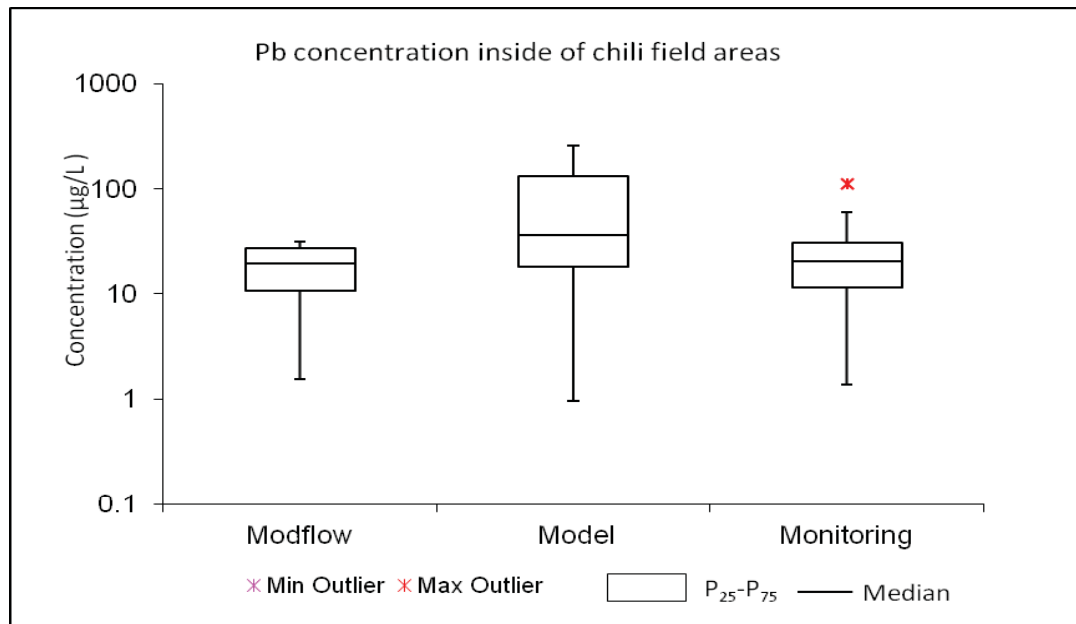
รูปที่ 7.8 Boxplot ใน Logarithmic scale เปรียบเทียบความเข้มข้นของตะกั่ว (Pb) จากบ่อน้ำบาดาลที่อยู่ใน พื้นที่
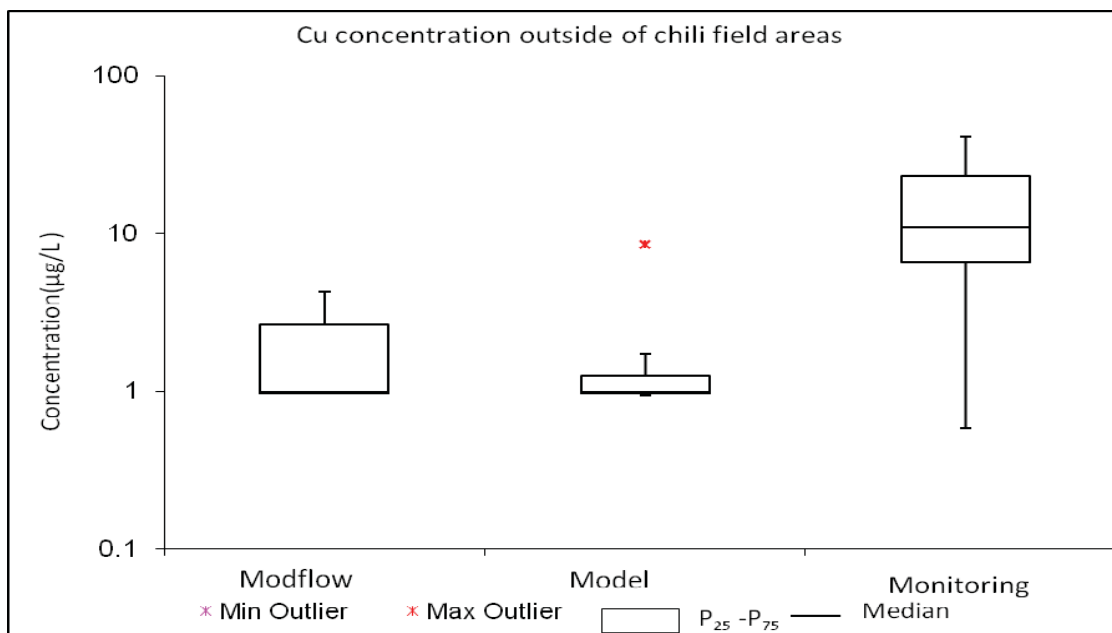ไร่พริก
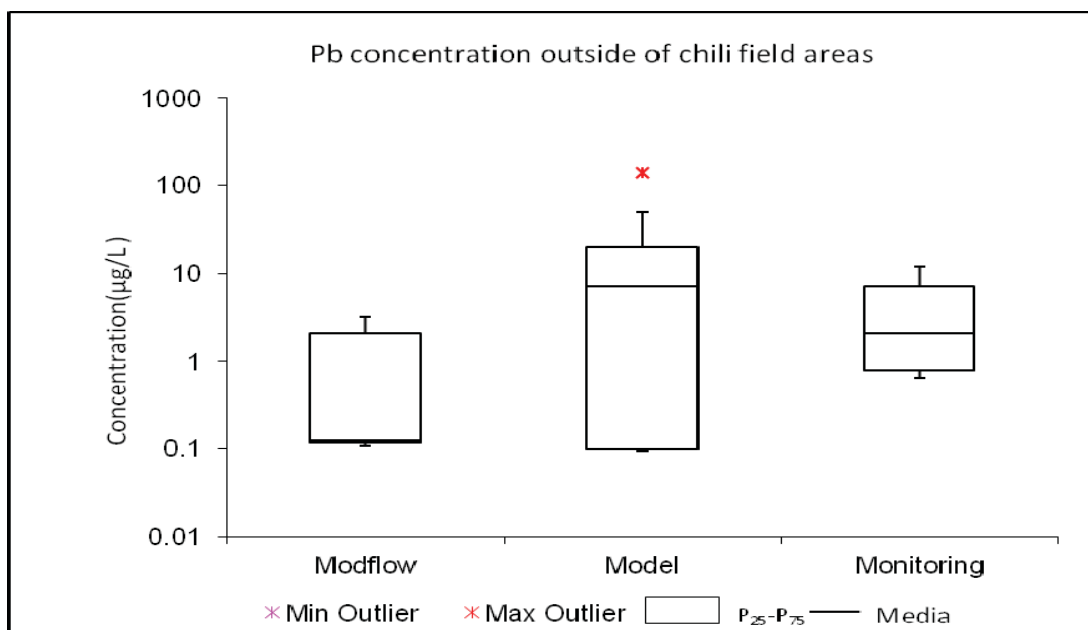
รูปที่ 7.9 Boxplot ใน Logarithmic scale เปรียบเทียบความเข้มข้นของตะกั่ว (Pb) จากบ่อน้ำบาดาลที่อยู่ นอก
พื้นที่ไร่พริก
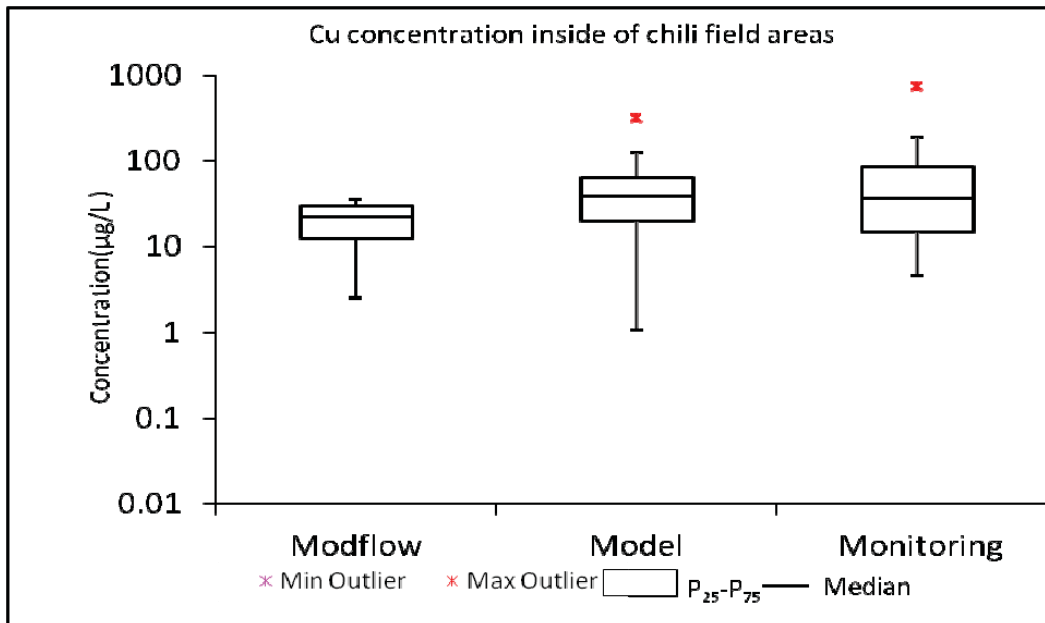
รูปที่ **7.10** Boxplot ใน Logarithmic scale เปรียบเทียบความเข้มข้นของทองแดง(Cu) จากบ่อน้ำบาดาล
ที่อยู่ในพื้นที่ไร่พริก

รูปที่ **7.11** Boxplot ใน Logarithmic scale เปรียบเทียบความเข้มข้นของทองแดง (Cu) จากบ่อน้ำบาดาลที่อยู่
นอกพื้นที่ไร่พริก

บาดาลที่อิ่มตัวด้วยน้ำ และสุดท้ายใน Box plot ที่ 3 เป็นค่าความเข้มข้นจริงที่ตรวจวัดได้ในภาคสนามของบ่อน้ำ
บาดาลที่ตั้งอยู่ในพื้นที่ไร่พริกและนอกไร่พริก

จากการวิเคราะห์ข้อมูลความเข้มข้นของโลหะหนักตะกั่ว (Pb) และทองแดง(Cu) พบว่าในพื้นที่ไร่พริก ซึ่ง
เป็นพื้นที่ที่ได้รับโลหะหนักจากสารเคมีเกษตร ซึ่งมีโลหะหนักเป็นองค์ประกอบอยู่ด้วยนั้น ทำให้ความเข้มข้นของ
โลหะหนักตะกั่ว (Pb) และทองแดง(Cu)ในน้ำบาดาลของบ่อที่ตั้งอยู่ในไร่พริกมีค่าความเข้มข้นสูงกว่าน้ำจากบ่อน้ำ
บาดาลที่ตั้งอยู่นอกไร่พริก นอกจากนี้ยังมีปัจจัยเรื่องของสภาพความเป็นกรดค่อนข้างสูงของน้ำบาดาลส่งผลให้
โอกาสในการเคลื่อนตัวของโลหะหนักลงสู่น้ำบาดาลมากขึ้น นอกจากนี้เมื่อพิจารณาความน่าเชื่อถือของความ
เข้มข้นที่ได้จากการสร้างแบบจำลองพบว่า แบบจำลองร่วมระหว่าง Hydrus 1D และ Modflow มีความถูกต้อง
น่าเชื่อถือมากกว่าแบบจำลองที่ใช้เพียง Modflow เท่านั้น และมีค่าใกล้เคียงกับค่าการตรวจวัดในภาคสนาม แสดง
ว่าแบบจำลองที่มีการนำเข้าข้อมูลของความเข้มข้นของตะกั่ว (Pb) และทองแดง (Cu) ของดินบริเวณรอบปากบ่อน้ำ
บาดาลในโปรแกรม HYDRUS 1D ซึ่งมีการกำหนดปัจจัยต่างๆ เช่น ปริมาณน้ำฝนที่ตกในพื้นที่ ค่าการระเหย และ
ค่าความสามารถในการดูดติดผิว เป็นต้น มีผลต่อการประเมินการปนเปื้อนของปริมาณโลหะหนักในชั้นน้ำบาดาล
ระดับตื้น

บทที่ 8
ผลผลิตที่เกิดขึ้นจากโครงการวิจัย

8.1 งานประชุมวิชาการระดับนานาชาติ

ผลจากการศึกษานี้ได้นำเสนอในงานประชุมระดับนานาชาติดังนี้

1. **Chotpantarat, S.**, Sutthirat, C., and Srisuk, K. 2012. Transport modeling of single and binary metal systems of Pb and Cu through unsaturated soil in an agricultural area: A case study of Hua Rua area, Thailand. The 4th IWA Asia-Pacific Young Water Professionals Conference. Japan, 7-10 Dec., 2012 (Full paper and Oral presentation) (ภาคผนวก ก)

2. **Chotpantarat, S.** and Masipan, T. 2013. Sequential Fractionation of Heavy Metals in Agricultural Soils: A Case Study of Hua Rua Area, Ubon Ratchatani Province. International Conference on Environmental and Hazardous Substance Management, Bangkok, Thailand, 21-23 May, 2013. (Full paper and Oral presentation) (ภาคผนวก ก)

8.2 บทความวิชาการที่ตีพิมพ์ในวารสารระดับชาติ

1. **Chotpantarat, S.**, 2011. Causes and potential acid generation techniques of acid mine drainage (AMD). Engineering Journal 64(4): 59-66. (ภาคผนวก ข)

8.3 บทความวิชาการที่ตีพิมพ์ในวารสารระดับนานาชาติ

ผลจากการศึกษานี้ได้รับตีพิมพ์ในการบทความวิชาการระดับนานาชาติ ดังนี้

1. **Chotpantarat, S.**, Limpakanwech, C., and Sutthirat, C. 2011. Effect of soil water characteristic curves on simulation of nitrate vertical transport in a Thai agricultural soil. Sustainable Environmental Research 21(3): 187-193(Formerly, Journal of Environmental Engineering and Management, JEEAM, indexed in the Chemical Abstracts Service, Cambridge Scientific Abstracts, EBSCO and INSPEC). **Corresponding author.** (ภาคผนวก ค)

2. **Chotpantarat, S.**, Ong, S.K., Sutthirat, C., and Osathaphan, K. 2012. Sorption and transport of Pb^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+} under single, binary and multi-metal systems through lateritic soil: Modeling. Geoderma 189-190: 278-287. **Impact factor 2.318. Corresponding author.** (ภาคผนวก ค)

3. Wongsasuluk, P., **Chotpantarat, S.**. Siriwong, W., Borjan, M, and Robson, M. 2013. Heavy metal conctamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area at Ubon Ratchathani Province, Thailand. Environmental Geochemistry and Health Journal. DOI: 10.1007/s10653-013-9537-8**. Impact factor 2.076.** (Accepted) **Corresponding author.** (ภาคผนวก ค)

8.4 ผลิตบัณฑิต

       ค่าใช้จ่ายในงานวิจัยมีส่วนในการสนับสนุนงานวิจัยและผลิตบัณฑิตดังนี้

-     ปริญญาบัณฑิต จำนวน 3 คน และ

-     มหาบัณฑิต จำนวน 1 คน

เอกสารอ้างอิง

กรมโยธาธิการ. 2538. โครงการศึกษาความเหมาะสมโครงการอนุรักษ์และฟื้นฟูน้ำใต้ดิน จ.กำแพงเพชร.

คณะกรรมการสิ่งแวดล้อมแห่งชาติ. 2547. มาตรฐานคุณภาพดิน. ตามประกาศคณะกรรมการสิ่งแวดล้อม แห่งชาติฉบับที่ 25 พ.ศ. 2547. กระทรวงวิทยาศาสตร์เทคโนโลยีและสิ่งแวดล้อม.

ธนัท ธนาบูรณ์. 2554. แบบจำลองการไหลของน้ำบาดาลและการเคลื่อนตัวของโลหะหนัก บริเวณ ต.หัวเรือ อ.เมือง จ.อุบลราชธานีอุบลราชธานี. ปริญญาบัณฑิต ภาควิชาธรณีวิทยา คณะ วิทยาศาสตร์ จุฬาลงกรณ์ มหาวิทยาลัย.

พิศาล ชัยสายัณห์ และ บัญชา ขวัญยืน, 2547. การจำลองการเคลื่อนตัวของน้ำใต้ดินของโครงการ น้ำใต้ดินสุโขทัยโดยใช้โปรแกรม MODFLOW. วิทยาสารกำแพงแสน. ปีที่ 2. ฉบับที่ 1. หน้า 61-71.

ปัทมา โชติกวิน. 2553. การดูดซับและจำลองการเคลื่อนตัวของตะกั่วและทองแดงในชั้นดินที่ไม่อิ่มตัวด้วยน้ำ กรณีศึกษา ตำบลหัวเรือ จังหวัดอุบลราชธานี. ปริญญาบัณฑิต ภาควิชา ธรณีวิทยา คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย.

สุธาสินี ซื่อสัตย์. 2553. การกระจายตัวและศักยภาพในการเคลื่อนตัวของโลหะหนักในดินและชั้นน้ำ บาดาลระดับ ตื้นบริเวณพื้นที่เกษตรกรรม: กรณีศึกษาตำบลหัวเรือ จังหวัดอุบลราชธานี. ปริญญาบัณฑิต ภาควิชา ธรณีวิทยา คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย.

Allen, T. 1974. Particle Size Measurement. Chapman&Hall, London.

Appel, C., Ma, L., Rhue, R., and Reve, W,. 2008. Sequential sorption of lead and cadmium in three tropical soils. Environmental Pollution 155:132-140.

ASTM D 6386-02. 2003. Test methods for determination of the soil water characteristic curve for desorption using a hanging column, pressure extractor, chilled mirror hygrometer, and/or centrifuge, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA.

ASTM D 7100. 2006. Standard test method for hydraulic conductivity compatibility testing of soils with aqueous solutions, West Conshohocken, PA.

Ayenew, T., Demlie, M. and Wohnlich, S., 2008. Application of Numerical Modeling for Groundwater Flow System Analysis in the Akaki Catchment, Central Ethiopia. Mathematical Geosciences 40: 887-906.

Blake, G.R. and Hartge, K.H. 1986. Bulk density. In: Klute, A. (Ed.), Methods of soil analysis Part 1, 2nd ed. Monogr. 9, ASA and SSSA, Madison, Winsconsin, pp.363-375.

Brooks, R.H. and A.T. Corey. 1964. Hydraulic Properties of Porous Media. Hydrology Papers 3, Colorado State University, Fort Collins, CO.

Chaturvedi, P., Seth, C., and Misra, V. 2006. Sorption kinetics and leachability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite). Chemosphere 64:1109-1114.

Chen G., Zeng, G., Du, C., Huang, D., Tang, L., Wang, L., and Shen, G. 2010. Transfer of heavy metals from compost to red soil and groundwater under simulated conditions. Journal of Hazardous Materials 181: 211-216.

Chotpantarat, S., and Sutthirat, C. 2009. Influence of Unsaturated Soil Hydraulic Parameters on Nonequilibrium Transport of Mn^{2+} under Single and Multiple Metals through Lateritic Aquifer: A Case Study of Gold Mine in Thailand. Paper presented at GEOSEA 2009, Kuala Lumpur, Malaysia, 8-10 June.

Chrostophoridis, C., Dedepsidis, D. and Fytisnos, K. 2009. Occurrence and distribution of selected heavy metals in the surface sediments of Thermiakos Gulf, N.Greece. Assessment using pollution indicators. Journal of Hazardous Materials 168: 1082-1091.

Claesson, M. and Fagerberg, J. 2003. Arsenic in groundwater of Santiago del Estero—source, mobility pattern and remediation with natural materials. Master Thesis, Dept. of Land and Wat Res. Eng., KTH, Stockholm, Sweden, TRITA-LWRLEXL-03-05, p. 59.

Covelo, E., Vega, F., and Andrade, M,. 2007. Heavy metal sorption and desorption capacity of soils containing endogenous contaminants. Journal of Hazardous Materials 143:419-430.

Dong, D., Zhao, X., and Gao, M. 2009. Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China. Journal of Hazardous Materials 162: 1261-1268.

EU. EU's drinking water standards [Online]. 1998. Available from: http://www.lenntech.com/applications/drinking/standards/eu-s-drinking-water-standards.htm [2011, April]

Eugenia, G.G., Vicente, A., and Rafael, B. 1996. Heavy metals incidence in the application of inorganic fertilizers and pesticides to rice farming soil, Environmental Pollution 92: 19-25.

Gowd S.S., Reddy M.R. and Govil P.K. 2010. Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. Journal of Hazardous Materials 174: 113-121.

Hansen, A., and Maya P., 1997. Adsorption-desorption behaviors of Pb and Cd in lake Chapala, Mexico. Environment International 27:553-56.

Hakanson, L. 1980. An Ecological Risk Index for Aquatic Pollution Control: A Sedimentological Approach. Water Research, 14: 975–1001.

Kaasalainen, M., and Yli-Halla, M. 2003. Use of sequential extraction to assess metal partitioning in soils. Environmental pollution 126: 225-233.

Karbassi, A., Saeedi, M. and Amirnejad, R. 2008. Historical changes of heavy metals content and sequential extraction in a sediment core from the Gorgan Bay, Southeastern Caspian Sea.

Indian Journal of Marine Sciences, 37(3): 267-272.

Keivan N., Bakar N.K.A, Abas, M.R. 2009. Investigation of heavy metals mobility in shrimp aquaculture sludge — Comparison of two sequential extraction procedures. Microchemical Journal 91: 227–231.

Kookana, R.S., Naidu, R., and Tiller, K.G. 1994. Sorption non-equilibrium during cadmium transport through soils. Australian Journal of Soil Research 32: 635-651.

Li, Q. 2000. Effect of surfactants on the sorption and transport of Cu (II) in a sandy soil: batch and column experiments and modeling. Master's Thesis. Department of Building, Civil and Environmental Enginerring. Concordia University.

Li, Y., Gou, X, Wang, G., Zhang, Q., Su, Q., and Xiao, G. 2008. Heavy metal contamination and source in arid agricultural soil in central Gansu Province, China. Journal of Environmental Sciences 20: 607–612.

Ma, L., Xu, R., and Jiang, J. 2010. Adsorption and desorption of Cu(II) and Pb(II) in paddy soils cultivated for various years in the subtropical China. Journal of Environmental Science 22(5): 689-695.

Merian, E., 1991. Metals and their compounds in the environment, VCH Verlaggesellschaft, Germany, pp: 1438.

Miretzky, P., Muñoz, C., and Carrillo-Chávez, A. 2006. Experimental Zn (II) retention in a sandy loam soil by very small columns. Chemosphere 65: 2082-2089.

Muller G. 1969. Index of geoaccumalation in sediments of the Rhine River, GeoJournal 2:108-118.

Nouri, J.,Mahvi, A.H.,Babaei, A.A., 2006. Investigation of Heavy Metals in Groundwater. Pakistan Journal of Biological Sciences 9(3): 377-384.

Pang, L., Close, M., Greenfield, H., and Stanton, G. 2004. Adsorption and transport of cadmium and rhodamine WT in pumice sand columns. New Zealand Journal of Marine and Freshwater Research 38: 367-378.

Pansu M., Gautheyrou J. 2006. Handbook of soil analysis mineralogical, Organic and inorganic methods. Spring Verlag, Heidelberg, Berlin.

PCD. 2004. Ministry of Natural Resources and Environment. Drinking Water Standards. Available at http://www.pcd.go.th/info_serv/en_reg_std_water01.html#s1. Accessed 20 Jan 2012

Perez G., and Valiente M. 2005. Determination of pollution trends in an abandoned mining site by application of a multivariate statistical analysis to heavy metals fractionation using SM&T-SES. Journal of Environmental Monitoring 7: 29-36. 10.

Pueya M., Mateu J., Rigol A., Vidal M., Lopez-Sanchez, J.F. and Rauret, G. 2008. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environmental Pollution 152: 330-341.

Reimann, Th., Liedl, R. and Walther, W., 2007. Transport of solutes in the transition zone of saturated and unsaturated underground. Beiträge zur Hydrogeologie 56: Jahrgang 2007/2008.

Rogan, N., Dolenec, T. and Serafimovski, T., 2010. Distribution and mobility of heavy metals in paddy soils of the Kocani Field in Macedonia. Environ Earth Science 61: 899-907.

Rybicka, E., Calmano, W., and Breeger, A., 1995. Heavy metals sorption/desorption on competing clay minerals; an experimental study. Applied Clay Science 9:369-381.

Santos, A. and Alonso, E., 2002. Heavy metal content and speciation in groundwater of the Guadiamar river basin. Chemosphere 48: 279–285.

Sawyer, R.H., Washington, L.D., Salvatore, B.A., Glenn, T.C., Knapp, L.W. 2003. Origin of archosaurian integumentary appendages: The bristles of the wild   turkey beard express feather-type β keratins. Journal of Experimental Zoology: 27-34.

Sayen, A., Mallet, J., and Guillon, E. 2009. Aging effect on the copper sorption on a vineyard soil: Column studies and SEM-EDS analysis. Journal of Colloid and Interface Science 331: 47-54.

Sastre J., Rauret G. and Vidal M. 2007. Sorption-desorption tests to assess the risk derived from metal contamination in mineral and organic soil. Environmental International 33: 246-256.

Srithongdee, T., Chotpantarat, S., Siriwong, W., Siripattanakul, S., and Sutthirat, C. 2010. Nitrate and Pesticide contamination of shallow groundwater under chilli field of Hua Rua, Ubon   Ratchathani Province. Paper presented at APRC-2010, Ubon Ratchathani, Thailand, 24-27   March, 2010.

Takeno, N. (2005). Atlas of Eh-pH diagrams. Intercomparison of Thermodynamic Databases, National Institute of Advanced Industrial Science and Technology Research Center for Deep Geological Environments: Geological Survey of Japan Open File Report No. 419.

Tsou, M. and Whittlemore, D., 2001. User Interface for Ground – Water Modeling, Arcview Extension. Journal of Hydrologic Engineering 6: 251-257.

Walkey, A. and Black, I.A. 1934. An examination of the Degtjareff method for determinating soil   organic matter, and a proposed modification of the chromic acid titration method. Soil Science   34: 29-38.

Williams, L.E., Mark, O.B., Kramer, T.A., and Melville, J.G. 2003. Adsorption and transport of   Arsenic (V) in experimental subsurface systems. Journal of Environmental Quality 32: 841-850.

WHO (World Health Organization). (2011). Guidelines for drinking-water quality (4th ed.). http://www.whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf. Accessed 01/15/2011.

Wong, S.C., Li, X.D. and Zhang, G. 2002. Heavy metals in agricultural soils of the Pearl River Delta,South China. Environmental Pollution 119: 33–44.

Van der Grift, B. and Griffioen, J. 2008. Modelling assessment of regional groundwater contamination due to historic smelter emissions of heavy metals. Journal of Contaminant Hydrology 96: 48–68.

van Genuchen M.Th., F.J. Leij and S.R. Yates. 1991. The RETC Code for Quatifying the Hydraulic Functions of Unsaturated Soils. US Satinary Laboratory, US Department of Agriculture, Agricultural Research Services, Riverside, California 92501,85 p.

Vega, F., Covelo, E., and Andrade, M. 2006. Competitive sorption and desorption of heavy metals in mine soils: Influence of mine soil characteristics. Journal of Colloid and Interface Science 298: 582-592.

Yolcubal, I. and Akyol, N.H. 2007. Retention and transport of hexavalent chromium in Calcareous Karst soils. Turkish Journal of Earth Sciences 16: 363-379.

ภาคผนวกที่ ก

เอกสารนำเสนอในงานประชุมวิชาการระดับนานาชาติ

1. **Chotpantarat, S.**, Sutthirat, C., and Srisuk, K. 2012. Transport modeling of single and binary metal systems of Pb and Cu through unsaturated soil in an agricultural area: A case study of Hua Rua area, Thailand. The 4th IWA Asia-Pacific Young Water Professionals Conference. Japan, 7-10 Dec., 2012 (Full paper and Oral presentation)

2. **Chotpantarat, S.** and Masipan, T. 2013. Sequential Fractionation of Heavy Metals in Agricultural Soils: A Case Study of Hua Rua Area, Ubon Ratchatani Province. International Conference on Environmental and Hazardous Substance Management, Bangkok, Thailand, 21-23 May, 2013. (Full paper and Oral presentation)

Program

[December 8, 2012]

Registration (8:00-9:00)

Plenary Session (9:00-10:30)
Chairperson: Ryo Honda, Kanazawa University
   Opening Remark: Hisashi Satoh (Chair of APYWP2012), Hokkaido University
   Welcome Remark: Tao Li, IWA China Regional Office
   Welcome Remark and Introduction of Japan-YWP: Ikuro Kasuga (Chair of Japan-YWP), The University of Tokyo
  Keynote Speech 1:
   Sustainability and sustainable technologies for a better world
   Dr. Subhas K. Sikdar, US EPA
  Keynote Speech 2:
   Sustainability science – An approach to tackle complicated problems
   Dr. Kensuke Fukushi, The University of Tokyo
  Group Photo

Academic Session A-1: Membrane bioreactor (12:45-14:15)
Chairperson: Hiroshi Yamamura, Chuo University
  Combination of photocatalysis and membrane bioreactor for TFT-LCD wastewater treatment
        Sheng-Jie You, Galilee Uy Semblante, Yu-Pu Chen, Tien-Chin Chang, Taiwan
  Development of energy saving technologies for MBR
        Kousuke Kajiyama, Kouji Fukumoto, Masaki Tsuzawa, Shigehide Hirata, Japan
  Feasibility of an innovative anaerobic forward osmosis membrane bioreactor (AnFOMBR) based on hybrid FO-NF configuration for wastewater treatment and energy recovery
        Melvin Tang, How Yong Ng, Singapore
  Synthesis of mesoporous magnetic r-Fe_2O_3 and its application in membrane bioreactor (MBR)
        Nien-Yu Lee, Galilee Semblante, Sheng-Jie You, Taiwan
  Effect of chemical coagulation and microfiltration pre-treatment on reverse osmosis fouling in leachate treatment plant at full scale operation
        Weerapong Rukapan, Chart Chiemchaisri, Wilai Chiemchaisri, Banyapa Khananthai, Thirdpong Srisukphun, Thailand
  Transformation of dissolved organic matter (DOM) during treatment of partially stabilized leachate by membrane bioreactor
        Samunya Sanguanpak, Chart Chiemchaisri, Wilai Chiemchaisri, Kazuo Yamamoto, Thailand

Academic Session A-2: Wastewater treatment 1 (15:15-16:45)
Chairperson: Takashi Onodera, National Institute for Environmental Studies
  Characterization of ultrasonic and microwave pretreated municipal mixed sludge and its anaerobic biodegradability
        Anteneh Mesfin Yeneneh, Siewhui Chong, Tushar kanti Sen, Ha ming Ang, Ahmet Kayaalp, Australia
  Effects of temperature on anaerobic biodegradation of polyhydroxybutyrate accumulated in the cells of waste activated sludge microorganisms
        S. M. Shamsul Huda, Hiroyasu Satoh, Takashi Mino, Japan
  Anaerobic treatment of pharmaceutical wastewater using sequencing batch reactor (AnSBR)

Xueqing Shi, Olivier Lefebvre, Kok Kwang Ng, How Yong Ng, Singapore

Biodegradation of fluorophenol using sequential batch reactor

Basavaraju Manu, Dibya Ranjan Dash, India

Successful treatment of high azo dye concentration wastewater using combined anaerobic/aerobic granular activated carbon-sequencing batch biofilm reactor (GAC-SBBR): Simultaneous adsorption and biodegradation processes

E. Hosseini Koupaie, M.R. Alavi Moghaddam, S.H. Hashemi, Iran

Effects of organic loading rates for the simultaneous removal of organic and odorous compounds using an electrochemical oxidation system

Hae Young Ahn, Ji Hyeon Song, Hyeong Kyu Namgung, Jin Sung Kim, Yun Ki Nam, South Korea

Academic Session A-3: Treatment of radioactive materials/ Disaster (16:55-18:25)

Chairperson: Seung Joo Lim, Korean Atomic Energy Research Institute

Selection of suitable sites for small hydropower generation using GIS and remote sensing

H. RAMESH, S. VANI, India

Evaluation of the effect of the Great East Japan Earthquake on the coastal environment in Kamaishi Bay

Mitsuo Yamamoto, Daisuke Kitazawa, Takayoshi Kato, Shinji Komatsuda, Motoyuki Matsuo, Katsumi Shozugawa, Shigeru Tabeta, Japan

Removal of radioactive Cesium along drinking water treatment processes

Soichi Watanabe, Yasuhiro Kobayashi, Kaori Tsuchiya, Makoto Sasaki, Tomo Oikawa, Japan

Cesium behavior in a dam reservoir at Fukushima Prefecture

Wenhan LI, Jiefeng LI, Alif SAMSEY, Toshiyuki KAWAGUCHI, Fusheng LI, Japan

Academic Session B-1: Micropollutants 1 (12:45-14:15)

Chairperson: Liou Ya-Hsusan, National Taiwan University

Dissolved organic matter (DOM) removal mechanisms by anion exchange resins (AERs)

Athit Phetrak, Satoshi Takizawa, Jenyuk Lowhwacharin, Michio Murakami, Kumiko Oguma, Hiroshi Sakai, Japan

Degradation of emerging contaminant ibuprofen by electrochemical anodic oxidation

Chih-Han Hsu, Chiung-Fen Chang, Ching-Yuan Chang, Taiwan

Identification and toxicological evaluation of intermediates from photodegradation of diuron by zinc oxide

Esara Sadudeewong, Hiroaki Tanaka, Varong Pavarajarn, Alisa S. Vangnai, Japan

A multi-tracer approach for analyzing occurrence and sources of perfluorinated compounds (PFCs) in groundwater in Tokyo

Keisuke Kuroda, Michio Murakami, Kumiko Oguma, Hideshige Takada, Satoshi Takizawa, Japan

Emerging pollution of PPCPs and estrogen and seasonal factors in Gyeongan River, South Korea

Lee SangJung, Vimal Kumal, Norihide Nakada, Han Ihnsub, Hiroaki Tanaka, Japan

Academic Session B-2: Micropollutants 2 (15:15-16:45)

Chairperson: Hsin-hsin Tung, National Taiwan University

Assessment of urban road dust toxicity as a non-point pollution source contaminating water environment

Rajendra Khanal, Hiroaki Furumai, Fumiyuki Nakajima, Japan

Effects of precipitation on the concentrations of veterinary medicines using QSAR

Seung Joo Lim, Tak-Hyun Kim, Sang-hun Kim, Byung-hak Yoo, Sun-Kyoung Kim, South Korea

Transport modeling of single and binary metal systems of Pb and Cu through unsaturated soil in an agricultural area: a case study of Hua Rua area, Thailand

Srilert CHOTPANTARAT, Chakkaphan SUTTHIRAT, Kriengsak SRISUK , Thailand

A low cost novel waste based inorganic adsorbent in the removal of cationic dye methylene blue (MB) from aqueous solution by adsorption: Equilibrium, thermodynamic, kinetics, mechanism and process design

Tushar Kanti Sen, Tam Doung and Hiroshi Nishioka, Australia

Direct and indirect photolysis of antineoplastic drugs in surface water systems

Wan-Ning Lee, Angela Yu-Chen Lin, Taiwan

Academic Session B-3: Micropollutants 3 (16:55-18:25)

Chairperson: Keisuke Kuroda, The University of Tokyo

Occurrence of pharmaceuticals in Feitsui reservoir and their sources in upstream watersheds in northern Taiwan

Xiao-Huan Wang, Wan-Ning Lee, Angela Yu-Chen Lin, Taiwan

Performance and kinetics of estrogens removals by aquatic plants

Yoshihiko INAGAKI, Taishiro FUJITA, Andre Rodrigues dos REIS, Shima SUZUKI, Yutaka SAKAKIBARA, Japan

Removal of methylene blue from aqueous solution using raw and modified pine tree leaves as adsorbent

Mustafa T. Yagub, Tushar Kanti Sen, H. M. Ang, Australia

Trend in biodegradability improvement of azo dyes by ozonation

Muhammad Ridwan Fahmi, Che Zulzikrami Azner Abidin, Nazerry Rosmady Rahmat, Ong Soon An, Malaysia

Special Session 1: Pathogens and indicators in water (15:15-16:45)

Chairperson: Daisuke Sano, Hokkaido University

PCR-based monitoring and multivariate statistical analysis benefit exploration of fecal pollution in water environments

Fusheng Li, Japan

Improvement of virus detection efficiency by removing organic matters in virus concentrate

Akihiko Hata, Hiroyuki Katayama, Hiroaki Furumai, Japan

Bacteroides-Prevotella genetic markers as fecal pollution indicators for microbiologically safe water management

Ayano Kobayashi, Daisuke Sano, Satoshi Ishii, Satoshi Okabe, Japan

Basic consideration of detection of pathogens using next generation sequencer

Masaru Ihara, Tomonari Matsuda, Suntae Lee, Hiroaki Tanaka, Japan

Special Session 2: Pathogen control and risks in water management (16:55-18:25)

Chairperson: Daisuke Sano, Hokkaido University

Estimation of norovirus infection risk in the reclaimed water for agriculture irrigation

Nobuhito Yasui, Mamoru Suwa, Tsutomu Uchida, Japan

Estimation of illness-to-infection rate of Campylobacter jejuni based on epidemiological study

Yasuhiro Asada, Yumiko Ohkouchi, Sadahiko Itoh, Japan

Virus removal by a coagulation-microfiltration process

Nobutaka Shirasaki, Taku Matsushita, Yoshihiko Matsui, Japan

Risk assessment for viral infection via drinking water considering age-dependent susceptibility

Toru Watanabe, Hiroaki Ito, Daisuke Sano, Satoshi Okabe, Japan

Recovery of wastewater treatment plant damaged by the 2011 flood in Thailand: From the viewpoint of health risk due to reuse of treated wastewater

Chittima Charudacha, Panja Yaithavorn, Toru Watanabe, Yoshifumi Masago, Ryo Honda, Tatsuo Omura, Thailand

[December 9, 2012]

Academic Session A-4: Water/ Wastewater treatment (9:00-10:30)

Chairperson: Masashi Hatamoto, Nagaoka University of Technology

The effects of recycling algae and controlling solid retention time in high rate algal pond

    Hina DERABE MAOBE, Masazumi ONODERA, Masahiro TAKAHASHI, Hisashi SATOH, Tatsuya Fukazawa, Japan

Characterization and identification of manganese oxides present in naturally coated filter media from conventional aeration-filtration groundwater treatment plants

    Jantinus H. Bruins, Branislav Petrusevski, Yness M. Slokar, Maria D.Kennedy, The Netherlands

Evaluation on suitable disinfection processes for sewage effluent during disaster restoration

    Kyoungsoo Park, Inkoo Park, Naoyuki Yamshita, Hiroaki Tanaka, Japan

Mesophilic co-digestion of sewerage sludge in the oxidation-ditch process and wasted fried tofu

    Tingting GU, TaketoTogari, Takahiro Nakade, Ryoko Yamamoto-Ikemoto, Eri Nakakihara, Ryo Honda, Japan

Mesophilic aerobic digestion of waste activated sludge pretreated by hybrid microwave-alkali method

    Vinay Kumar Tyagi, Shang-Lien Lo, Taiwan

Treatment of municipal sewage in snowy region by using anaerobic-oxic biological filter reactor equipped with swinging carbon fibers

    Yuerui Chen, Ryoko Yamamoto-Ikemoto, Eri Nakakihara, Ryo Honda, Japan

Academic Session A-5: Wastewater treatment 2 (10:45-12:15)

Chairperson: Kengo Kubota, Tohoku University

Experience of full scale sewage treatment plant in a developing country: a case study of sewage treatment plant 1-9, Islamabad

    Moazzam Shahzad, Sher Jamal Khan, Shahid Sohai, Pakistan

Development of the DHS-USB system for nitrification and denitrification of marine aquarium water

    Ayato Furukawa, Akinobu Nakamura, Masanobu Takahashi, Masahito Mori, Mutsumi Kawamata, Masahiro Nishimura, Takashi Yamaguchi, Japan

Nitrogen removal from treated wastewater through rice cultivation with circulated irrigation

    Ayumi Muramatsu, Toru Watanabe, Atsushi Sasaki, Akihiko Kajihara, Japan

Sequential carbon removal and SND (simultaneous nitrification and denitrification) for landfill leachate treatment by microbial fuel cell

    Chunhua Feng, Haixia Du, Zaiji Yu, Wenhan Li, Fusheng Li, Japan

Enhancement of nitrification and denitrification for treatment of landfill leachate with high-concentration ammonia nitrogen by dilution

    Zaiji YU, Chunhua FENG, Fusheng LI, Japan

Academic Session A-6: Wastewater management (13:30-14:45)

Chairperson: Akihiko Terada, Tokyo University of Agriculture & Technology

Reuse of wastewater from rubber sheet production for agriculture in Northeast Thailand

    Chuleemas Boonthai Iwai, Sasiwath Titapan, Mongkon Ta-Oun, Thailand

Development of carbon electrode for the desalination of seawater by means of capacitive deionization (CDI)

    Andre, Ginno Lizano, Shoukei Yuki, Yoshinobu Yoshihara, Japan

Investigation of whole effluent toxicity (WET) program for wastewater management in Japan

    Haruna Watanabe, Norihisa Tatarazako, Japan

Mathematical modeling of industrial water systems

Pavel Gotovtsev, Julia Tichomirova, Russia

Treatbility study of waste activated sludge in the presence of PCBs and transformer oil

Devrim Kaya, Ipek Imamoglu, F. Dilek Sanin, Turkey

Academic Session A-7: Energy efficent and recovery (15:15-16:45)

Chairperson: Daisuke Inoue, Kitasato University

Availability of organic suspended solid as substrate for power generation in microbial fuel cell

Jia Jin, Kayako Hirooka, Osamu Ichihashi, Fusheng Li, Japan

N_2O formation mechanism and control technology in wastewater treatment

Sheng-Jie You, Wei-Chun Chien, Taiwan

Kinetics of nitrification and denitrification in two-chamber MFC reactors for treatment of wastewater containing high content of ammonia nitrogen

Haixia Du, Chunhua Feng, Zaiji Yu, Wenhan Li, Fusheng Li, Japan

Photocatalytic hydrogen production from formic acid solution over platinum deposits on CdS/Titanium nanotubes with visible light illumination

Yi-Chun Lai, Hsiu-Yu Chen, Hsin-Hung Ou, Shang-Lien Lo, Taiwan

Water supply operation intended for greater energy efficiency

Yoshihiro Sakurai, Norikazu Suzuki, Japan

Grazing preference of bacteria by *Bodo saltans separated from activated sludge*

Yurie Shirakawa, Osamu Nishimura, Ryuichi Sudo, Japan

Academic Session B-4: Water treatment/management 1 (9:00-10:30)

Chairperson: Muhammad Ridwan Fahmi, University Malaysia Perlis

A study on the perceptions of drinking water quality and risk in Shenyang, China

Lu Gao, Naoya Abe, Japan

Household survey on water sources and point-of-use water treatment systems in Hanoi, Vietnam

Do Thuan An, Keisuke Kuroda, Satoshi Takizawa, Takeshi Hayashi, Tran Thi Viet Nga, Kumiko Oguma, Japan

Competition in Water: IPART's approach to regulating Sydney Water's third party water access regime

Justin Robinson, Australia

Ultrafiltration of natural surface waters: Fouling effects of nanoparticles

Jenyuk Lohwacharin, Satoshi Takizawa, Japan

Introduction of Asia-Pacific Drinking Water Technology Information Network (Aswin)

Kunihisa Takahashi, Tatsuo Takeuchi, Shigeru Ando, Masahiro Fujiwara, Japan

Academic Session B-5: Water treatment/management 2 (10:45-12:15)

Chairperson: Nobutaka Shirasaki, Hokkaido University

Public relations activities of Tokyo metropolitan government to promote the understanding of water conservation forests among elementary school children

Kyohei Yamazaki, Kenji Sakai, Kunio Kinoshita, Japan

Study of private participation influence on the efficiency performance of municipal water management in Indonesia

Nirmala Hailinawati, Naoya Abe, Japan

Counting planktons to examine the water mass movement in raw water conveyance facilities

Rumiko Yano, Japan

The contribution of organic nitrogen and inorganic chloramines on nitrogenous disinfection byproducts formation from natural waters

Yi-Hsueh Chuang, Hsin-hsin Tung, Taiwan

Importance of autotrophic denitrification and formation of DON in ammonia nitrogen transformation in drinking water biofiltration

    Xin Yu, Bing Liu, Zihong Fan, Huining Zhang, Shenghua Zhang, China

Academic Session B-6: Microbiology 1 (13:30-14:45)

Chairperson: Yoshifumi Masago, Tohoku University

Viruses in stream channels in residential areas that receive effluent of on-site wastewater treatment facilities

    Ahmad S. SETIYAWAN, Toshiro YAMADA, Fusheng LI, Denny HELARD, Joni A. FAJRI, Akihiro HORIO, Min KOU, Japan

Multiple peaks expression of enteric virus density in environmental water

    Daisuke Sano, Tsuyoshi Kato, Ayano Kobayashi, Takayuki Miura, Satoshi Okabe, Japan

Comprehensive detection of bacterial pathogens in the shallow well groundwater in Kathmandu valley, Nepal, using a DNA microarray

    Daisuke Inoue, Noriko Suzuki, Takuji Hinoura, Kaori Miyauchi, Junqin Pang, Saroj K. Chapagain, Hiroaki Matsuzawa, Yasuhiro Tanaka, Michihiko Ike, Kei Nishida, Kazunari Sei, Japan

Analysis of effect on edible root crops by microcystin toxin in blue-green algae

    Kakeru Ruike, Yuki Kanzo, Ryuhei Inamori, Kai-Qin XU, Yuhei Inamori, Japan

Simultaneous reduction of azo dye and sulfates by mixed anaerobic sulfate reducing bacteria culture

    Kashif Rasool, Gajanan Ghodake, Hye Min Ahn, Suk Hyang Kim, Dae Sung Lee, South Korea

Comparison of eukaryotic communities in wastewater treatment processes as revealed by 18S rRNA gene clone library

    Kengo MATSUNAGA, Kengo KUBOTA, Yasuyuki TAKEMURA, Hideki HARADA, Japan

Academic Session B-7: Microbiology 2 (15:15-16:45)

Chairperson: Xin Yu, Chinese Academy of Sciences

Development of sediment chronic toxicity test for freshwater ostracod Heterocypris incongruens

    Kenta Tsukahara, Fumiyuki Nakajima, Japan

Escherichia coli contamination and its relation to stormwater quality in Yongin watershed, South Korea

    Ma. Cristina A. Paule, Sheeraz Memon, Bum Yeong Lee, Chang-Hee Lee, Hor Gil Hul, South Korea

Adsorption of viruses onto activated carbon and their infectivity changes

    Shinta INDAH, Fusheng LI, Keita TANIOKA, Japan

Variation of nitrogen removal bacterial community in a full-scale landfill-leachate treatment plant

    Yu-Tzu Huang, Shiou-Shiou Chen, Jih-Gaw Lin, Taiwan

Microbial communities involved in anaerobic sulfur-oxidation in UASB reactor treating municipal sewage

    Aida Azrina AZMI, Masashi HATAMOTO, Masamitsu YAMAMOTO, Shinya ONO, Akinobu NAKAMURA, Masanobu TAKAHASHI, Takashi YAMAGUCHI, Japan

Special Session 3: Water education workshop (9:00-10:30)

Chairperson: Tomoko Takeda, Showa Kankyo System K. K.

Introduction

Project WET activity

Review of project WET activity

IWA world water monitoring challenge activity

Review of WWMC activity

Group discussion

Wrap-up

Special Session 4: International cooperation and water business (10:45-12:15)

Chairpersons: Ryo Honda, Kanazawa University, Takashi Hashimoto, Metawater Co. Ltd.

Invited Talks

Toshiyuki Shimizu, Japan

Samreth Sovithiea, Cambodia

Koichi Matsubara, Japan

Hironori Hamasaki, Japan

Floor Discussion

Academic Session C-6: Sustainable water environment 1 (13:30-14:45)

Chairperson: Jenyuk Lohwacharin, The University of Tokyo

Development of nutrients runoff behavior model in river water based on watershed survey

Koichi Sato, Keisuke Sato, Japan

A comparative study of electrosorption of ions by nanoporous carbon electrodes for capacitive deionization

Nei-Ling Liu, Chia-Hung Hou, Taiwan

Understanding chemical weathering rate and associated CO_2 consumption of the Brahmaputra River Basin (india) in the context of climate change and sustainability

Pallavi Das, Manish Kumar, K. P. Sarma, India

Sustainable water resources management in vietnam under climate change condition

Pham Ngoc Bao, Toshiya Aramaki, Japan

Practical aspects of indicators for measuring sustainability of certified products

Oscar David Matallana-Tost, Germany

Academic Session C-7: Sustainable water environment 2 (15:15-16:45)

Chairperson: Pham Ngoc Bao, Toyo University

Remediation of eutrophic sediments using industrial byproducts

Satoshi ASAOKA, Tamiji YAMAMOTO, Hideo OKAMURA, Japan

Water distribution system configurations analysis based on link importance measures

Li Shuping, Zhou Weiwei, Hou Yudong, Huang Lu, China

Evaluating annual rainfall trends using man-kendall test in Yom river basin, Northern Thailand

Pawee KLONGVESSA, Srilert CHOTPANTARAT, Thailand

Biodegradation characteristics of photosynthetic organic matter under the coexistence of a ciliate

Kei Suzuki, Naoyuki Kishimoto, Seiko Furuta, Satoshi Ichise, Japan

Closing Session (16:50-17:30)

Chairperson: Akihiko Terada, Tokyo University of Agriculture & Technology

Closing Remark: Hisashi Satoh (Chair of APYWP2012), Hokkaido University

Best Research Awards and Best Poster Awards Ceremony: Hisashi Satoh, Hokkaido University

Announcement of the 5th APYWP2014: Hsin-hsin Tung, National Taiwan University

Announcement of the 5th IWA-ASPIRE: Tao Li, IWA China Regional Office

Announcement of the Technical Tour: Akihiko Terada, Tokyo University of Agriculture & Technology

Transport Modeling of Single and Binary Metal Systems of Pb and Cu through Unsaturated Soil in An Agricultural Area: A Case Study of Hua Rua Area, Thailand

Srilert CHOTPANTARAT[1,2], Chakkaphan SUTTHIRAT[1] and Kriengsak SRISUK[3]

[1] Department of Geology, Faculty of Science, Chulalongkorn University, Bangkok, 10330 Thailand

[2] Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Chulalongkorn University, Bangkok, 10330 Thailand

[3] Department of Geotechnology, Faculty of Technology, Khonkaen University, Khonkaen, Thailand

E-mail: csrilert@gmail.com

Abstract

Most of agricultural areas in Tambon Hua Rua, Changwat Ubon Ratchatani have long been intensively applied fertilizer and pesticide in agricultural activities that may in turn impact negatively to the environment including human health. Results from the analysis of heavy metal and fertilizer from groundwater wells in the agricultural area found the amounts of Pb(II) and Cu(II) were greater than the standard of the Department of Pollution Control (PCD). So, this study focused on sorption and transport of such two heavy metals through shallow groundwater system.

This research divided into two parts. Firstly, the experiment was conducted to estimate the physical properties of the unsaturated soils, or soil water characteristic curve (SWCC), and batch experiments were performed in order to describe the sorption of Pb(II) and Cu(II). For batch experiments, loamy sand samples were carried out in 50 mL polypropylene tubes and were shaken at 180 rpm to homogenize and facilitate the reactions. The proportion of soil and water (g:mL) was 1:20 and were shaken for 48 hours at room temperature under the pH 4 (4 ± 0.2). Batch experiments were well fitted by linear isotherm sorption. Secondly, the parameters obtained batch experiments and SWCC used as input parameters for simulating by Hydrus-1D to illustrate water flow and transport of Pb(II) and Cu(II) through soil throughout a year. It showed that Cu(II) can move faster than Pb(II), which in lined with sorption properties of these metals. At 132 cm deep, average groundwater level, below ground surface, the amount of Pb(II) and Cu(II) contamination was 2.56×10^{-7} mg/L and copper 2.50×10^{-4} mg/L for single system and was 3.77×10^{-7} and 3.89×10^{-4} mg/L for competitive system, respectively.

Keywords: Freundlich isotherm, Competitive sorption, Hydrus-1D

1. Introduction

Trace substances from anthropogenic activities, for example, industrial activities, mining areas, agricultural production and atmospheric deposition, has been released to environment (Kim et al., 2003). Thailand is an agricultural country so that the farmers has long used pesticides and fertilizers for several decades. The result from using pesticides and fertilizers may cause the heavy metal contamination. People and animals may be then adversely affected by touching or drinking those polluted groundwater. One of the most agricultural areas, Tambon Hua Ruea, Ubon Ratchatani Province, has intensively applied pesticides and fertilizers in agricultural activities (Chotpantarat et al., 2011). Furthermore, the results from the analysis of heavy metal and fertilizer from groundwater wells the agricultural area found the amounts of Pb(II) and Cu(II) were greater than the standard of the Department of Pollution Control. Moreover, the pH of shallow groundwater measured in field revealed pH values around 3-4, acidic condition, that may accelerate the migration of heavy metals into groundwater system. In order to propose the specific management practices managing nonpoint source and protecting groundwater resources, the long-term effect from such agro-chemical would be derived. The mathematical models are the tool to describe the water flow and solute movement from ground surface into groundwater. Hydrus-1D is widely used to simulate solute transport in variable saturated flow system. However, there has been not yet clearly understood about heavy metals movement and also Hydrus-1D is suitable for chilly field. Therefore, the objective of this study were: 1) to characterize the soil water characteristics curve of soil collected from Hua Ruea area and 2) to apply a numerical modeling to estimate the transport of Pb(II) and Cu(II) from soil surface through shallow groundwater system.

2. Materials and methods

In this study, triplicate cores of undisturbed soil samples of 2 locations from 0-30 cm depth below the ground surface and cores of disturbed soil samples of 12 locations were sampled in the vicinity of cultivated chili fields (Fig.1). This research divided into two parts. First, the experiment was conducted to describe the physical properties of the unsaturated soils and batch experiments were performed in order to describe the sorption properties of Pb(II) and Cu(II) under single metal and multi-metal systems. According to ASTM D 6836, the pressure chamber apparatus was applied to determine the relationship between soil moisture and water pressure in soil (SWCC) by using the van Genuchten equations (VG). By batch experiments, loamy sand samples with the proportion between soil and water (g:ml) 1:20 were shaken for 48 hours at room temperature and controlled by the pH 4. Results derived from batch experiments were well fitted by Freundlich isotherm and sorption coefficient (K_f and n) can be derived. As mentioned, the parameters obtained from the previous experiments applied as input parameters for simulating by the Hydrus 1D to further describe the transport of lead and copper in soil throughout a year.
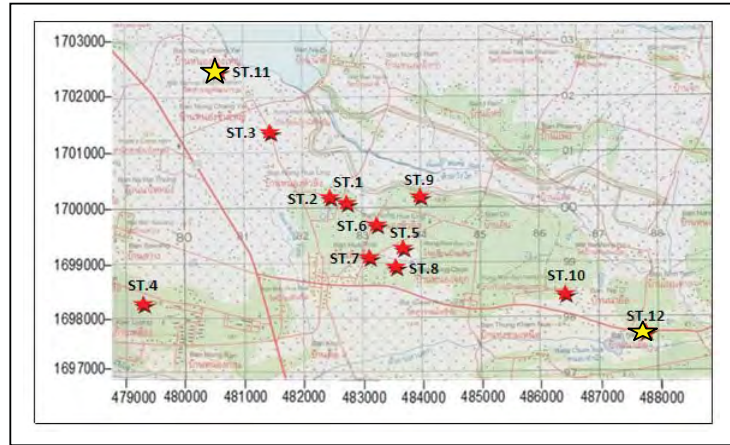
★ Locations of disturbed samples

☆ Locations of undisturbed samples

Fig. 1 Location of 12 disturbed and 2 undisturbed soil sampling sites
(in red and yellow marks, respectively)

3. Results and discussions

3.1 Physical and chemical properties

The textures of such agricultural soils were classified as loamy sand (Table 1). pH measurement of soils revealed that all top soils are mildly acid.

Table 1. Physical and chemical properties of soil in the study area

Site	Soil texture	Sand	Silt	Clay	Hydraulic conductivity, Ks	Organic matter	CEC	Bulk density	Porosity
		%	%	%	cm day^{-1}	%	cmol kg^{-1}	g cm^{-1}	cm^3 cm^{-3}
1-12	Loamy sand	77.0	15.0	8.0	11.73±4.57	1.06	2.3	1.56±0.06	0.43±0.06

3.2 Soil Hydraulic Properties

By applying the RETC program to fit SWCC results and estimate unsaturated parameters, the VG model could explain the SWCC behavior superior than BC model (Fig.2).
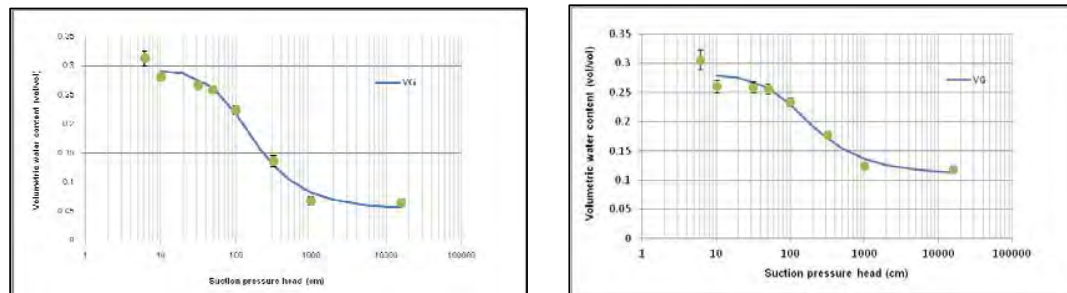

Fig.2 Soil water characteristic curve of soils explained by VG model

3.3 Sorption-desorption of Pb (II) and Cu (II)

The linear relationship of Qs versus Ce reveals that the sorption isotherms for Cu(II) and Pb(II) fit well to the linear equation (Fig.3). The batch experiment was designed to derive sorption coefficient (Kd) value yielding 0.0004 L/kg for Cu(II) and 0.043 L/kg for Pb(II) (Appel et al., 2008; Chaturvedi et al., 2006, Covelo et al., 2007a, 2007b). The results of the desorption of the previously sorbed Cu(II) and Pb(II) show that the desorption coefficient value yielding 0.0003 L/kg for Cu(II) and 0.0008 L/kg for Pb(II).
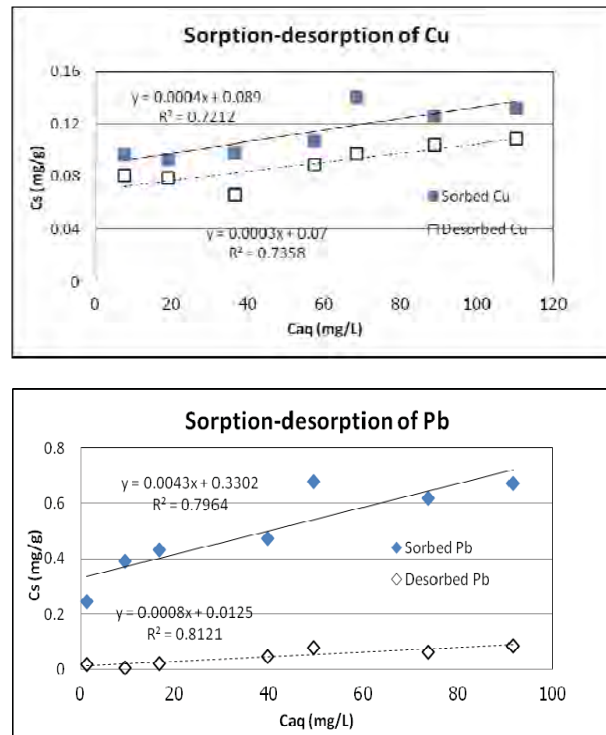

Fig.3 Adsorption-desorption isotherms for Cu(II) and Pb(II) by a chile soils

3.4 Movement of Pb (II) and Cu (II) in variable saturated zone

The simulation results of Pb (II) and Cu (II) transport through loamy sand affected by the rainfall in March and July, 2009 as shown in Fig.4. The heavy metal concentrations were found to decrease with increasing depth from the ground surface both summer and rainy seasons, especially Pb. The mobility of elements in soils depends on the infiltration of water into the soil domain and also its reaction with the soil and liquid phase could be taken into consideration. The infiltration rate is influenced by the hydraulic conductivity (K), which is strongly related to soil texture and water content. So, the distribution of soil moisture content was affected the degree of water infiltration, based on the weather data in terms of precipitation. However, since the saturated hydraulic conductivity of sandy loam relative higher than the rainfall rate, the distribution of water content may not show a constant shape, but rather was lower at the soil surface and increase with depth. Therefore the sorption

behavior would be more influence on metal migration than that of water content. As mentioned, the results of metal movement simulation of two scenarios both in summer and rainy seasons would not show significant different. At 132 cm deep, below ground surface, the amount of Pb and Cu contamination was 2.56×10^{-7} mg/L and 2.50×10^{-4} mg/L for single system, respectively, which is in lined with sorption mechanism from batch experiments.
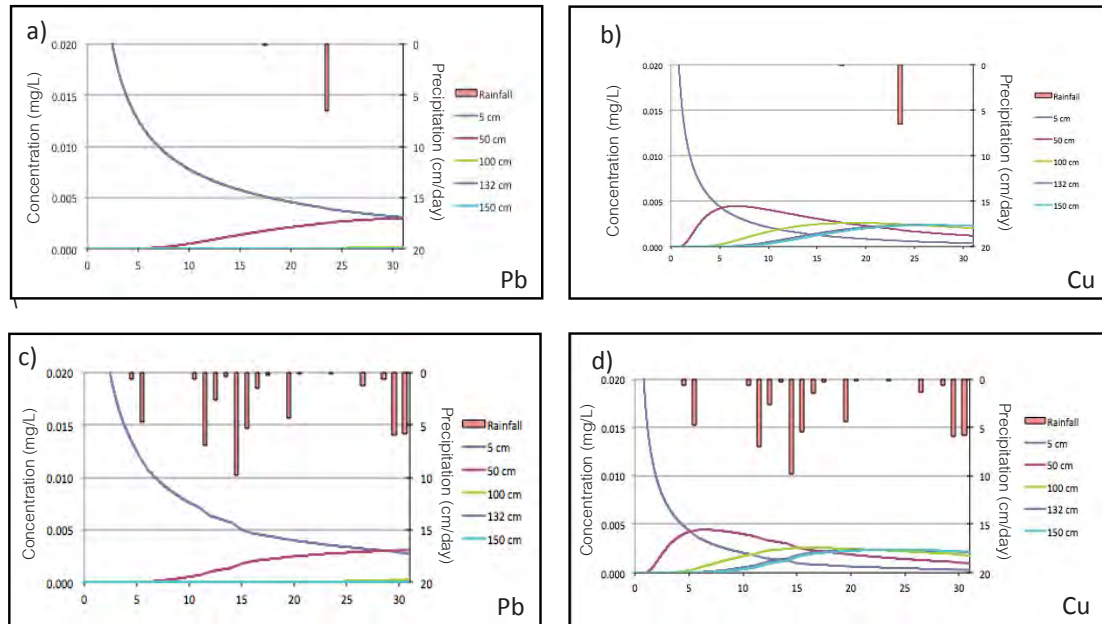

Fig.4 The simulated heavy metal concentrations at different depths below the soil surface in (a) March for Pb(II) (b) March for Cu(II) (c) July for Pb(II) (b) July for Cu(II)

4. Conclusions

The sorption coefficient of soils is quite important for assessing potential of transport of heavy metals from the ground surface to the subsurface environment, especially shallow groundwater system. HYDRUS-1D modeling showed that Pb (II) and Cu (II) transported through the topsoil with an approximate depth at 132 cm deep below ground surface, the amount of Pb (II) and Cu (II) contamination was 2.56×10^{-7} mg/L and copper 2.50×10^{-4} mg/L, respectively.

5. Acknowledgement

6. References

Appel, C., Ma, L., Rhue, R., and Reve, W. 2008. Sequential sorption of lead and cadmium in three tropical soils. Environmental Pollution 155:132-140

Chaturvedi, P., Seth, C., and Misra, V. 2006. Sorption kinetics and leachability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite). Chemosphere 64:1109-1114

Chotpantarat, C., Limpakanwech, C., Siriwong, W., Siripattanakul, S., and Sutthirat, C. 2011. Effects of soil water characteristic curve on simulation of nitrate vertical transport in a Thai agricultural soil. Sustainable Environmental Research 21(3): 187-193.

Covelo, E., Vega, F., and Andrade, M. 2007. Heavy metal sorption and desorption capacity of soils containing endogenous contaminants. Journal of Hazardous Materials 143:419-430

Covelo, E., Vega, F., and Andrade, M. 2007. Simultaneous sorption and desorption of Cd, Cr,Cu, Ni, Pb, and Zn in acid soils I. Selectivity sequences. Journal of Hazardous Materials147:852-861

Kim, I.S., Kand, K.H., Green, P.J. and Lee, E.J. 2003. Investigation of heavy metal accumulation in polygonum thunbergil for phytoextraction. Environmental Pollution 126: 235-143.

CONFERENCE PROGRAM

Tuesday 21 May 2013

Room: Queen's Park 1

07.30-09.00   Registration

09.00-09.30   **Opening Ceremony**

Reporting address
by Asst. Prof. Dr. Somporn Kamolsiripichaiporn
Director of Center of Excellence on Hazardous Substance Management, Conference Chair

Welcome address
by Assoc. Prof. Dr. Boonsom Lerdhirunwong
Dean of Faculty of Engineering, Chulalongkorn University

Opening address
by Prof. Pirom Kamolratanakul, M.D.
President of Chulalongkorn University

09.30-10.10   **Keynote I: Convergence of Nanotechnology and Microbiology: Emerging Opportunities for Water Disinfection Integrated Urban Water Management, and Risk Assessment**
by Prof. Dr. Pedro J.J. Alvarez
Rice University, USA

Room: Queen's Park 1

Session A: Industrial Ecology / Life Cycle Analysis
Chairs: Dr. Am Jang , Korea and Dr. Chanathip Pharino, Thailand

10.30-11.00   **Special Lecture I: SCP Policy Options towards Green Economy with Eco-Industrial Development Practices and Material Flow Accounting Tools**
by Prof. Dr. Anthony Chiu
De La Salle University, Philippines

11.00-11.20   Greenhouse Gas Emission in the Production of Microemulsion-based Biofuel
O-A-01   *Noulkamol Arpornpong*

11.20-11.40   Environmental Impact Evaluating of CRT and LCD Computer Screens End of Life
O-A-02   Management between Landfilling and Recycling Approaches
Tatthap Veeratat

11.40-12.00   Comparison of Environment Impacts for End-of-Life (EOL) Management of
O-A-03   Smartphone
Witthawin Sangprasert

Room: Queen's Park 4

Session B: Pollution Prevention / Waste Utilization
Chairs: Dr. Maria Fuerhacker, Austria and Dr. Patiparn Punyapalakul, Thailand

10.30-10.50   Parametric and Kinetic Studies of Sodium Diclofenac Adsorption onto Activated
O-B-01   Carbon Derived from Waste Rice Hulls
Judilyn Q. Filipinas

10.50-11.10   Adsorption of Diclofenac from Aqueous Solution Using Fe-Mn Binary Oxides:
O-B-02   Parametric and Kinetic Study
Benny Marie B. Ensano

11.10-11.30	Characterisation of Ten Organic Waste Biochars and their Use Potential for
O-B-03	Contaminant Removal: A Feasibility Study
	Ajit K Sarmah

Room: Queen's Park 5

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Tjandra Setiadi, Indonesia and Dr. Benjaporn Suwannasilp, Thailand

10.30-10.50	Development of Photo-Biohydrogen Process for Treatment of Starch Residue
O-G-01	*Supaknapar Rattanagumpol*

10.50-11.10	Potential and Reality of Bio-fermented Solution on Treating Polluted Water
O-G-02	*Sukanya Kaewruang*

11.10-11.30	The Response of Perturbation on Performance of Anaerobic Partial Mixed Reactor
O-G-03	Treating High Strength Wastewater
	Amornrat Boonmee

11.30-11.50	Current Production Increase by Biofilm and Nano-Pili Attached to the Electrode in
O-G-04	the Microbial Fuel Cell
	Numfon Eaktasang

Room: Queen's Park 6

Session F: Remediation of Contaminated Soil and Groundwater
Chairs: Dr. Say Kee Ong, USA and Dr. Pichet Chaiwiwatworakul, Thailand

10.30-10.50	Assessing and Communicating the Sustainability of Land Remediation Options
O-F-01	*Daniel C.W. Tsang*

10.50-11.10	Modelling of Salt Intrusion under Heavy Rainfall Infiltration
O-F-02	*Nattachat Boonchukusol*

11.10-11.30	Electromagnetic Induction Heating of Polymer-Modified Nanoscale Zerovalent Iron
O-F-03	(NZVI) Accelerates Remediation of Dense Non-aqueous Phase Liquid (DNAPL)
	Source Zone via Enhanced Dechlorination and NAPL Dissolution
	Tanapon Phenrat

11.30-11.50	Using Multi-Criteria Evaluation (MCE) and Geographic Information System (GIS)
O-C-01	for Assessing Flood Vulnerable Areas of Shrimp Farm in Chacheongsao Province
	Chaiyaporn Seekao

Room: Queen's Park 1

13.00-14.15	**Panel I: Green Economy Concept and Policies - Pathways to Sustainable Development?**

Moderator: *Prof. Dr. Thongchai Panswad*

- Perspectives on Green Economy
  Dr. Stefanos Fotiou, Senior Regional Coordinator, Resource Efficiency,
  Regional Office for Asia and the Pacific, United Nations Environment Programme
- Green Growth Strategy and Best Practices in South Korea
  Assoc. Prof. Dr. Heekwan Lee, Director, Incheon Regional Technology
  Development Center, and Lecturer at School of Urban and Environmental
  Engineering, Incheon National University
- Green Growth Strategy and Its Implementation in Thailand
  Dr. Wijarn Simachaya, Deputy Permanent Secretary, Ministry of Natural Resources
  and Environment

<div align="right">**Room: Queen's Park 1**</div>

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Eakalak Khan, USA and Dr. Patiparn Punyapalakul, Thailand

14.30-15.00	**Special Lecture II: Emerging Contaminants - How Can We Cope with this Challenge?** *by Prof. Dr. Maria Fuerhacker* *University of Natural Resources and Applied Life Sciences, Austria*
15.00-15.20 O-G-05	Comparison of Sorption of Dissolved Phosphorus onto Various Surface Modified Activated Carbon (SMAC) for Advanced Phosphorus Removal *Sangmin Lee*
15.20-15.40 O-G-06	Determination of Antibiotics (Tetracyclines And Sulfonamides) In Swine Wastewater By Liquid Chromatography-Tandem Mass Spectrometry *Jirawan Deeraksa*
15.40-16.00 O-G-07	Influence of Biofilm Carrier on Ammonia Oxidation in a Moving Bed Biofilm Reactor *Wannipha Dokbua*

<div align="right">**Room: Queen's Park 4**</div>

Session B: Pollution Prevention / Waste Utilization
Chairs: Dr. Takashi Yamaguchi, Japan and Dr. Alisa Vangnai, Thailand

14.30-15.00 O-B-04	Isolation and Characterization of an Alkaliphilic and Metal-tolerant Microorganism from A Landfill Site for Fly Ash Bioleaching *Yen-Peng Ting*
15.00-15.20 O-B-05	Optimization of Sewage Sludge, Swine Waste, and Food Waste Co-Digestion *Kim Sang-Hyoun*
15.20-15.40 O-B-06	Biosurfactant Production from Glycerol Waste And Its Applications for Enhancing Solubilization, Dispersion, and Emulsification of Petroleum *Ekawan Luepromchai*
15.40-16.00 O-B-07	Bioproduct from Shrimp Shell for Manipulating Soil borne Root Rot Fungi: Fusarium oxysporum, Rhizoctonia solani, and Sclerotium rofsii *Bajaree Lolium*

<div align="right">**Room: Queen's Park 5**</div>

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Marjorie Valix, Australia and Dr. Sumana Ratpukdi, Thailand

14.30-15.00 O-G-08	Influence of Aeration and Hydraulic Retention Time to Membrane Bioreactor Performances in Treating High Nitrogen Wastewater *Tjandra Setiadi*
15.00-15.20 O-G-09	Effect of Ammonia on Enrichment of Ammonia-Oxidizing Microorganism Inoculums for Ammonia Removal in Shrimp Ponds *Thanasita Chodanon*
15.20-15.40 O-G-10	Effects of Nitrite on Kinetics of Nitrite Oxidizing Bacteria Inoculums for Nitrite Removal in Shrimp Ponds *Wipasanee Tangkitjawisut*
15.40-16.00 O-C-02	Decentralized Composting of Institutional Wastes *Ajay S. Kalamdhad*

Room: Queen's Park 6

Session I: Environmental Policy, Law and Economics
Chairs: Dr. Say Kee Ong, USA and Dr. Chaiyaporn Puprasert, Thailand

14.30-15.00
O-H-01
Study on the Characteristics of the Activity Data for General Vessels in the Maritime Sector
Heekwan Lee

15.00-15.20
O-I-01
Evaluation of Municipal Solid Waste Characteristics via Self-Appraisal Technique
Amornchai Challcharoenwattana

15.20-15.40
O-I-02
Avoidance of Greenhouse Gas Emissions By Passive Aeration of Landfill: Case study in Tropical Environment
Komsilp Wangyao

15.40-16.00
O-I-03
Investigation of Solid Waste Open Burning Activity in Thailand
Saphawan Wattanakroek

Room: Queen's Park 1

Session J: Emerging Issues
Chairs: Dr. Petros Gikas, Greece and Dr. Manaskorn Rachakarakij, Thailand

16.00-16.20
O-J-01
Electronic Waste: an Insight from Saudi Arabia
Zayed Ali Huneiti

16.20-16.40
O-J-02
Assessment of E-Waste Management in Dhaka City: Issues and Strategies towards Sustainable Development
Tanzim Alam

16.40-17.00
O-J-03
Assessing the Potential of Acidithiobacillus thiooxidans in Bioleaching of Electronic Waste
Marjorie Valix

Room: Queen's Park 4

Session J: Emerging Issues
Chairs: Dr. Pedro Alvarez, USA and Dr. Pisut Painmanakul, Thailand

16.00-16.20
O-J-04
Kinetics and Copper Dissolution Behaviour from Copper-Rich E-Waste Using Acidophilic Bacteria
Alex Cheung

16.20-16.40
O-J-05
A Multimedia Data Mining System and Its Applications for Global Environmental Analysis
Yasushi Kiyoki

16.40-17.00
O-J-06
Material Flow Analysis of Municipal Solid Wastes in Bangkok: Case Study On-Nuch Transfer Station
Saravanee Singtong

Room: Queen's Park 5

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Takashi Yamaguchi, Japan and Dr. Sang-Min Lee, Korea

16.00-16.20
O-G-11
Study of Bubble Hydrodynamic and Mixing Parameters from Induced Air Flotation (IAF) with Mixing Devices in Plastic Separation Process
Pattarasiri Fagkaew

16.20-16.40 O-G-12	The Microbial Distribution in Fluidized Bed Reactor Under Various Operating Conditions *Phatchariya Rungkitwatananukul*
16.40-17.00 O-A-04	Life Cycle Assessment of Vehicle Batteries *Chuleekorn Sawettavong*

Room: the Terrace

17.00-18.00	**MOU Signing Ceremony**
18.00-20.30	**Conference Reception**

Wednesday 22 May 2013

Room: Queen's Park 1

09.00-10.20 **Panel II: Sustainable Consumption and Production Policy for Waste Management**
(co-hosted by United Nations Environment Programme)

Moderator: *Dr. Stefanos Fotiou,* **Regional Office for Asia and the Pacific, UNEP**

- *Ms. Shalimar Vitan,* Asia Pacific Coordinator for the Global Alliance of Incinerator Alternatives (GAIA), Philippines
- *Mr. Mohammad Helmy*, vice Chair, Indonesia Solid Waste Association, Indonesia
- *Mr. Donovan Storey*, Chief, Sustainable Urban Development Unit, UN-ESCAP, Thailand
- *Assoc. Prof. Dr. Alice Sharp*, Head, Department of Common and Graduate Studies, Sirindhorn International Institute of Technology, Thammasat University

Room: Queen's Park 1

Session F: Remediation of Contaminated Soil and Groundwater
Chairs: Dr. David A. Sabatini, USA and Dr. Chakkaphan Sutthirat, Thailand

10.40-11.10	**Special Lecture III: PAH Bioavailability Estimation Using Various Chemical Extraction Methods** *by Prof. Dr. Say Kee Ong* *Iowa State University, USA*
11.10-11.30 O-F-04	Effects of Different Rates of Boiler Ash, Filter Cake and Vinasse Amendments on the Fractionation of Cd And Zn in Cd Contaminated Soil *Pensiri Akkajit*
11.30-11.50 O-F-05	Effect of Arbuscular Mycorrhiza Fungi on Heavy Metal Co-contamination in the rhizosphere of L. philippensis (Cham.) Benth. Growing in the Contaminated Sediment *Kallaya Suntornvongsagul*
11.50-12.10 O-F-06	Waste Treatment Using Vermifiltration *Meena Khwairakpam*

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Kim Sang-Hyoun, Korea and Dr. Tawan Limpiyakorn, Thailand

10.40-11.00 O-G-13	Utility of Constructed Wetlands in Treating Domestic Wastewater in Indian Environmental Conditions *Akhilendra B. Gupta*
11.00-11.20 O-G-14	Ready-To-Use Serratia Sp. W4-01 Inoculum for Treatment of Lipid-Rich Wastewater and Its Potential Application in Petrol Station *Onruthai Pinyakong*
11.20-11.40 O-G-15	Enhancement of Nitrate and Sulfate Removal Efficiency in Anaerobic Baffled Reactor (ABR) by Iron Addition *Monchai Pumkaew*
11.40-12.10 O-G-16	Toxic Phenol-Production Wastewater Treatment by Fenton and Biological Processes *Kamonreuthai Tudthiam*

Session C: Sustainable Consumption and Production
Chairs: Dr. Chantra Tongcumpou, Thailand and Dr. Noppadon Kitana, Thailand

10.40-11.00 O-C-03	An Ecologically Sustainable Aquaponic System : Lettuce and Puntius Carp *Dhiti Cheochanvit*
11.00-11.20 O-B-08	Effect of Coir Pith and Modified Coir Pith as Soil Amendments in Arsenic Uptake in Rice Plants *Suteera Arnamwong*
11.20-11.40 O-F-07	Effect of Nitrilotriacetic Acid (NTA) and Ethylenediaminetetraacetic Acid (EDTA) on Arsenic Uptake from Contaminated Soil by Mimosa Pudica L. *Khamla Nanthavong*

Session E: Eco-toxicity/ Environmental and Human Risk Assessment
Chairs: Dr. Yen-Peng Ting, Singapore and Dr. Tassanee Prueksasit, Thailand

10.40-11.00 O-I-04	Non-Combustion Technology for The Destruction of Polychlorinated Biphenyls (Pcb) in The Philippines: An Evaluation of Its Affordability And Accessability for Government-Managed Electric Cooperatives *Luisa P. Martinez*
11.00-11.20 O-E-01	Health risk assessment from rice and vegetables in the vicinity of abandon lead smelter, Bo-Ngam lead mine, Karnchanaburi, Thailand *Teerawit Poopa*
11.20-11.40 O-E-02	Health Risk Assessment of Volatile Organic Compounds in Painting Process in the Automotive Industry *Charanya Daengthongdee*
11.40-12.00 O-E-03	Distribution of BTEX from Incense Smoke and The Potential Health Risk for The Workers at Worship Places in Bangkok, Thailand *Vee Maspat*
12.00-12.20 O-J-07	Investigation of Volatile Organic Compounds in the Cabin of a New Car : Concentrations and Effects of the In - Cabin Temperature and Car Age *Thabthim Chatsuvan*

<div align="right">**Room: Queen's Park 1**</div>

13.30-14.10 **Keynote II: Green Industry Initiative for Sustainable ASEAN Economic Community**

by Mr. Kan Trakulhoon
  President and CEO of the Siam Cement Group

<div align="right">**Room: Queen's Park 1**</div>

Session F: Remediation of Contaminated Soil and Groundwater
Chairs: Dr. David A. Sabatini, USA and Dr. Chantra Tongcumpou, Thailand

15.00-15.30 **Special Lecture IV: Carbon Nanotube Enabled Environmental Remediation and Water Treatment**

by Prof. Dr. Somenath Mitra
  New Jersey Institute of Technology,USA

15.30-15.50 Application of Rotary Chip Disc for On-Site Heavy Metals Measurement
O-F-08   *Am Jang*

15.50-16.10 Decomposition of 4-Chlorocatechol Using the Immobilized Hydroxyquinol 1,2-
O-F-09   Dioxygenase onto Single-Walled Carbon Nanotubes
  Yanasinee Suma

16.10-16.30 Optimizing N_2 Selectivity using Nzvi-Based Trimetal for Nitrate Reduction
O-F-10   *Yingyote Lubphoo*

<div align="right">**Room: Queen's Park 4**</div>

Session B: Pollution Prevention / Waste Utilization
Chairs: Dr. Yasushi Kiyoki, Japan and Dr. On-anong Larpparisudthi, Thailand

15.00-15.20 Bioleaching Of Gold From Electronic Scrap Material Using Mutated
O-B-09   Chromobacterium violaceum
  Yen-Peng Ting

15.20-15.40 Effective Management of LiPF6 in Lithium ion Battery: Pollution control and
O-B-10   Alternation Route to Preparation of Li2SiF6
  Bankole Oluwatosin Emmanuel

15.40-16.00 Barium Recovery Using Fluidized-bed Crystallization Process
O-B-11   *Resmond L. Reano*

16.00-16.20 Comparison Study of Environmental Standards of Soil In East Asian Region In
O-B-12   Relation to Utilization of Recycling Materials
  Rieko Kubota

<div align="right">**Room: Queen's Park 5**</div>

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Marjorie Valix, Australia and Dr. Chaiwat Rongsayamanont, Thailand

15.00-15.20 UASB-DHS-A2SBR System without External Aeration for Removal of Organic
O-G-17   matter, Nitrogen and Phosphorus in Domestic Wastewater
  Takashi Yamaguchi

15.20-15.40 Optimization of Hydrogen Production from Tapioca Wastewater by Anaerobic Mixed
O-G-18   Culture Using Central Composite Design
  Phatlapha Thanwised

15.40-16.00   Removal of Micro-Pollutants By Foulant Layer on Membrane Surface in Membrane
O-G-19   Bioreactor Treating Municipal Landfill Leachate
Samunya Sanguanpak

16.00-16.20   Role of Attached Sludge on P-Nitrophenol Acclimatization in Combined Suspended-
O-G-20   Attached Growth System
Niyapran Lertlaokul

Room: Queen's Park 6

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Heekwan Lee, Korea and Dr. Pisut Painmanakul, Thailand

15.00-15.20   Performance of Tiny Microbubbles Enhanced with Normal Cyclone Bubbles in
O-G-21   Separation of Fine Oil-In-Water Emulsions
Tsuyoshi Imai

15.20-15.40   Wastewater Treatment Plants as Net Energy Production Factories
O-G-22   *Petros Gikas*

15.40-16.00   COD Reduction from TFT-LCD Wastewater by Adsorption Using Chitosan-Coated
O-G-23   Bentonite: Optimization and Adsorption Studies
Mayzonee V. Ligaray

16.00-16.20   Phosphate Recovery from TFT-LCD Wastewater by Crystallization as Magnesium
O-G-24   Phosphate in Fluidized Bed Reactor: Effect of pH and Mg:P Ratio
Maria Lourdes Dalida

Thursday 23 May 2013

Room: Queen's Park 3

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Eakalak Khan, USA and Dr. Manaskorn Rachakarakij, Thailand

09.00-09.30   **Special Lecture V: Water Supply Sustainable Management of Tap Water**

by Sompodh Sripoom
Managing Director of Thai Tap Water Supply PCL

09.30-09.50   Confidence of Tap Water for Drinking Purpose in Bangkok Metropolitan and Its
O-J-08   Vicinity after Flooding Crisis
Sopa Chinwetkitvanich

09.50-10.10   Development of Hybrid Process (Adsorption And Hydrocyclone) for the Treatment of
O-G-25   Humic Acid Presence in Liquid Phase
Lucksiga Kongvichen

10.10-10.30   Study of In-line Coagulation and Flocculation Processes for Turbidity Removal: Floc
O-G-26   Size Prediction
Ratchanan Chamnanmor

Room: Queen's Park 4

Session D: Fate and Transport of Pollutants in the Environment
Chairs: Dr. Somenath Mitra, USA and Dr. Noppadon Kitana, Thailand

09.00-09.20   Dispersion of Arsenic in Environment of Gold Mine Area at Wangsaphung
O-D-01   District, Loei Province, Thailand
Wanpen Wirojanagud

09.20-09.40 O-D-02	Estimating Annual Cadmium Load via Surface Runoff into Songkhla Lake, Thailand *Kitipan Kitbamroong*
09.40-10.00 O-D-03	Influence of Electric Fields on the Stability of Titanium Dioxide and Zinc *Natalia Monroy*
10.00-10.20 O-D-04	Sequential Fractionation of Heavy Metals In Agricultural Soils: A Case Study of Hua Rua Area, Ubon Ratchatani Province *Tulaya Masipan*

Room: Queen's Park 5

Session H: Air Quality Model and Technology
Chairs: Dr. Prapat Pongkiatkul, Thailand and Dr. Tassanee Prueksasit, Thailand

09.00-09.20 O-H-02	Study on The Impact of Breeze Pattern on Dispersion Characteristics of Air Pollution *Heekwan Lee*
09.20-09.40 O-H-03	Photocatalytic Oxidation of Benzene, Toluene, Ethylbenzene and Xylenes (Btex) by Titanium Dioxide (TiO_2) Cementitious Materials for Air Pollution Control *Tanutcha Meechaiyo*
09.40-10.00 O-H-04	Height Variations and Characteristic Fluctuation of Roadside Fine Particulate Matter *Chatkrita Ratanaphain*
10.00-10.20 O-H-05	Assessment of Indoor Air Pollution in a Hospital *Chotikoon Bunditboondee*

Room: Queen's Park 6

Session F: Remediation of Contaminated Soil and Groundwater
Chairs: Dr. David A. Sabatini, USA and Dr. Alisa Vangnai, Thailand

09.00-09.20 O-F-11	Microbial Diversity in a Volatile Organic Compounds (VOCs) - Contaminated Groundwater Site at Rayong *Nipa Milintawisamai*
09.20-09.40 O-F-12	Characterization of Biosurfactants Produced by Bacillus Sp. GY19 and Potential Applications in Soil Washing *Alice Rau*
09.40-10.00 O-F-13	Novosphingobium pentaromativorans PCY: the newly PAH-degrading inoculum for bioremediation of contaminated site *Wanwasan Wongwongsee*
10.00-10.20 O-F-14	The Enhancement of Reductive Dechlorination of 234-Trichlorobiphenyl And 2345-Tetrachlorobiphenyl by Using Halogenated Primers *Wichidtra Sudjarid*

Room: Queen's Park 3

Session C: Sustainable Consumption and Production
Chairs: Dr. Maria Fuerhacker, Austria and Dr. Chantra Tongcumpou, Thailand

| 10.45-11.15 | **Special Lecture VI: Surfactant-Microemulsion-based Environmental Technologies: From Subsurface Remediation to Oilseed Extraction to Biodiesel** |
| | *by Prof. Dr. David A. Sabatini* *University of Oklahoma, USA* |

11.15-11.35 O-C-04	Effects of Manufacturing Variables on the Transesterification Reaction for Biodiesel Fuel
	Tsair-Wang Chung

11.35-11.55 O-C-05	Vegetable oil-Based Reverse Micelle Microemulsion Biofuel Using Biodegradable Surfactants
	Chodchanok Attaphong

11.55-12.15 O-B-13	Properties Improvement of Microemulsion Fuel from Ethanol-Jatropha Oil-Diesel by Surfactant Selection
	Akechai Sankumgon

Room: Queen's Park 4

Session J: Emerging Issues
Chairs: Dr. Wanpen Wirojanagud, Thailand and Dr. Srilert Chotpantarat, Thailand

10.45-11.05 O-J-09	Mechanistic Investigation of the Bioleaching of E-Wastes Using Acidophilic Bacteria and Fungi
	Marjorie Valix

11.05-11.25 O-J-10	Emerging Issue in a Proper Recycling Technology for The Non-Metallic Portion Separated From Printed Circuit Board Scrap : A Case Study Of Recycling by Using Pyrolysis Process
	Songpol Boonsawat

11.25-11.45 O-I-05	Investigation of the Biological and Medical Waste Management in Riyadh, Saudi Arabia
	Abdullah Alhadlaq

11.45-12.05 O-J-11	Effect of Air Temperature Change on Electricity Demand of Urban and Suburban Areas of Ho Chi Minh City
	Tran Thi Thu Thao

Room: Queen's Park 5

Session G: Water and Wastewater Science and Engineering
Chairs: Dr. Yasushi Kiyoki, Japan and Dr. Pichet Chaiwiwatworakul, Thailand

10.45-11.05 O-G-27	Pareto Analysis for The Design Optimization of a River Monitoring Network with Multiple Objectives
	Huei-Tau Ouyang

11.05-11.25 O-G-28	Impacts of Land Use Changes on River Runoff in Yom Basin During 1988-2009 Using Swat Hydrologic Model
	Supattra Kitichuchairit

11.25-11.45 O-G-29	Spatial-Temporal Variations of Nitrate Concentration in Yom River
	Satika Boonkaewwan

Room: Queen's Park 6

Session E: Eco-toxicity/ Environmental and Human Risk Assessment
Chairs: Dr. Benjaporn Suwannasilp, Thailand and Dr. Thunyalux Ratpukdi, Thailand

10.45-11.05 O-E-04	Bioavailability of Heavy Metals from Root Vegetables by Using Digestive Tract Fluids
	Siti Najyan Said

11.05-11.25 O-E-05	Contamination and Footprints of Chlopyrifos (Organophosphate Pesticide) on Rice-Growing Farmers' Body: A Case Study in Nakhon Nayok Province, Central Thailand
	Sattamat Lappharat

11.25-11.45   Effect of Ammonia Concentration on Ammonia-Oxidizing Microorganisms
O-E-06   Population in Nitrifying Sludge
Angkana Jantanaprasartporn

11.45-12.05   The influence of PROPER Award Towards Products Innovation and Control of The
O-E-07   Waste Disposal by Small and Medium Enterprises (SME) in Bandung
Khairul Huda

Room: Queen's Park 3

13.15-15.30   **Panel III: Opportunities and Impact of ASEAN Economic Community on the Environment: Future Research Needs** (co-hosted by Thailand Research Fund)

Opening Remark: *Prof. Suthipun Jitpimolmard,* **MD, TRF Director**

Moderator: *Prof. Dr. Methi Wecharatana*, **New Jersey Institute of Technology**
Commentator: *Assoc. Prof. Dr. Sitanon Jesdapipat*, **Rangsit University**

- *Assoc. Prof. Dr. Niramon Sutummakid*, Lecturer, Faculty of Economics, Thammasat University
- *Prof. Dr. Mario Tabucanon*, Visiting Professor, United Nations University-Institute of Advanced Studies
- *Assoc. Prof. Dr. Adis Israngkura*, Advisor, Thailand Development Research Institute and Dean of School of Development Economics, National Institute of Development Administration
- *Mr. Aboejoewono Aboeprajitno*, Former Director, Basel Convention Regional Centre for South-East Asia (BCRC-SEA)
- *Dr. Chaiyod Bunyagidj*, Technical Advisor, United Analyst and Engineering Consultant Co. Ltd
- *Dr. Peter King*, Senior Policy Advisor, Institute for Global Environmental Strategies (IGES) Regional Centre

15.30-16.00   **Open Discussion**

16.00-16.15   **Closing Remark**

POSTER PRESENTATIONS

Wednesday 22 May 2013
14.10 – 15.00, Foyer of Queen Park's 1

P-B-01 Improvement of Soybean Oil Solubility in Short-Chain Alcohol Using a Fatty Alcohol Ethoxylate
Nattapong Tuntiwiwattanapun

P-B-02 Influence of Membrane Polymorphism on Barrier Properties of Biodegradable Composite Films
Boonyong Punantapong

P-B-03 Degradation of Phorbol Esters in Jatropha Curcas Seed and Oil in Different Storage Conditions
Naphatsarnan Phasukarratchai

P-B-04 Effect of Rice Varieties and Fertilizer Type on Methane Emission From Paddy Fields
Yuttapong Pongaksorn

P-B-05 Effect of Fertilizers on Methane Emissions from Paddy Field
Sarinee Chomkaew

P-B-06 Sulfur Oxidizing Bacterial Biofilter for Removal of Hydrogen Sulfide from Biogas
Kawin Rujisangvittaya

P-B-07 Fabrication of Cassava Peel-Based Edible Film Using Ultrasound Reduced Biopolymer Size
Aomjai Worthong

P-B-08 Development of a Selective Bulk Optode Membrane Containing Benzothiazolecalix[4]Arene for Determination of Silver Ion
Rawiwan Wattanayon

P-C-01 Kinematic Viscosity of Jatropha Biodiesohol in Various Ratio and Content of Ethanol-Fatty Alcohol Ethoxylate Nonionic Surfactant Mixture
Mongkolchai Assawadithalerd

P-C-02 Automatic Meter Reading Based on Visual Management System for Improve Energy Efficiency in Factory
Bancha Jitsong

P-D-01 Hydrogeochemical Characteristics of Groundwater Surrounding Gold Mine Area
Jirawan Thamrongsrisakul

P-E-01 A Study of The Effects of Nano-Scale Iron and Zeolite on the Toxicity of Chemical Mixtures Employing a Rapid Assessment Method
Boontida Uapipatanakul

P-E-02 Quantifying Zinc Uptake in Barley Plants after Exposure to Engineered Nano-Scale Zinc Oxide
Cordelia P N Rampley

P-E-03 Evaluation of Phytotoxicity And Benifitial Effects of Multi-Walled Carbon Nanotubes in Maize Plant
Wuttipong Mahakham

P-E-04 Site-Related Difference in Herbicide Contamination and Associated Biomarkers in the Freshwater Mussel Uniandra Contradens in Agricultural Catchments, Nan Province
Tongchai Thitiphuree

P-E-05   Herbicide Utilization in Paddy Fields Increases Fluctuating Asymmetry of The Populated Rice
Frog *Fejervarya limnocharis*
Panupong Thammachoti

P-E-06   Enzymatic And Cellular Responses In Rice Field Crab *Esanthelphusa Nani* Living In Herbicide
Utilization Paddy Fields, Nan Province
Rachata Maneein

P-E-07   Herbicide Utilization in Paddy Field Alters Immune Response of the Rice Frog Fejervarya
Limnocharis Living in Agricultural Area at Nan Province, Thailand
Khattapan Jantawongsri

P-F-01   Behavior of Dibutyltin Dichloride Affecting the Aquifer Remediation by Surfactant Technique
Seelawut Damrongsiri

P-F-02   Bacterial Diversity in Antarctic Soils and Detection of Hydrocarbon Degradative Genes
Chanokporn Muangchinda

P-F-03   Properties of Biosurfactant Powder from *Bacillu*s Sp. Gy19 for Enhancing Petroleum Removal
Witchaya Kaewtip

P-F-04   Biological Treatment of Lipid-Rich Wastewater by Ready-To-Use Serratia sp.W4-01
Nanthorn Paorach

P-F-05   Degradation of Diesel in Fresh Water Samples by Bacterial Consortia SJ42 and SJ51
Suthasinee Jittimanee

P-F-06   Biosurfactant Production by Immobilized Gordonia sp. GY40 Cells and its Potential Application
as Petroleum Dispersant
Supattra Laorrattanasak

P-F-07   Pyrene-Degrading Bacteria on Ornamental Plant Leaves Along Urban Roadsides
Weerayuth Siriratruengsuk

P-F-08   Effects of Sub-CMC Sodium Dihexyl Sulfosuccinate on Tributyltin Bioavailability and
Biodegradation in Subsurface soil
Lada Mathurasa

P-F-09   Phytoremediation of Copper by Water Hyacinth (Eichhornia Crassipes) and Water Lettuce (Pistia
Stratiotes)
Jakwida Choowongsirikul

P-F-10   Effect of Combined Bioaugmentation and Biostimulation on Carbofuran Degradation in
Contaminated Soil
Patcharaporn Pimmata

P-F-11   Cadmium and Zinc Tolerate Properties of Cupriavidus Taiwanensis KKU2500-3 and Study of
Gene in Response to Cadmium Stress
Surasak Siripornadulsil

P-F-12   Isolation and Characterization of Engine Oil-Degrading Bacteria
Surasak Siripornadulsil

P-G-01   Treatment of Organic Wastewater Containing High Sulfate Using a Single Chamber Air-
Breathing Microbial Fuel Cell
Atiwich Lorwirachsutee

P-G-02   Determination of Iron Contaminated in Water by Digital Image-Based Analysis
Worawit Wongniramaikul

P-G-03 Phenols and Color Removal from Treated Palm Oil Mill Effluent by Immobilized Bacteria and White Rot Fungi
Wipaporn Ekamornthanakul

P-G-04 Colorimetric Detection of Arsenic(Iii) in Aqueous Solution Using Difluoroboron-Curcumin
Sirinya Sirawatcharin

P-G-05 Application of Ultrasound with Chemical Coagulation
Chalermkiat Boonlue

P-G-06 Degradation of 17α-methyltestosteron in Water Using UV Radiation
Kattinat Sagulsawasdipan

P-J-01 The 2011 Flood Altered Nesting Activities of the Freshwater Turtle Malayemys macrocephala at Phra Nakhon Si Ayutthaya Province, Central Part of Thailand
Rangsima Pewphong

SEQUENTIAL FRACTIONATION OF HEAVY METALS IN AGRICULTURAL SOILS: A CASE STUDY OF HUA RUA AREA, UBON RATCHATANI PROVINCE

Srilert Chotpantarat[1, 2*] and Tulaya Masipan[3]

[1] Department of Geology Faculty of Science Chulalongkorn University, Thailand.
[2] Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Thailand
[3] Inter-department of Environmental Science, Graduate School, Chulalongkorn University, Thailand

Email address: csrilert@gmail.com

Key words: Heavy metals, Mobility, BCR scheme, Ubon Ratchatani province

ABSTRACT

Anthropogenic may cause to continuous release of heavy metals in agricultural soils. In few decades, there has long been used agrochemical, i.e. fertilizers and pesticides, in many areas in Thailand. Heavy metals contained in such chemicals may release into soils and may eventually transfer into the food chain or reach through shallow groundwater. In this study, soil samples were collected 12 locations from chili field in Hua Rua area, Ubon Ratchathani Province, which has long been applied agro-chemicals for agricultural activities for many decades. Mobility potential of heavy metals in soils was analyzed by the BCR scheme, which was divided into four sequential fractionation phases and then measured the amount of heavy metals by inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The study found that the soil was contaminated by arsenic (As), copper (Cu), lead (Pb) and zinc (Zn). The results showed that summation of fraction 1 (exchangeable fraction) and fraction 2 (reducible fraction) of copper (Cu) and zinc (Zn) in most soils were higher than 50%, ranged from 68.71 to 78.79%, except soils collected from point no. 8 and 11, indicating such metals may be easily leached into shallow ground water, which may cause harmful to subsurface environment. Furthermore, the mobility potential in term of sequential fractionation revealed the decreasing of mobility potential in the order of: Zn > Cu > Pb > As.

Keywords: Heavy metals, Mobility, BCR scheme, Ubon Ratchatani province

INTRODUCTION

Groundwater resources have been currently developed for use in both the industrial sector and agricultural areas where mostly are far from the irrigation system (Kumar et al., 2007; Manika et al., 2012). Ground water resourcesare the source of water that is cleaner than surface water (Manish et al, 2010; Carlson et al., 2011) but recent years, many areas found contramination in groundwater such as high concentration of heavy metals in the vicinity of abandoned and active mines (Rogen et al., 2009). Moreover, Due to an important approach to increase crop yield in agricultural areas, fertilizer application may change soil properties and also supply heavy metals in agricultural soils (Smith, 1996; Tsadilas et al., 2005). This consequence may adversely affect on ecosystem such as the loss of

soil fertility, the erosion of soil, the disease of crop and livestock including health of local people and associated animals by contacting or consuming these polluted soils and groundwater.

Hua Rua located in Muang district, Ubon Ratchatani province, is an intensively agricultural area with a lot of chilli farming and farmers have been used of chemical fertilizers and pesticides. Also, we found different types of chilli farms spreading throughout the area and all groundwater wells are located in such chilli fields. Most farmers have been consuming water from the groundwater well. Number of groundwater wells appeared to be increased (Department of Groundwater Resources, 2548) that is currently a problem with the many environments in which environmental issues are one of the contaminated groundwater (Anat and Paul, 2003) due to modern agricultural practice with the use of chemicals to increase agricultural productions. As a result, the risk of contamination of heavy metals, which are components in fertilizers and pesticides, in shallow groundwater may be more concerned (Yu et al., 2008; Pepijn et al., 2011; Parinya et al., 2012; Pepijn and Prasnee, 2012).

In this research, the objectives of the present study were to assess the contamination of heavy metals in soil and the mobility potential of heavy metals by the BCR Scheme (Perez et al., 2005) which may be used to describe heavy metals migration in shallow groundwater.

MATERIALS AND METHODS

Study area and collection of samples

The study area is located in Hua Rua, Muang district, Ubon Ratchatani province, Northern Thailand (Fig. 1) This area is one of largest areas of chilli farming in Thailand and the use of chemical fertilizers.

Soil sampling and analysis

Twelve Soil samples were collected from chili field in Hua Rua area, Ubon Ratchathani Province. Soil samples were disaggregated and sieved through smaller than 90 μm to remove plant debris, pebbles, and stones prior to analyzing concentrations of heavy metal, i.e., arsenic (As), copper (Cu), lead (Pb) and zinc (Zn).

BCR sequential extraction scheme

The binding forms of heavy metals in soil samples were established according to the BCR sequential extraction scheme method (Perez and Valiente, 2005). This scheme normally classified heavy metals in four chemical fractions as follows: exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction.
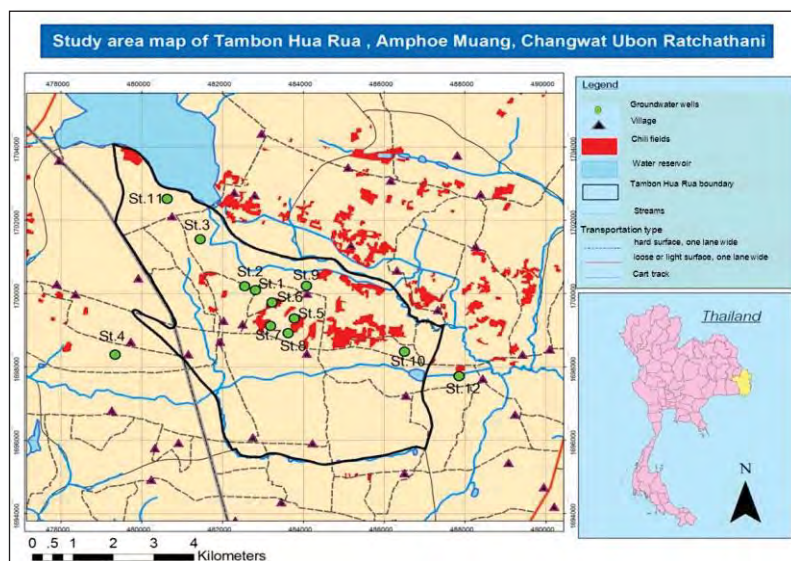
Figure 1. Study areas and soil sampling locations

RESULTS AND DISCUSSION

Fractionation concentrations of heavy metals in soils

The total concentrations of heavy metals (i.e., As, Cu, Pb and Zn) in all chili field in Hua Rua area, Ubon Ratchathani Province were shown in Fig.1. The results revealed that sum. of fraction 1 (Exchangeable fraction) and fraction 2 (reducible fraction) of copper (Cu) and zinc (Zn) in most soil samples were higher than 50% ranged from 68.71 to 78.79%, except soils collected from location 8 and 11. Concentration of copper (Cu) are the most at location 12 approx. 88.15% and Concentration of zinc (Zn) is the most at location 1 approx. 77.66% (Fig.2 and Table 1).
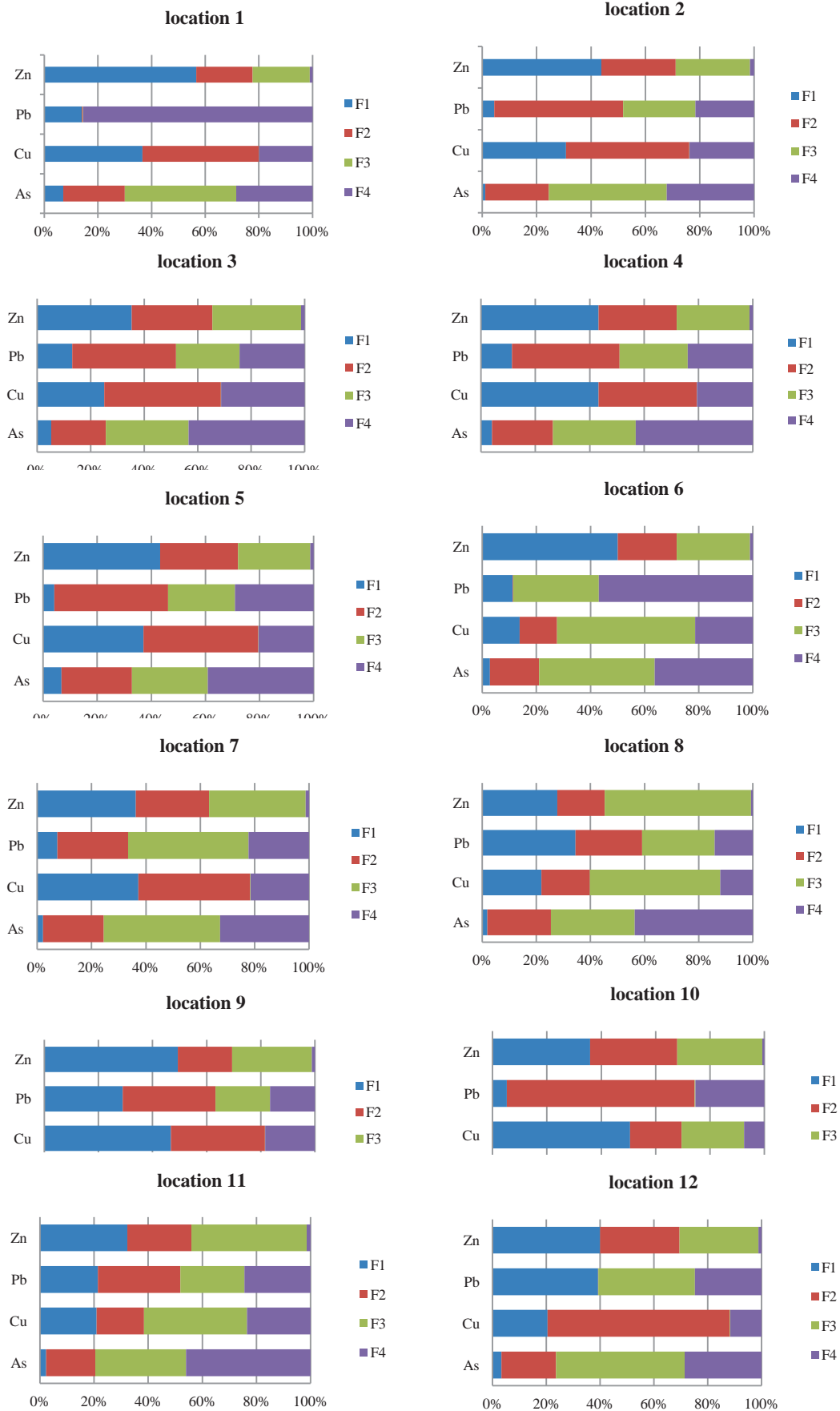
Figure 2. The total concentrations of heavy metals for 12 locations

Average percentage (ug / g) of four sequentially extracted phases of As, Cu, Pb and Zn in soils for 12 samples assessed by BCR scheme showed that the proportion in the chemical fraction 1 and 2, which summation of two fractions were higher than 50%, indicating that such metals could be easily dissolved in water and finally reach into soils and shallow groundwater. The summation of average percentage of fraction of 1 and fraction 2 were shown as the descending order as follows: Zn (66.83) > Cu (59.47) > Pb (52.76) > As (27.87). The study showed that concentrations (Fig.3) of zinc (Zn) were mostly found in leachable forms or Fractions 1 and 2, which were higher than 50%, suggesting that Zn can be easily dissolved in natural and eventually percolated through groundwater. The exchangeable fraction held weakly bound heavy metal species, which could be leached by ion-exchange mechanisms (Filgueiras et al., 2002).

Site 1-12	Exchangeable, F1	Reducible, F2	Oxidizable, F3	Residual,F4
As	5.84± (31.169)	22.03± (54.677)	37.21± (264.904)	34.91± (140.582)
Cu	27.42± (997.459)	32.06± (1639.728)	21.43± (1459.204)	19.10± (451.972)
Pb	22.25± (1769.748)	30.51± (2048.848)	23.27± (1625.211)	23.97± (834.550)
Zn	40.21± (26724.428)	26.62± (20644.042)	32.07± (42187.363)	1.09± (785.204)

Table 1. Average percentage and standard deviation (mean ± SD, ug/g) of four sequentially extracted phases of As, Cu, Pb and Zn in soils for 12 locations
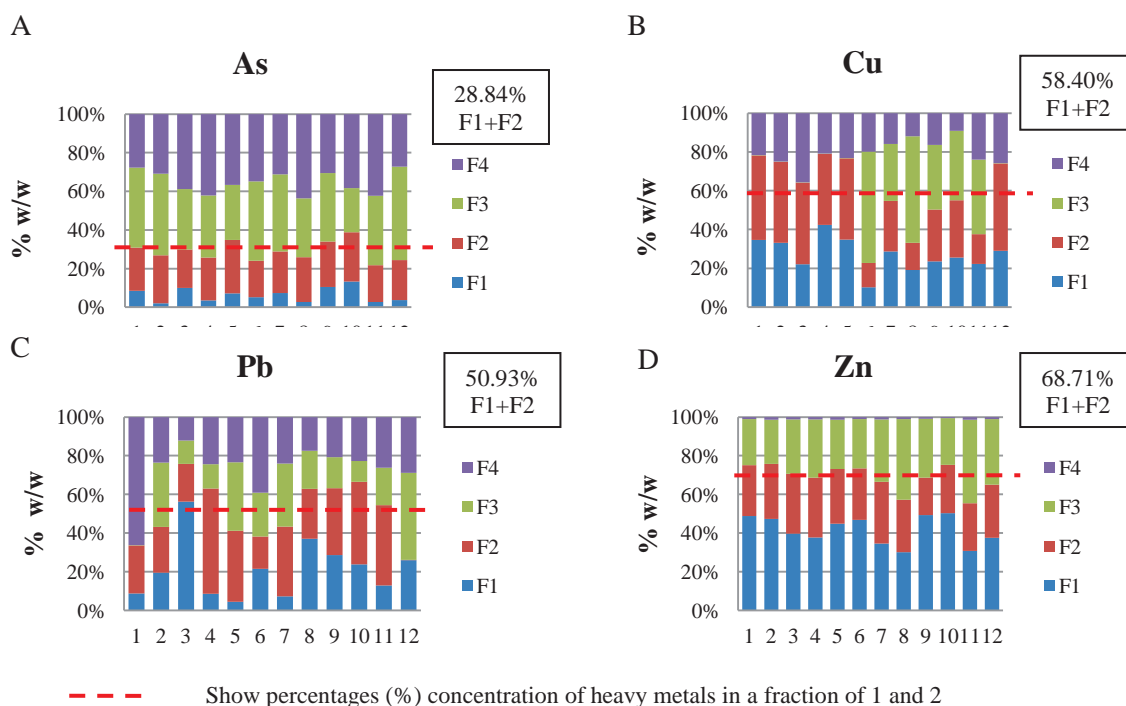

Figure 3. BCR sequential extraction scheme of 12 samples

Mobility potential of heavy metals

The mobility, immobility, and consequently the toxicity of heavy metals in chili field depend most of all on their types of binding forms. Table 2 displayed the mobility potential of heavy metals in different forms. All the heavy metals investigated were extracted in the exchangeable fraction zinc (Zn) and reducible fraction copper (Cu). The Zn and Cu had the highest percentage mobility in the exchangeable fraction, indicating that they should be the most readily available elements from the environmental point of view. Zn and Cu had the highest ability, susceptibility, and mobility potential to be released from the soil by a simple ion exchange mechanism. As represent the highest proportions in the oxidizable and residual fractions, which indicated that these two elements are the most non-mobile and thus potentially the least harmful. The residual concentration of any heavy metal was considered to be the non-mobile fraction.

Step	Condition	Mobility
1	Exchangeable fraction	Zn > Cu > Pb > As
2	Reducible fraction	Cu > Pb > Zn > As
3	Oxidizable fraction	As > Zn > Pb > Cu
4	Residual	As > Pb > Cu > Zn

Table 2. Mobility potential of heavy metals in chili field

CONCLUSIONS

In this study, the distribution and mobility characteristics of heavy metals (i.e., As, Cu, Pb, and Zn) in soil samples chili field in Hua Rua area, Ubon Ratchathani Province were investigated. The results showed that the fraction 1 (exchangeable fraction) and fraction 2 (reducible fraction) of copper (Cu) and zinc (Zn) in most soils were higher than 50%, indicating such metals may be easily leached into the shallow groundwater, which may cause harmful to subsurface environment. Furthermore, the mobility potential based on sequential fractionation results in the descending order of: Zn > Cu > Pb > As.

ACKNOWLEDGEMENTS

REFERENCES

Antanaitis, D., Antanaitis, A., 2004. Migration of heavy metals in soil and their concentration in sewage and sewage sludge. Ekologija 1, 42 – 45.

Anat, T., Paul, F.H., 2003. Use of geographic information systems for assessing groundwater pollution potential by pesticides in Central Thailand. Environment International 29, 87 – 93.

Filgueiras, A.V., Lavilla, I., Bendicho, C., 2002. Chemical sequential extraction for metal partitioning in environmental solid samples. J Environment Monit 4, 823 – 857.

Gupta, M., Garg, N.K., Himanshu J., Sharma, M.P., 2012. Persistence and mobility of 2,4-D in unsaturated soil zone under winter wheatcrop in sub-tropical region of India. Agriculture, Ecosystems and Environment 146, 60 – 72.

Mark, A., Carlson, K., Lohse, A., Jennifer McIntosh, C., Jean E.T.M., 2011. Impacts of urbanization on groundwater quality and recharge in a semi-arid alluvial basin. Journal of Hydrology 409, 196 – 211.

Manish, K., Pankaj, K., Ramanathan, A.L., Prosun, B., Roger, T., Umesh K.S., Tsujimura, M., Ondra S., 2007. A comparative evaluation of groundwater suitability for irrigation and drinking purposes in two intensively cultivated districts of Punjab, India. Environmental Geology 53, 553 – 574.

Panuwet, P., Siriwong, W., Prapamontol, T., Ryan, P. B., Fiedler, N., Mark G.R., Dana B.B., 2012. Agricultural pesticide management in Thailand: status and population health risk. Environmental science & policy 17, 72 – 81.

Perez, G., Valiente, M., 2005. Determination of pollution trends in an abandoned mining site by application of a multivariate statistical analysis to heavy metals fractionation using SM&T-SES. Journal of Environmental monitoring 7, 29 – 36.

Rogan, N., Dolenec, T., Todor, S., Tasev, G., Dolenec, M., 2009. Distribution and mobility of heavy metals in paddy soils of the Kočani in Macedonia. Environ Earth Sci. 5, 899 – 907.

Schreinemachers, P., Sringarm, S., Sirijinda, A., 2011. The role of synthetic pesticides in the intensification of highland agriculture in Thailand. Crop Protection 30,1431 – 1437.

Schreinemachers, P., Tipraqsa, P., 2012. Agricultural pesticides and land use intensification in high, middle and low income countries. Food Policy 37. 616 – 626.

Wongsasuluk, P., 2010. Human health risk assessment associated with heavy metals in drinking shallow groundwater wells at Ubon Ratchathani province, Thailand. A Thesis Submitted in Partial Fulfillment of

the Requirements for the Degree of Master. Science Program in Environmental Management, Graduate School Chulalongkorn University.

Yu, L., Xin, G., Gang, W., Qiang Z., Qiong S., Guoju X., 2008. Heavy metal contamination and source in arid agricultural soil in central Gansu Province, China. Journal of Environmental Sciences 20, 607 – 612.

ภาคผนวกที่ ข

บทความวิชาการที่ตีพิมพ์ในวารสารระดับชาติ

1. **Chotpantarat, S.**, 2011. Causes and potential acid generation techniques of acid mine drainage (AMD). Engineering Journal 64(4): 59-66.

อาจารย์ ดร.ศรีเลิศ โชติพันธรัตน์

ภาควิชาธรณีวิทยา คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

วิศวกรรมสาร

สาเหตุและเทคนิคการประเมินศักยภาพ
การเกิดน้ำเหมืองเป็นกรด

Causes and potential acid generation techniques of acid mine drainage (AMD)

บทคัดย่อ

การเกิดน้ำเหมืองเป็นกรดเป็นปัญหาที่เกิดจากการประกอบกิจการเหมืองแร่ที่ส่งผลเสียอย่างรุนแรงต่อสภาพแวดล้อมรอบข้างอย่างมากโดยเฉพาะดิน น้ำผิวดินและน้ำใต้ดิน ปัญหาดังกล่าวส่วนใหญ่จะเกิดขึ้นภายหลังการปิดเหมืองไปแล้ว สำหรับประเทศไทยมีสถานประกอบกิจการเหมืองเป็นจำนวนมาก หากไม่มีการจัดการที่ดีหลังจากปิดกิจการไป ส่งผลให้เร่งการเกิดสภาพน้ำเหมืองเป็นกรดเมื่อแร่ซัลไฟด์สัมผัสกับออกซิเจนและน้ำ ทำให้มลสารต่างๆ ถูกชะออกมาง่ายขึ้น เช่น โลหะหนักต่างๆ เป็นต้น และปนเปื้อนสู่สิ่งแวดล้อมในที่สุด ในบทความนี้กล่าวถึงสาเหตุการเกิด และเทคนิคที่ใช้ในการประเมินศักยภาพการเกิดน้ำเหมืองเป็นกรด ซึ่งประกอบด้วยวิธี acid base accounting (ABA) และอีกวิธีคือ net acid generation (NAG) ตลอดจนเกณฑ์ที่ใช้ในการประเมินน้ำเหมืองเป็นกรด นอกจากนี้ยังได้มีการพิจารณาร่วมระหว่างวิธี ABA และ NAG เพื่อช่วยให้การประเมินศักยภาพน้ำเหมืองเป็นกรดมีความถูกต้องและน่าเชื่อถือมากขึ้น จากที่กล่าวมาแล้วดังนั้นในการดำเนินกิจการเหมืองจำเป็นที่จะต้องประเมินโอกาสการเกิดน้ำเหมืองเป็นกรดในพื้นที่เพื่อวางแผนในการป้องกันและบรรเทาผลกระทบที่จะเกิดขึ้นในอนาคต

Abstract

Acid mine drainage (AMD) is one of the serious environmental problems caused by mining activities and adversely impacts on surrounding environments, especially for soil, surface water and groundwater. Major AMD problems may occur after closure of mines. In Thailand, many mining areas may have not been taken care of properly. They may, in turn, promote the AMD generation as sulfide-bearing material is exposed to oxygen and water. Consequently, other contaminants containing in acidic water, such as some heavy metals will be easily released and eventually pollute the environment. This paper described causes of acid mine drainage and acid producing potential tests, which consist of acid base accounting (ABA) and net acid generation test (NAG), including their criteria used to evaluate acid producing potential in mining areas. In addition, the ABA test is used association with the NAG test to verify the acid generating potential of a sample. As mentioned, the acid producing potential tests should be encouraged to assess acid-generating potential to prevent and mitigate such impacts of acidic water in the future.
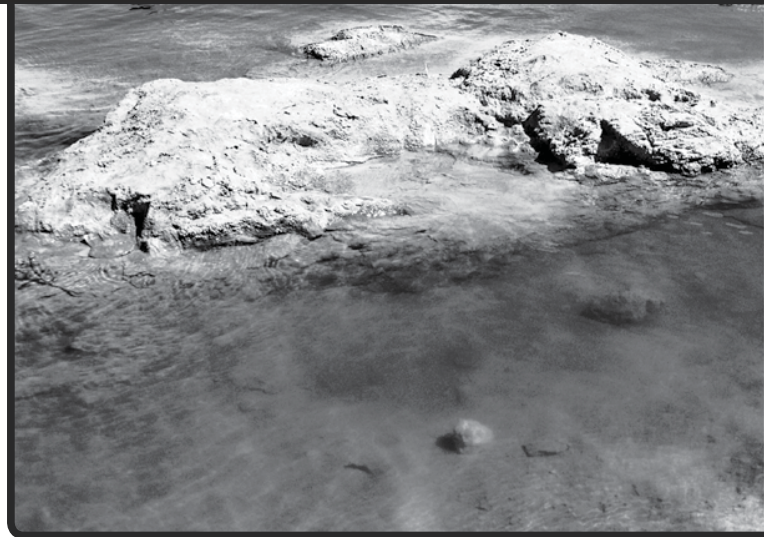
1. บทนำ

การประกอบกิจการเหมืองแร่เป็นอุตสาหกรรมหนึ่งที่ก่อ
ให้เกิดปัญหาต่อสิ่งแวดล้อมเนื่องจากมีกระบวนการเปิดหน้า
เหมืองและการทิ้งกากของเสียหลังจากได้สกัดโลหะที่มีคุณค่า
ออกไป เช่น หินทิ้ง (Waste rocks) และกากแร่ (Tailings) เป็นต้น
ซึ่งจะเป็นแหล่งของมลสารที่จะส่งผลกระทบต่อสิ่งแวดล้อมต่อ
ไปหากไม่มีการจัดการที่ดีภายหลังจากปิดกิจการไป การเกิด
สภาพน้ำเหมืองเป็นกรดจากการประกอบกิจการเหมืองแร่เป็น
อีกปัญหาที่หลีกเลี่ยงไม่ได้ และเป็นปัญหาหลักของการ
ประกอบกิจการเหมืองแร่ โดยเฉพาะเมื่อสิ้นสุดกิจการเหมืองแร่
เพราะปฏิกิริยาดังกล่าวจะช่วยเร่งในเกิดการชะเอาโลหะหนัก
ต่างๆ ที่มีอยู่ในหินทิ้งและกากแร่ เช่น ตะกั่ว (Pb) อาร์เซนิก
(As) สังกะสี (Zn) แคดเมียม (Cd) เป็นต้น ลงในระบบน้ำผิวดิน
และน้ำบาดาลในที่สุด [1] น้ำเหมืองเป็นกรด (Acid mine
drainage, AMD) คือน้ำชะที่มีฤทธิ์เป็นกรดที่เกิดจากพื้นที่
ประกอบกิจการเหมืองแร่ มีค่าพีเอชต่ำ ดังแสดงในรูปที่ 1
เป็นสภาพน้ำเหมืองเป็นกรดในพื้นที่เหมืองแร่เหล็กที่ปิดกิจการ
ไปแล้ว ประเทศสาธารณรัฐแอฟริกาใต้ [2] การเกิดน้ำเหมือง
เป็นกรดสามารถเกิดขึ้นได้เองอย่างช้าๆ เนื่องจากการสึกกร่อน
ผุพังตามธรรมชาติของชั้นดินและชั้นหิน แต่อัตราการเกิดน้ำที่มี
ฤทธิ์เป็นกรดจะเพิ่มขึ้นอย่างรวดเร็ว เมื่อมีการเปิดหน้าดินทำให้
ชั้นดินและหินที่มีกลุ่มแร่ซัลไฟด์สัมผัสกับอากาศและน้ำได้
มากขึ้น นอกจากนี้แบคทีเรียซึ่งเกิดขึ้นตามธรรมชาติ เช่น

Thiobacillus ferrooxidans เป็นต้น ยังสามารถเร่งปฏิกิริยาการ
เกิดน้ำเหมืองเป็นกรดเร็วขึ้นอีกด้วย [3-4] ดังนั้นอาจกล่าวได้ว่า
ปัญหาสภาพน้ำเหมืองเป็นกรดจะส่งผลกระทบต่อสิ่งแวดล้อม
และสิ่งมีชีวิตต่างๆ ตลอดจนระบบนิเวศน์ในที่สุด ปัจจุบันพบ
ปัญหาการเกิดสภาพน้ำเหมืองเป็นกรดเกิดขึ้นในหลายๆ
ประเทศ เช่น เหมืองถ่านหิน ประเทศสาธารณรัฐแอฟริกาใต้
[2] เหมือง Black swan (BS) ทางตะวันตกของประเทศ
ออสเตรเลีย [5] และเหมือง Tinto Santa Rosa ประเทศสเปน
[6] เป็นต้น ในการบำบัดและฟื้นฟูพื้นที่ที่เสียหายเนื่องจาก
สภาพน้ำเหมืองเป็นกรดจำเป็นต้องใช้งบประมาณมหาศาล
สำหรับประเทศไทยมีเหมืองเปิดกว่า 700 แห่งทั่วประเทศ ซึ่ง
มีโอกาสเสี่ยงที่จะเกิดปัญหานี้ในอนาคต จากที่กล่าวมาข้างต้น
การประเมินศักยภาพในการเกิดน้ำเหมืองเป็นกรดและมาตรการ
ในการควบคุมเพื่อลดความเสี่ยงในการเกิดสภาพดังกล่าว
ให้น้อยที่สุดจึงมีความสำคัญอย่างมากในการประกอบกิจการ
เหมืองแร่

สำหรับเนื้อหาในบทความนี้ได้อธิบายกระบวนการการเกิด
น้ำเหมืองเป็นกรด และเทคนิคที่นิยมใช้ในการประเมินศักยภาพ
การเกิดน้ำเหมืองเป็นกรดเพื่อระบุพื้นที่ที่อาจก่อให้เกิดน้ำเหมือง
เป็นกรด สำหรับเทคนิคเพื่อประเมินศักยภาพการเกิดกรด
ของพื้นที่นั้นๆ ได้แก่ วิธี acid base accounting (ABA test)
[7-8] และวิธี net acid generation (NAG test) [7, 9] ซึ่ง
จะกล่าวในรายละเอียดต่อไป

รูปที่ 1 น้ำเหมืองเป็นกรด บริเวณเหมืองแร่เหล็ก ประเทศสาธารณรัฐแอฟริกาใต้ [2]

2.การเกิดน้ำเหมืองเป็นกรด

ในส่วนนี้จะขอกล่าวถึงกระบวนการการเกิดน้ำเหมือง
เป็นกรด เมื่อมีการเปิดหน้าดินทำให้ชั้นดินและหินที่มีแร่ซัลไฟด์
เป็นองค์ประกอบสัมผัสกับอากาศและน้ำบนผิวดิน ส่งผลให้
อัตราการเกิดน้ำที่มีฤทธิ์เป็นกรดเพิ่มขึ้นอย่างรวดเร็ว เนื่องจาก
ในอากาศมีปริมาณออกซิเจนสูงทำให้เกิดปฏิกิริยาออกซิเดชั่น
ได้เร็วยิ่งขึ้น ได้เป็นกรดซัลฟิวริก (H_2SO_4) และอาจเกิดตะกอน
ของเหล็กเฟอริก ($Fe(OH)_3$) ถูกชะลงในระบบน้ำผิวดินและน้ำ
บาดาลทำให้น้ำมีสภาพเป็นกรด น้ำจากปฏิกิริยาดังกล่าวมีค่า
พีเอชต่ำ มีค่าการนำไฟฟ้าสูง ปริมาณของเหล็ก อลูมิเนียม
แมงกานีสสูง และมีโลหะหนักอื่นๆ ด้วย ปฏิกิริยาของการเกิด
กรดสามารถอธิบายได้โดยใช้แร่ไพไรต์ (pyrite) ซึ่งเป็นแร่ซัลไฟด์
ที่ก่อให้เกิดน้ำเหมืองเป็นกรด นอกจากนี้ยังมีแร่กลุ่มซัลไฟด์
ชนิดอื่นๆ เช่น chalcocite (Cu_2S), enargite (Cu_3AsS_4),
arsenopyrite (FeAsS) เป็นต้น ปฏิกิริยาเคมีของการเกิด
น้ำเหมืองเป็นกรดจากปฏิกิริยาออกซิเดชั่นของแร่ไพไรต์พอจะ
แบ่งได้ 4 ขั้นตอนดังนี้ [10]

ขั้นตอนแรก เกิดจากแร่ไพไรต์เกิดปฏิกิริยาออกซิเดชั่น
ด้วยออกซิเจนทำให้ซัลเฟอร์ถูกออกซิไดซ์กลายเป็นซัลเฟต (Sulfate,
SO_4^{2-}) เหล็กเฟอร์รัส (Ferrous, Fe^{2+}) และไฮโดรเจนไอออน (H^+)
ดังแสดงในปฏิกิริยาที่ 1 จากขั้นตอนนี้จะพบว่า ปริมาณ
ของแข็งละลายน้ำ (Total dissolved solid, TDS) จะมีปริมาณ
สูงขึ้นและมีความเป็นกรดสูงซึ่งทำให้ค่าพีเอชลดต่ำลง

$$FeS_2 + 7/2O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

ขั้นตอนที่สอง หากปริมาณออกซิเจนมากเพียงพอจะ
เกิดปฏิกิริยาออกซิเดชั่นเปลี่ยนจากเหล็กเฟอร์รัส (Ferrous,
Fe^{2+}) เป็นเหล็กเฟอร์ริก (Ferric, Fe^{3+}) โดยปฏิกิริยาจะเกิดขึ้น
อย่างช้าๆ ภายใต้สภาวะที่เป็นกรด พีเอชอยู่ในช่วง 2-3
นอกจากนี้แบคทีเรียบางชนิดมีส่วนช่วยในการเร่งปฏิกิริยาเพิ่ม
ขึ้นอีกด้วยที่ค่าพีเอชต่ำกว่า 3.5 เช่น *Thiobacillus ferrooxidans*
เป็นต้น ทั้งนี้อัตราการเกิดปฏิกิริยาขึ้นอยู่กับค่าพีเอชของระบบ
หากแบคทีเรียไม่ได้อยู่ในสภาพที่เหมาะสม อิทธิพลของ
แบคทีเรียต่อการก่อให้เกิดน้ำเหมืองเป็นกรดน้อยมากดังแสดง
ในปฏิกิริยาที่ 2

$$Fe^{2+} + 1/4O_2 + H^+ \longrightarrow Fe^{3+} + 1/2H_2O \qquad (2)$$

ขั้นตอนที่สาม ที่ค่าพีเอชระหว่าง 2.3 ถึง 3.5 เหล็ก
เฟอร์ริก (Ferric, Fe^{3+}) จากขั้นที่สองจะเกิดการไฮโดรไลซิสของเหล็ก
เกิดเป็นตะกอนของเหล็กเฟอริก $Fe(OH)_{3\ solid}$ มีสีส้มเหลือง
หรือเรียกว่า yellow boy ทั้งนี้ตะกอนจะเกิดขึ้นที่พีเอชสูงกว่า
3.5 หากพีเอชต่ำกว่า 3.5 จะไม่เกิดการตกตะกอน ทั้งนี้ขั้นตอน
นี้มีไฮโดรเจนไอออนเกิดขึ้นด้วยทำให้ค่าพีเอชลดลง ดังแสดง
ในปฏิกิริยาที่ 3

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_{3\ solid} + 3H^+ \qquad (3)$$
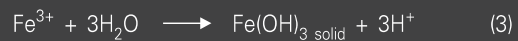
ขั้นตอนสุดท้าย เหล็กเฟอร์ริก (Ferric, Fe^{3+}) ที่เหลือ
จากขั้นตอนที่ 2 และไม่ตกตะกอนในขั้นตอนที่ 3 จะถูกใช้เพื่อ
ออกซิไดซ์ไพไรต์ โดยปฏิกิริยาจะเกิดขึ้นเป็นวัฏจักรอย่าง
ต่อเนื่องและรวดเร็วจนกว่าเหล็กเฟอร์ริกหรือไพไรต์จะหมด
ดังแสดงในปฏิกิริยาที่ 4

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

สรุปภาพรวมของการเกิดปฏิกิริยาโดยรวมปฏิกิริยาที่ 1- 3 ได้
ดังแสดงในปฏิกิริยาที่ 5

$$FeS_2 + 15/4O_2 + 7/2H_2O \longrightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \qquad (5)$$

จากปฏิกิริยาข้างต้นจะได้กรดซัลฟิวริกซึ่งจะชะลงสู่
แหล่งน้ำบริเวณใกล้เคียงทำให้เกิดน้ำเหมืองเป็นกรด และการ
ปนเปื้อนของโลหะหนักส่งผลกระทบต่อพืชและสัตว์ในบริเวณ
นั้น โดยทิศทางการเกิดปฏิกิริยาแสดงในรูปที่ 2 [10] และ
ชะเอาโลหะต่างๆ ออกมาได้ เช่น อาร์เซนิก (As) แคดเมียม
(Cd) โคบอลล์ (Co) นิกเกิล (Ni) ตะกั่ว (Pb) เป็นต้น ลงสู่
แหล่งน้ำในบริเวณใกล้เคียง

โดยทั่วไปน้ำเหมืองเป็นกรดมักแสดงลักษณะดังนี้
- น้ำมีค่าพีเอชน้อยกว่า 5.5
- พบพืชและสัตว์ในพื้นที่ถูกรบกวนหรือมีอาการขาดน้ำ
- เกิดตะกอนทั่วไปทั้งในท้องน้ำและพื้นดิน
- น้ำมีสีขุ่นหรือสะอาดเป็นพิเศษ
- พบแบคทีเรียสกุล slime
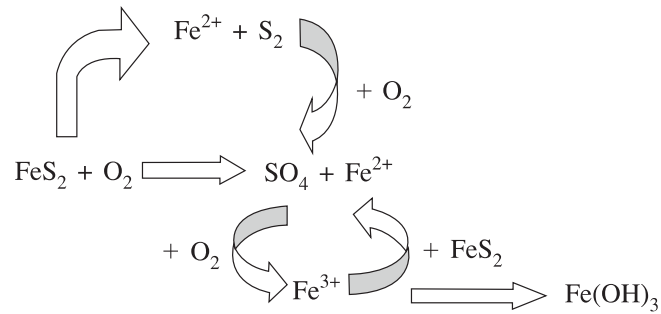
รูปที่ 2 แผนภาพอย่างง่ายแสดงทิศทางปฏิกิริยาออกซิเดชั่นของไพไรต์ [10]

อย่างไรก็ตามไม่ใช่ทุกเหมืองที่มีแร่ซัลไฟด์ในหินจะก่อให้เกิดน้ำเหมืองเป็นกรด เนื่องจากการปนเปื้อนสู่สิ่งแวดล้อมไม่ได้จำกัดเฉพาะการเกิดน้ำเหมืองเป็นกรด แต่มีการระบายอัลคาไลค์ลงสู่สิ่งแวดล้อมด้วย นอกจากนี้ยังมีปัจจัยอื่นๆ ที่มีผลต่อการเกิดน้ำเหมืองเป็นกรด ปัจจัยทางกายภาพ เช่น พื้นที่ผิวสัมผัสของแร่ซัลไฟด์กับอากาศ ค่าความสามารถในการซึมผ่านของน้ำ (Permeability) ในกองหินทิ้ง เป็นต้น [11]

การเกิดปฏิกิริยาออกซิเดชั่นในกองหินทิ้งที่เกิดจากการเคลื่อนที่ของออกซิเจนและน้ำเข้าไปในกองหินทิ้งแสดงในรูปที่ 3 และหากอุณหภูมิภายในกองหินทิ้งสูงถึง 60 องศาเซลเซียสจะส่งผลให้เพิ่มการเคลื่อนที่ของออกซิเจนเข้าสู่กองหินทิ้งมากยิ่งขึ้นเป็นผลมาจากการเคลื่อนที่ด้วยการพา (Convective transport of atmospheric oxygen) ซึ่งเป็นการเร่งให้เกิดน้ำเหมืองเป็นกรดเร็วขึ้นด้วย [11]
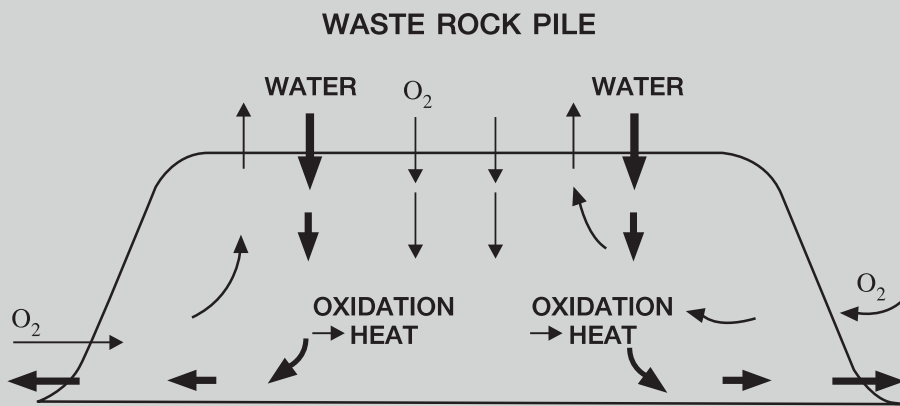
รูปที่ 3 แผนภาพแสดงการเกิดปฏิกิริยาออกซิเดชั่นของไพไรต์ในกองหินทิ้ง [11]

3. การประเมินศักยภาพน้ำเหมืองเป็นกรด

ในบทความนี้ขออธิบายการวิเคราะห์ทางธรณีเคมี (Geochemical tests) ซึ่งในช่วงสามสิบปีที่ผ่านมาได้มีการพัฒนาเทคนิคต่างๆ ที่จะใช้ในการประเมินศักยภาพการเกิดกรดในเหมืองมากมาย [12] ในบทความนี้จะขอกล่าวถึง 2 วิธีที่ใช้อย่างแพร่หลายได้แก่ วิธี acid base accounting (ABA) [13] ซึ่งเป็นวิธีที่นิยมใช้แถบอเมริกาเหนือและออสเตรเลียแต่จะมีความแตกต่างกัน

เล็กน้อยซึ่งจะกล่าวในรายละเอียดต่อไป และวิธี net acid generation (NAG) [7] โดยทั้ง 2 วิธีเป็นการทดสอบทางธรณีเคมีของแร่ซัลไฟด์ที่มีอยู่ในหินทิ้งหรือกากแร่เพื่อใช้ทำนายศักยภาพการเกิดกรดจากตัวอย่างนั้นๆ สำหรับประเทศไทยได้นำวิธี ABA และ NAG มาใช้ในการประเมินศักยภาพน้ำเหมืองเป็นกรดของเหมืองแร่ทองคำอัครา จังหวัดพิจิตร [14] และเหมืองถ่านหินแม่ทา จังหวัดลำปาง [15] สำหรับรายละเอียดวิธีการประเมินโดยใช้วิธี ABA และ NAG มีรายละเอียดดังต่อไปนี้

3.1 การทดสอบด้วยวิธี acid base accounting (ABA)

วิธี ABA เป็นวิธีการทดสอบเพื่อประเมินศักยภาพในการเกิดน้ำเหมืองเป็นกรดซึ่งในเบื้องต้นขอกล่าวถึงตัวย่อต่างๆ และวิธีการประเมินของเทคนิคนี้ที่ใช้ในแถบอเมริกาเหนือก่อน ซึ่งประกอบด้วย 2 ส่วน คือ

1. ค่าศักยภาพความเป็นกรดของหินทิ้งหรือกากแร่ (Acid potential, AP) ซึ่งได้จากการนำค่าร้อยละของซัลเฟอร์คูณด้วย 31.25 ซึ่งพิจารณาจากปฏิกิริยาที่ 6 ร้อยละ1 ของซัลเฟอร์ในหิน 1 ตันต้องใช้ $CaCO_3$ 31.25 กิโลกรัมในการทำให้เป็นกลาง ปริมาณซัลเฟอร์ได้จากการวิเคราะห์ด้วยเครื่อง Carbon/ Sulfur analyzer

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \longrightarrow Fe(OH)_3 + 2SO_4^{2-} + 2\ Ca^{2+} + 2CO_2 \qquad (6)$$
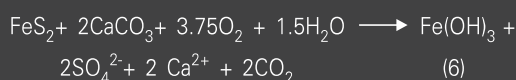
2. ค่าศักยภาพความเป็นกลางของหินทิ้งหรือกากแร่หรือปริมาณคาร์บอเนต (NP) ได้จากการคำนวณปริมาณโซเดียมไฮดรอกไซด์ที่ใช้ในการไทเทรตกับกรดที่เหลืออยู่ภายหลังจากเติมกรดไฮโดรคลอริกลงในตัวอย่าง 2 กรัม และนำไปต้มจนหมดฟอง (หรือสิ้นสุดปฏิกิริยา) ทิ้งไว้ให้เย็นไทเทรตจนค่าพีเอชเท่ากับ 7 และคำนวณค่าหาปริมาณคาร์บอเนตต่อไปสามารถดูรายละเอียดได้จาก Sangtong et al. (2011) [15]

นำค่า AP และ NP ที่ได้มาหาศักยภาพความเป็นกลางสุทธิ (Net Neutralization Potential, NNP = NP-AP) ซึ่งคำนวณจากผลต่างของ AP กับ NP [10] นอกจากนี้ยังประเมินศักยภาพการเกิดกรดจากอัตราส่วนศักยภาพความเป็นกลาง (Neutralization Potential Ratio, NPR= NP/AP) [16] และ

พิจารณาศักยภาพการเกิดน้ำเหมืองเป็นกรดตามเกณฑ์ในตารางที่ 1 ซึ่งได้จากการศึกษาของ Skousen et al. (2002) [16] ซึ่งได้ประยุกต์ใช้วิธี ABA เพื่อการทำนายคุณภาพน้ำในพื้นที่หลังประกอบกิจการเหมืองแร่ โดยนำตัวอย่างจากเหมืองทางตะวันตกของรัฐเวอร์จิเนีย 56 แห่ง และหาค่า AP และ NP และคำนวณค่า NNP และ NPR ผลที่ได้พบว่าค่า NNP กับ NPR มีความสัมพันธ์ที่ดีต่อการทำนายคุณภาพน้ำผิวดิน จากการศึกษานี้พบว่า ABA เป็นเครื่องมือที่ดีในการคาดการณ์คุณภาพน้ำผิวดินภายหลังการทำเหมือง ซึ่งเกณฑ์ในตารางที่ 1 ได้สรุปภายหลังทำการเปรียบเทียบกับงานวิจัยต่างๆ ที่ผ่านมา [16]

ตารางที่ 1 เกณฑ์การพิจารณาศักยภาพการเกิดกรดโดยวิธี ABA ที่นิยมใช้ในแถบอเมริกาเหนือ [16]

ตัวแปรของ ABA	เกณฑ์ (kg $CaCO_3$/t)	ศักยภาพ
NP	< 10	กรด (net acid)
	> 21	เบส (net alkaline)
NNP	< 0	กรด (net acid)
	>12	เบส (net alkaline)
NPR	< 1	กรด (net acid)
	>2	เบส (net alkaline)

นอกจากนี้จากที่กล่าวมาข้างต้นในออสเตรเลีย และแถบเอเชียแปซิฟิกได้ใช้วิธี ABA เช่นกันแต่มีความแตกต่างของตัวย่อและการประเมินน้ำเหมืองเป็นกรดที่ต่างในรายละเอียดดังนี้ ใช้ตัวย่อ ค่าศักยภาพความเป็นกรดสูงสุดของหินทิ้งหรือกากแร่ (Maximum potential acid, MPA) และ ค่าความเป็นกลางของหินทิ้งหรือกากแร่ (Acid neutralization capacity, ANC) และค่าศักยภาพความเป็นกรดสุทธิ (Net acid production potential, NAPP) แทนตัวย่อที่แถบอเมริกาเหนือใช้คือ AP NP และ NNP ตามลำดับ

ค่า MPA หาได้จากตัวอย่าง 1 ตันที่มีซัลเฟอร์ 1% ในรูปของ แร่ไพไรต์จะให้กรดซัลฟูริก 30.6 กิโลกรัมหลังทำปฏิกิริยา ในปฏิกิริยาที่ 5 และสำหรับค่า ANC นั้นคำนวณได้เช่นเดียวกัน กับวิธีคำนวณค่า NP ที่นิยมใช้ในแถบอเมริกาเหนือ ภายหลัง การคำนวณทั้งค่า MPA และ ANC คำนวณค่า NAPP = MPA-ANC และเทียบกับเกณฑ์การพิจารณาศักยภาพการเกิดกรดใน ตารางที่ 2

ตารางที่ 2 เกณฑ์การพิจารณาศักยภาพการเกิดกรด จากค่า NAPP [17]

NAPP (kg H_2SO_4/t)	ศักยภาพ
> 20	Partially acid generating
< -20	Non-acid generating
Between -20 and +20	Zone of uncertainty

3.2 การทดลองด้วยวิธี net acid generation (NAG)

วิธี NAG เป็นอีกหนึ่งวิธีที่ใช้ประเมินศักยภาพการเกิด น้ำเหมืองเป็นกรด ซึ่งวิธีนี้นิยมใช้ในการประเมินศักยภาพ น้ำเหมืองเป็นกรดในประเทศออสเตรเลีย แสดงใน รูปที่ 4 โดยการเติมไฮโดรเจนเปอร์ออกไซด์ (H_2O_2) ลงในตัวอย่างและ ต้มเพื่อเร่งปฏิกิริยาจนเกิดฟอง ทิ้งไว้ให้เย็นแล้ววัดค่าพีเอช สุดท้าย (NAG pH) ด้วยเครื่องพีเอชมิเตอร์ และนำสารละลาย หลังทำปฏิกิริยาไปไทเทรตกับโซเดียมไฮดรอกไซต์จนได้ค่า พีเอชเท่ากับ 4.5 หรือ 7 แล้วนำค่าที่ได้มาคำนวณหาค่า NAG สำหรับรายละเอียดเพิ่มเติมสามารถศึกษาจากงานวิจัยของ Liao et al. (2007) [7]

รูปที่ 4 แผนภาพแสดงขั้นตอนการทดสอบโดยวิธี NAG

การพิจารณาการเกิดน้ำเหมืองเป็นกรดตามเกณฑ์ในตารางที่ 3 [7] ซึ่งจะพิจารณาค่าความเป็นกรดสุดท้าย (NAG pH) ควบคู่ กับค่าปริมาณกรดซัลฟิวริก ที่คำนวณได้จากค่า NAG

ตารางที่ 3 เกณฑ์การพิจารณาศักยภาพความเป็นกรด จากการทดสอบด้วยวิธี NAG test [7]

NAG pH	Calculated NAG (kg H_2SO_4/t)	ศักยภาพ
≥5	0 – 2	ไม่มีศักยภาพเป็นกรด
2.5 < NAG pH < 5	2 – 50	ศักยภาพเป็นกรดปานกลาง
≤2.5	>50	ศักยภาพเป็นกรด

นอกจากนี้ผลที่ได้จากวิธี ABA และ NAG สามารถนำมา พิจารณาร่วมกันเพื่อความน่าเชื่อถือของผลการประเมิน ศักยภาพการเกิดกรดดังที่กล่าวในหัวข้อ 3.3 ซึ่งเป็นวิธีที่เป็นที่ นิยมใช้ในการประเมินศักยภาพน้ำเหมืองเป็นกรดในออสเตรเลีย และแถบเอเชียแปซิฟิก

3.3 การประเมินศักยภาพการเกิดน้ำเหมือง เป็นกรดร่วมระหว่างวิธี ABA และวิธี NAG

เมื่อได้ค่าศักยภาพความเป็นกรดจากทั้ง 2 วิธีการ ทดสอบแล้ว สามารถนำค่าทั้งสองที่ได้มาพิจารณาร่วมเพื่อ ความถูกต้องแม่นยำและน่าเชื่อถือของการประเมินศักยภาพ น้ำเหมืองเป็นกรด โดยการนำค่าศักยภาพการเกิดกรดสุทธิ (NAPP) ที่ได้จากการนำผลต่างระหว่างศักยภาพความเป็นกรด สูงสุด และค่าความเป็นกลางของหินทิ้งหรือกากแร่จากการ ทดสอบด้วยวิธี ABA (NAPP = MPA-ANC) นำมาพิจารณาร่วม กับค่าพีเอชสุดท้าย (NAG pH) จากการทดสอบด้วยวิธี NAG โดยมีเกณฑ์การพิจารณาดังแสดงในตารางที่ 4 สามารถแบ่งได้ 3 กลุ่ม คือ 1.ไม่มีศักยภาพในการเกิดกรด (Non acid forming) 2.มีศักยภาพในการเกิดกรด (Potential acid forming) และ 3.ไม่สามารถระบุได้ชัดเจน (Uncertainty)

ตารางที่ 4 เกณฑ์การพิจารณาศักยภาพความเป็นกรด จากการพิจารณาผลของ ABA และ NAG pH [9]

NAPP (AP − NP) kg H_2SO_4/t	NAG pH	ศักยภาพ
> 0	< 4.4	Potential acid forming (PAF)
≤0	< 4.5	Uncertainty
> 0	≥4.5	
≤0	≥4.4	Non acid forming (NAF)

4. สรุป

น้ำเหมืองเป็นกรดเป็นสาเหตุของปัญหาทางด้านสิ่งแวดล้อม ส่งผลกระทบต่อสิ่งมีชีวิตต่างๆ และระบบนิเวศน์ โดยมีแร่ไพไรต์เป็นสาเหตุหลักของการเกิดน้ำเหมืองเป็นกรด โดยทั่วไปเกิดขึ้นภายหลังปิดเหมือง ดังนั้นจำเป็นอย่างยิ่งที่จะต้องมีการประเมินศักยภาพการเกิดน้ำเหมืองเป็นกรด ตลอดจนมีมาตรการเพื่อป้องกันและบรรเทาปัญหาน้ำเหมืองเป็นกรดในอนาคต อย่างไรก็ตามจากที่กล่าวมาแล้วว่าการประเมินน้ำเหมืองเป็นกรด มีหลายวิธี วิธีที่นิยมใช้ได้แก่ ABA และ NAG ซึ่งในบางครั้งใช้การพิจารณาร่วมของ 2 วิธี เพื่อจะได้ผลการประเมินที่มีความน่าเชื่อถือมากยิ่งขึ้น การลดปัญหาที่จะเกิดขึ้นอย่างง่ายโดยการควบคุมไม่ให้น้ำฝนสัมผัสกับแร่ไพไรต์ หรือทำให้น้ำเหมืองมีค่าพีเอชเป็นกลาง เช่น การขุดคูเพื่อระบายน้ำจากพื้นที่เหมืองโดยมีการเติมหินปูน โดยให้การละลายของหินปูนช่วยเพิ่มค่าพีเอชของน้ำเหมืองให้มีสภาพเป็นกลางก่อนออกสู่สิ่งแวดล้อม เป็นต้น หรืออาจจะกล่าวได้ว่าเป็นวิธีการบำบัดด้วยกระบวนการธรรมชาติ (Passive Treatment) ซึ่งมีข้อดีหลายประการ เนื่องจากไม่ต้องมีการเติมสารเคมี และไม่เป็นกระบวนการที่สิ้นเปลือง ตลอดจนมีค่าใช้จ่ายในการดำเนินงานและการบำรุงรักษาระบบน้อย แต่จำเป็นต้องทราบพื้นที่ขอบเขตรวมถึงปริมาณกรดที่เกิดขึ้นอย่างชัดเจน เพื่อจะดำเนินการวางแผนการบรรเทาปัญหาน้ำเหมืองเป็นกรดในอนาคต ซึ่งต้องอาศัยการประเมินน้ำเหมืองเป็นกรดที่มีความน่าเชื่อถือ ดังที่กล่าวมาแล้ว สำหรับประเทศไทยมีเหมืองจำนวนมากทั้งที่ ดำเนินกิจการอยู่และปิดไปแล้ว ดังนั้นจำเป็นอย่างยิ่งที่จะต้องคำนึงถึงปัญหานี้ ตลอดจนภาครัฐควรมีการบังคับใช้กฎหมายที่เข้มงวดเพื่อให้บริษัทที่ดำเนินกิจการเหมืองมีมาตรการต่างๆ เพื่อควบคุม ป้องกันน้ำเหมืองเป็นกรดและมลสารต่างๆ ที่มาพร้อมกับน้ำเหมืองเป็นกรดทั้งขณะดำเนินกิจการและภายหลังการปิดกิจการไปแล้วด้วย

เอกสารอ้างอิง

[1] P.K. Pandey, R. Sharma, M. Roy. and M. Pandey, "Toxic mine drainage from Asia's biggest copper mine at Malanjkhand, India", Environmetal Geochemistry and Health, Vol. 29, 2007, pp.237-248.

[2] S. Koldas, "Notes of environmental inspections in South African Mines", Department of Minerals and Energy of South Africa, 2000, pp.125.

[3] A. Akcil and S. Koldas, "Acid mine drainage (AMD): causes, treatment and case studies", Journal of Cleaner Production, Vol. 14, 2006, pp. 1139-1145.

[4] S.R. Jennings, D.R. Neuman and P.S. Blicker, "Acid mine drainage and effects on fish health and ecology: A review", Reclamation Research Group Publication, Bozaman, MT, 2008.

[5] L. Liang-qi, S. Ci-an, X. Xiang-li, L. Yan-hong and F. Wang, "Acid mine drainage and heavy metal contamination in groundwater of metal sulfide mine at arid territory (BS mine, Western Australia)", Transactions of Nonferrous Metals Society of China, Vol. 20, 2010, pp. 1488-1493.

[6] P.M. Asta, C. Ayora, P. Acero and J. Cama, "Field rates for natural attenuation of arsenic in Tinto Santa Rosa acid mine drainage (SW Spain)", Journal of Hazardous Materials, Vol. 117, 2010, pp. 1102-1111.

[7] B. Liao, L.N., Z.H.Y. Huang, C.Y. Lan and W.S. Shu, "Cut-off net acid generation pH in predicting acid-forming potential in mine spoils", Journal of Environmental Quality, Vol. 36, 2007, pp. 887 – 891.

[8] S.R. Jennings and D.J. Dollhopf, "Acid-base account effectiveness for determination of mine waste potential acidity", Journal of Hazardous Materials, Vol. 41, 1995, pp. 161-175.

[9] W.A. Stewart, S.D. Miller and R. Smart, "Advances in acid rock drainage (ARD) characterization of mine wastes", In the 7th International Conference on Acid Rock Drainage (ICARD), St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502, 2006, pp. 2098-2119.

[10] B. Lottermoser, "Mine wastes: Characterization, Treatment and Environmental Impacts", Springer-Verlag, Berlin, Germany, 2003, 277 pp.

[11] D.W. Blowes, "The environmental effects of mine wastes", In Proceedings of Exploration 97: Fourth Decennial International Conference on Mineral Exploration edited by A.G.Gublins, 1997, pp. 887-892.

[12] P.A. Weber, W.A. Stewart, W.M. Skinner, C.G. Weisener, J.E. Thomas and R.St.C. Smart, "Geochemical effects of oxidation products and framboidal pyrite oxidation in acid mine drainage production techniques", Applied Geochemistry, Vol. 19, 2004, pp. 1953 – 1974.

[13] K. Lapakko and R.W. Lawrence, "Modification of the net acid production (NAP) test", In Proc. BC Mine Reclamation Symposium, Port Hardy, B.C., 1993, pp. 145-159.

[14] C. Changul, S. Chakkaphan, G. Padmanahban and C. Tongcumpou, "Assessing the acidic potential of waste rock in the Akara gold mine, Thailand", Environment Earth Science, Vol. 60, 2010, pp. 1065-1071.

[15] P. Sangtong, S.P umjan, S. Chotpantarat and C. Charngul, "The potential acidity of coal mine: A case study of Mae Ta lignite and ball clay mine, Lampang province", In the 5th International Workshop and Conference on Earth Resources Technology, Ipoh, Malaysia, 9-12 May, 2011.

[16] J. Skousen, J. Simmons, L.M. McDonald and P. Ziemkiewicz, "Acid-Base Accounting to predict post-mining drainage quality on surface mines", Journal of Environmental Quality, Vol. 31, 2002, pp. 2034 – 2044.

[17] L. Lei and R. Watkins, "Acid drainage reassessment of mining tailings, Black Swan Nickel Mine, Kalgoorlie, Western Australia", Applied Geochemistry, Vol.20, 2005, pp.661-667.

ภาคผนวกที่ ค

บทความวิชาการที่ตีพิมพ์ในวารสารระดับนานาชาติ

1. **Chotpantarat, S.**, Limpakanwech, C., and Sutthirat, C. 2011. Effect of soil water characteristic curves on simulation of nitrate vertical transport in a Thai agricultural soil. Sustainable Environmental Research 21(3): 187-193(Formerly, Journal of Environmental Engineering and Management, JEEAM, indexed in the Chemical Abstracts Service, Cambridge Scientific Abstracts, EBSCO and INSPEC). **Corresponding author.**

2. **Chotpantarat, S.**, Ong, S.K., Sutthirat, C., and Osathaphan, K. 2012. Sorption and transport of Pb^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+} under single, binary and multi-metal systems through lateritic soil: Modeling. Geoderma 189-190: 278-287. **Impact factor 2.318. Corresponding author.**

3. Wongsasuluk, P., **Chotpantarat, S.**. Siriwong, W., Borjan, M, and Robson, M. 2013. Heavy metal conctamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area at Ubon Ratchathani Province, Thailand. Environmental Geochemistry and Health Journal. DOI: 10.1007/s10653-013-9537-8**. Impact factor 2.076. Corresponding author.**

Sustain. Environ. Res., 21(3), 187-193 (2011)

187

EFFECTS OF SOIL WATER CHARACTERISTIC CURVES ON SIMULATION OF NITRATE VERTICAL TRANSPORT IN A THAI AGRICULTURAL SOIL

Srilert Chotpantarat,[1,2,*] Chutinun Limpakanwech,[1] Wattasit Siriwong,[3,4] Sumana Siripattanakul[5] and Chakkaphan Sutthirat[1,6]

[1]Department of Geology, Faculty of Science
Chulalongkorn University
Bangkok 10330, Thailand
[2]National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM)
Chulalongkorn University
Bangkok 10330, Thailand
[3]Thai Fogarty International Training and Research in Environmental and Occupational Health (ITREOH) Center
Chulalongkorn University
Bangkok 10330, Thailand
[4]College of Public Health Science
Chulalongkorn University
Bangkok 10330, Thailand
[5]Department of Chemical Engineering, Faculty of Engineering
Ubon Ratchathani University
Ubonratchathani 34190, Thailand
[6]Environmental Research Institute
Chulalongkorn University
Bangkok 10330, Thailand

ABSTRACT

One of the most intensive agricultural areas of Thailand, Tambon Hua Ruea in the Ubon Ratchatani Province, has routinely applied nitrate fertilizers at high levels over a long time as a part of the widespread agricultural activities, and in particular in the cultivation of chili and rice. Unsaturated soil characteristics are important properties for assessing potential nitrate movement from the ground surface to the subsurface environment. In this study, twelve undisturbed soil samples were collected, three from each of four sites, at 0-30 cm depth below ground surface in the vicinity of cultivated chili fields. By applying the retention curve (RETC) program to fit the experimental results of the soil water characteristic curve (SWCC), the van Genuchten (VG) model could explain the SWCC (correlation coefficient, R > 0.99) better than the Brooks and Corey (BC) model (R > 0.94). The simulations of the water content distribution did not show a constant shape, but the water content was lower at the soil surface (varying from 0.06-0.27) and then increased with depth. When incorporating the VG parameters, the maximum nitrate concentrations at depths of 0, 50 and 100 cm below the surface were 100, 0.80 and 0.55 mg L^{-1}, respectively. Furthermore, the rapid decrease in the nitrate concentration from 100 mg to 6 mg L^{-1} just 5 d after nitrate application, seen in both July and November, may be caused from an advection process under otherwise similar initial conditions. At 1 m depth, nitrate concentrations obtained from the VG and BC formulations after 15 d were similar (~ 0.55 mg L^{-1}), and were statistically significantly as well as numerically three-fold higher than that (~ 0.18 mg L^{-1}) derived from neural network predictions, indicating that these soil hydraulic properties play a major role in controlling nitrate transport. Furthermore, the nitrate front moved quite well with the infiltrated water because it was not sorbed onto soil media. According to the simulated results under rainy and summer seasons, the higher the wetted front, the faster was the movement of nitrate. As a result, in order to minimize losses of the nitrogen fertilizer, application rates need to be considered for crop needs, rain amounts and soil hydraulic properties, to identify the best management strategies associated with N-fertilizer application from the environmental and economic perspectives, and to prevent groundwater contamination.

* Corresponding author
Email: lertc77@yahoo.com

INTRODUCTION

Applied agrochemicals may be released rapidly from the ground surface through the unsaturated zone and eventually reach the groundwater systems [1]. Consequently, the ecosystem and diverse life forms, including people and associated vetinary animals, may be then adversely affected by contacting or drinking these polluted soils and groundwater, respectively. In crop production, high application rates of nitrogen fertilizers tend to be performed to obtain high yields of the crop. Nitrate (NO_3^-) is a leaching pollutant from fertilizer application in soil and groundwater. Moreover, nitrate can not only be uptaken by plants but it can also move rapidly through the unsaturated zone, eventually reaching the groundwater or being released to the surface water because it does not strongly sorbed onto the soil matrix. Thus, it is relatively easy to obtain groundwater pollution with nitrate concentrations that exceed the regulated standard [2,3]. Many factors impact on nitrate transport, including the fertilization application rates and amounts per application, irrigation times, soil texture and the structure of the soil profile [3]. In areas of intensive agriculture, the monitoring of nitrate concentration in aquifers needs to be complemented with the assessment of nitrate contents in the unsaturated zone or root zone. The main aim of such consideration is to revert or prevent nitrate levels from reaching or exceeding the allowable level established by the Thailand groundwater drinking standard [4]. This necessitates the strategic development of appropriate water and fertilization application to agricultural land in order to maximize their fertilizer efficiency and minimize nitrogen leaching into groundwater system [5]. Given that the unsaturated zone plays an important role in the transport of nitrate from the soil surface to the subsurface environment, especially unconfined aquifers [6], then if the characteristics of the unsaturated zone can be properly determined, the assessment of nitrate concentrations would be more accurate.

One of the highest density agricultural areas in Thailand, Tambon Hua Ruea in the Ubon Ratchatani Province, has intensively applied agrochemicals (pesticides and fertilizers) for a long period, and in particular for the cultivation of chili and rice. Thus, this is a prime example of where optimizing fertilizer application for maximal crop yield with minimal cost and ecosystem damage is required. However, only a few reports are available on the impact of the unsaturated soil properties and climate factors upon the nitrate movement in an agricultural area. To assess the risk of nitrate leaching into groundwater aquifer, there is a need for efficient tools capable of explaining the mechanism of nitrate leaching and quantifying the nitrate content varying with depth [7,8]. Therefore, the objective of this study were: 1) to characterize the soil water characteristics curve (SWCC) of soil cores collected from Hua Ruea area; and 2) to apply variable saturated modeling (Hydrus-1D) [9] to estimate the movement of nitrate from the soil surface through the shallow groundwater system under different unsaturated properties and different climates in this agricultural system.

MATERIALS AND METHODS

Triplicate cores of undisturbed soil samples taken from 0-30 cm depth below the ground surface were sampled at each of four locations (Fig. 1) in the vicinity of intensively cultivated chili fields. The texture of each agricultural soil was determined by sieve analysis and pipette method [10]. To describe the SWCC of these unsaturated agricultural soils, the relationship between the water content (θ) and the suction pressure head (h) of each soil was evaluated using a pressure plate apparatus according to ASTM D 6836. The SWCC of the soil cores was measured at h of 6, 10, 31.6, 50, 100, 316, 1000 and 15900 cm. The retention curve (RETC) program was used to fit the experimental results and to estimate the unsaturated parameters. From these, the fitting parameters for the van Genuchten (VG) formulation were estimated using a neural network prediction function (NNP). Finally, these unsaturated soil parameters were used to predict the water flow and nitrate vertical transport through the subsurface environment using Hydrus-1D modeling [11]. This model can be used to simulate water flow and contaminant transport in variably saturated soils and can be applied for different equilibrium and non-equilibrium flow and transport in both direct and inverse modes.
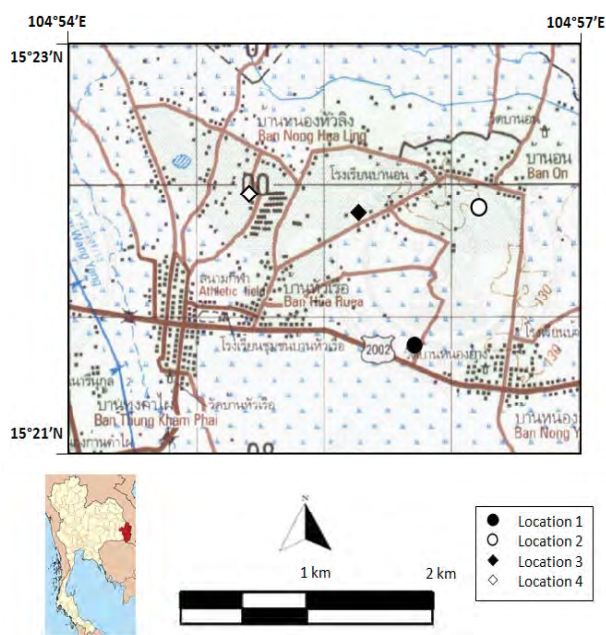

Fig. 1. Location of soil sampling sites (1-4) with three soil samples taken at each location site (next to intensive chilli cultivation plots).

1. Soil Hydraulic Properties

The SWCC is the relationship between the θ at the suction head ($\theta(h)$) and h. The two formulations often used to describe unsaturated soil are the VG and Brook and Corey (BC) formulations, which can be obtained from Eqs. 1 to 6. The unsaturated hydraulic conductivity function ($K(h)$) is given by the Mualem-VG [11,12] and BC [13] models as show below:

(a) VG equations

$$S_e = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \left[\frac{1}{1 + (\alpha h_m)^n}\right]^m \quad h < h_e \quad (1)$$

$$= 1 \quad\quad h \geq h_e \quad (2)$$

$$K(\theta) = K_s K_r(\theta) \quad h < 0 \quad\quad (3)$$
$$= K_s \quad\quad h \geq 0$$

$$K_r(\theta) = (S_e)^k \left[1 - \left(1 - (S_e)^{1/m}\right)^m\right]^2 \quad (4)$$

(b) BC equations

$$S_e = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \left[\frac{h_{m,a}}{h_m}\right]^\lambda \quad h_m < h_{m,a} \quad (5)$$

$$K(\theta) = K_s \left[\frac{\theta - \theta_r}{\theta_s - \theta_r}\right]^{3 + \frac{2}{\lambda}} = K_s (S_e)^N \quad (6)$$

where $\theta(h)$ is the soil θ at the suction head ($L^3 L^{-3}$) and $K(h)$ ($L\ T^{-1}$) are as defined above and h_m = the soil suction head (L), θ_r = the residual θ ($L^3 L^{-3}$), θ_s = the saturated θ ($L^3 L^{-3}$), K_s = the saturated hydraulic conductivity ($L\ T^{-1}$), $h_{m,a}$ = the air-entry potential (L^{-1}), $K(h)$ = unsaturated hydraulic conductivity ($L\ T^{-1}$), K_r = the relative hydraulic conductivity ($L\ T^{-1}$), S_e = the relative water saturation (-), N = constant of soil, λ = index of the pore distribution, k = 0.5 and m, n, α are the fitting parameters of soil water retention curve; m

= 1 - (1/n).

The fitting parameters and index of the pore distribution were derived by fitting Eqs. 1, 2 and 5 to the soil water retention data using the RETC program [11].

2. Water Flow Equation

The one dimensional transient water flow can be described by the Richard's equation (Eq. 7) [14]

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h)\right] \quad (7)$$

where: $\theta(h)$, h and $K(h)$ are as defined above and t is the time (T) and z is the vertical distance (L).

3. Solute Transport Equation

The one-dimensional convection-dispersion equation under transient water flow conditions in variable saturated porous medium (Eq. 8) is shown as [11]:

$$\frac{\partial \theta C}{\partial t} + \frac{\partial \rho_b S}{\partial t} = \frac{\partial}{\partial z}\left[\theta D \frac{\partial C}{\partial z}\right] - \frac{\partial q_w C}{\partial z} \quad (8)$$

where: C is the solute concentration in solution ($M\ L^{-1}$); S is the sorbed solute concentration on soil ($M\ M^{-1}$); ρ_b is the soil bulk density ($M\ L^{-1}$); D is the hydrodynamic dispersion coefficient ($L^2\ T^{-1}$) and q_w is the volumetric water flux ($L\ T^{-1}$).

4. Nitrate Leaching and Distribution Simulation under Different Scenarios

The various input parameters required in Hydrus-1D, namely the saturated hydraulic conductivity (K_s), θ_s, θ_r and empirical factors (α, n) for both VG and BC simulations for nitrate transport in sandy soil are shown in Table 1. The NNP option available in Hydrus-1D was used by assigning the values of bulk density as well as clay, silt and sand percentage composition. The simulation depth was taken at 50 and 100 cm depth below the ground surface. This

Table 1. Input parameters for the simulation of the vertical transport of nitrogen through sand (site 2 on Fig. 1) using Hydrus-1D simulations

Parameter	VG	BC	NNP
Saturated hydraulic conductivity (K_s)	49 ± 7	49 ± 7	49 ± 7
Residual water content (θ_r)	0.13 ± 0.02	0.01 ± 0.01	0.05
Saturated water content (θ_r)	0.34 ± 0.02	0.35 ± 0.05	0.38
Empirical fitting parameter α	0.008 ± 0.003	0.04 ± 0.04	0.036
Empirical fitting parameter n	2.36 ± 0.73	0.20 ± 0.09	4.15
Longitudinal dispersivity (cm)	10	10	10

Data are shown as the mean $\pm$ one standard deviation, and are derived from 3 repeats. In all simulations the Initial nitrate concentration (C_0) at the soil surface (0 cm) was 100 mg L^{-1}. Note that the Thailand drinking water standard for nitrate levels is not to exceed 45 mg L^{-1}

study simulated nitrogen distribution within the root zone and the cumulative nitrogen going below the root zone or unsaturated zone, prior to reaching the water table of 1 m depth.

RESULTS AND DISCUSSION

1. Soil Hydraulic Properties

The texture of each agricultural soil was classified as loamy sand, sand and sandy loam (Table 2). By applying the RETC program to fit the experimental results and estimate unsaturated parameters, the VG model (correlation coefficient R > 0.99) could explain the SWCC behavior better than the BC and NNP models (correlation coefficients R > 0.94 and 0.70, respectively).

2. Soil Moisture Distribution

The water flow and nitrate transport simulations in site 2, which had the highest hydraulic conductivity,

were carried out as the representative example of an area which is at a high risk of nitrate contamination into the groundwater. The simulation results of the soil moisture distribution (Fig. 2) in the sandy soil of site 2 was performed using the unsaturated soil parameters derived from the three formulations, VG, BC and NNP, and the weather data recorded at the nearby station in study area during July and November. The total precipitation levels were 51 and 0.03 cm in July and November, respectively.

The soil moisture distribution was affected by the level of water infiltration, based on the weather data in terms of the precipitation and evapotranspiration (Fig. 2). The θ distribution did not show a constant shape, but rather was lower at the soil surface and then increased with depth because the rainfall rate was less than the saturated hydraulic conductivity of sand (49.0 cm d^{-1}). This then led to non-uniform θ profiles in both July and November. The simulated θ distribution using the parameters derived from the NNP were lower than those obtained from the BC and VG models for depths of 0 to 80 cm below the surface,

Table 2. Physical and chemical properties of the surface soil (0-30 cm depth) in the study area[1]

Site	Soil texture	Sand (%)	Silt (%)	Clay (%)	Saturated Hydraulic conductivity (cm d^{-1})	Organic matter (%)	CEC (cmol kg^{-1})	Bulk density (g cm^{-1})	Porosity (cm^3 cm^{-3})
1	Loamy sand	77	18.5	4.5	3.4 ± 0.6	0.37	1.6	1.75 ± 0.03	0.36 ± 0.05
2	Sand	98.5	1.5	0.01	49 ± 7	0.47	2.1	1.62 ± 0.02	0.40 ± 0.02
3	Loamy sand	78	15.5	6.5	28 ± 11	0.52	3.6	1.56 ± 0.06	0.43 ± 0.06
4	Sandy loam	75.5	18.3	6.3	9 ± 5	1.87	2.8	1.68 ± 0.01	0.43 ± 0.01

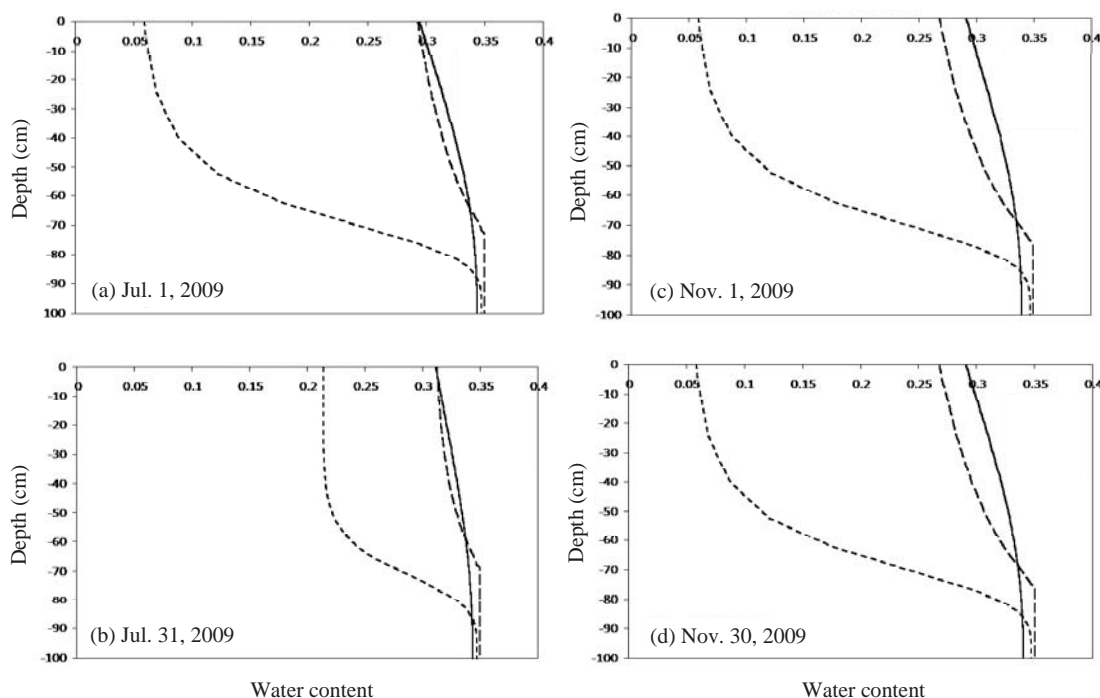[1]Data are shown as the mean ± 1 standard deviation and are derived from three replicates.

Fig. 2. The simulated soil water content (θ) distribution at different depths below the soil surface in (a) Jul. 1; (b) Jul. 31; (c) Nov. 1 and (d) Nov. 30, 2009 (—— VG; ---- BC; ------ NPP).

but they appeared to become closer at near the water table (90-100 cm). For example, on July 1, 2009, the θ distribution derived from the VG and BC model simulations (0.29) was approximately five times higher than that from NNP (0.06) near the surface. On July 31, the θ distribution was higher than that in the beginning of the month because the soil pores were filled with infiltrated water. In contrast, when comparing the two θ profiles between November 1 and 30, they were found to be broadly similar because only a small level of precipitation (0.03 cm) had occurred which would not be sufficient to significantly affect the soil water profile. This is in agreement with the fact that the degree of water saturation in sandy soils is sensitive to rainfall events [15].

3. Nitrate Concentration Distribution

The simulation of nitrate movement through the same sandy soil at site 2 that was affected by water infiltration due to different precipitation and evapotranspiration levels (Fig. 2) was performed for the different soil water characteristic parameters derived from the VG, BC and NNP models. The simulations were performed for three different soil depths (Fig. 3). In

these simulations, we assumed that a nitrate concentration of 100 mg L^{-1} would result from fertilizer leaching from the ground surface into the groundwater due to rainfall percolation. The lower boundary (100 cm) was assumed to be located at the water table surface. The nitrate concentrations were found to decrease with increasing depth from the surface, as expected if there is no absorption to the soil matrix. For example, in July the maximum simulated nitrate concentrations at a depth of 0, 50 and 100 cm from the surface were 100, 0.80 and 0.55 mg L^{-1}, respectively, when using the VG model. The nitrate concentration appeared to be decrease rapidly from 100 to approximately 6 mg L^{-1} during the initial simulation period (5 d after fertilizer application) in both July and November, probably caused by an advection process under the otherwise similar initial conditions (Figs. 2a and 2c). This implies that the soil hydraulic properties play a major role in controlling the vertical nitrate transport through the soil when it has a higher θ. These nitrate concentrations, derived from numerical simulations in both July and November, do not exceed the current Thailand groundwater regulated standard of 45 mg L^{-1} [15]. The influx of infiltrated water appeared to reduce the nitrate concentration. For example, the nitrate con-
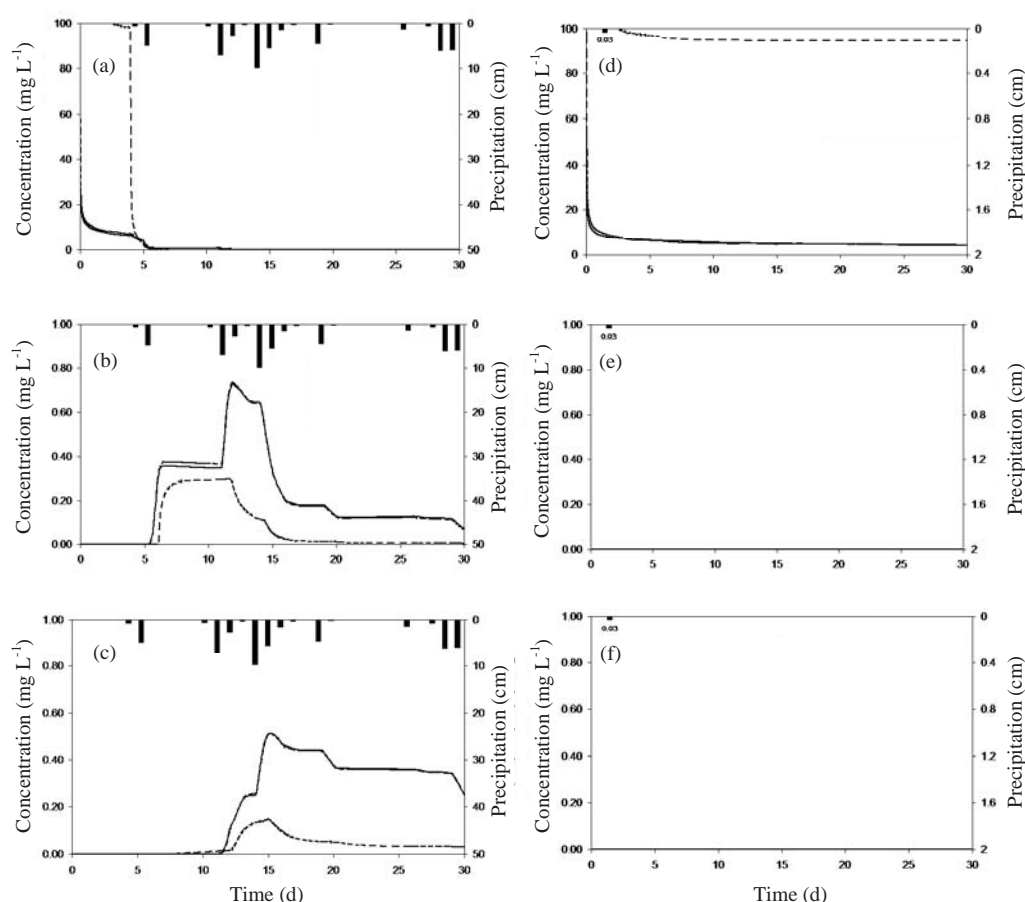

Fig. 3. The simulated nitrate concentration in (a-c) July and (d-f) November (2009) at (a, d) 0 cm, (b, e) 50 cm and (c, f) 1 m below the soil surface (■ Precipitation; — VG; ······ BG; – – NPP).

centration was reduced from 6 to 1.5 mg L^{-1} at the soil surface because of the rainfall (0.63 cm) on July 5 (Fig. 2a). The infiltrated water caused the θ in the soil to increase with depth (Figs. 2a and 2b), and consequently, the front of nitrate concentrations (Figs. 3b and 3c) moved faster under these conditions than those with a lower θ (Figs. 3e and 3f). The nitrate levels at the soil surface level in November were essentially constant because there was no rainfall after Nov. 2. As a result, the leaching of nitrate did not reach as far down as 50 and 100 cm below the surface (Figs. 3e and 3f). Moreover, under different soil hydraulic parameters, the simulation of nitrate concentrations obtained from NNP appeared to be significantly lower than those from simulations based upon the VG and BC models, indicating that the soil hydraulic parameters clearly affected the vertical nitrate movement through the unsaturated zone. For example, at a 1 m depth below the surface the nitrate concentrations obtained from VG and BC formulation after 15 d were similar (~ 0.55 mg L^{-1}), but statistically significantly ($P < 0.05$) and numerically 3-fold higher than that derived from NNP (~ 0.18 mg L^{-1}). Thus, local soil hydraulic properties should be carefully evaluated prior to simulating the fate and transport of contaminants. Furthermore, the nitrate front can move fairly efficiently along with the infiltrated water because the nitrate ions are poorly sorbed by the soil media [16,17]. Since the nitrification of nitrite to nitrate is a much faster reaction than the nitrification of ammonium, both nitrification reactions are often grouped together, thereby neglecting the nitrite species. Volatilization and gaseous state of nitrate is neglected. Its concentration depends on the oxygen level, pH and temperature [18], and the application of ammonium/nitrate fertilizer reduces this concentration [17]. Thus for these reasons the sorption of nitrate to the soil matrix and its redox reaction have not been considered in the nitrate simulation equations performed here.

CONCLUSIONS

Unsaturated soil hydraulic characteristics are quite important for assessing the potential movement of agrochemicals from the ground surface to the subsurface environment, and especially in shallow groundwater systems. Here, parameters derived from the VG equation (correlation coefficient, R > 0.99) could explain the SWCC behavior better than those from the BC and NNP models (R > 0.94 and 0.70, respectively). The higher the wetted front of the soil θ was, then the faster was the vertical movement of nitrate through the soil matrix. Furthermore, the soil hydraulic properties affect this vertical movement and so should be carefully estimated in any assessment of the water flow and movement of nitrate. For the proper agricultural management practices, N-fertilizer application rates should be suitable for crop needs and soil hydraulic properties in fields in order to minimize losses of nitrogen fertilizer and the protect groundwater resources.

REFERENCES

1. Kleveno, J.J., K. Loague and R.E. Green, Evaluation of a pesticide mobility index: Impact of recharge variation and soil profile heterogeneity. J. Contam. Hydrol., 11(1-2), 83-99 (1992).

2. Wang, C., Experimental study of nitrogen transport and transformation in soils. Adv. Water Sci. 8(2), 176-182 (1997) (in *Chinese*).

3. Chen, M., H. Wu and F. Wo, Nitrate vertical transport in the main paddy soils of Tai Lake region, China. Geoderma, 142(1-2), 136-141 (2007).

4. Pollution Control Department (PCD), Groundwater drinking standard. PCD, Bangkok, Thailand. http://www.pcd.go.th/info_serv/en_reg_std_water01.html#s3 (2010).

5. Ajdary, K., D.K. Singh, A.K. Singh and M. Khanna, Modelling of nitrogen leaching from experimental onion field under drip fertigation. Agr. Water Manage., 89(1-2), 15-28 (2007).

6. Al-Darby, A.M. and G. Abdel-Nasser, Nitrate leaching through unsaturated soil columns: Comparison between numerical and analytical solutions. J. Appl. Sci., 6(4), 735-743 (2006).

7. Gardenas, A.I., J.W. Hopmans, B.R. Hanson and J. Simunek, Two-dimensional modeling of nitrate leaching for various fertigation scenarios under micro-irrigation. Agr. Water Manage., 74(3), 219-242 (2005).

8. Rahil, M.H. and V.Z. Antonopoulos, Simulating soil water flow and nitrogen dynamics in a sunflower field irrigated with reclaimed wastewater. Agr. Water Manage., 92(3), 142-150 (2007).

9. Crevoisier, D., Z. Popova, J.C. Mailhol and P. Ruelle, Assessment and simulation of water and nitrogen transfer under furrow irrigation. Agr. Water Manage., 95(4), 354-366 (2008).

10. Allen, T., Particle Size Measurement. Chapman & Hall, London, UK (1974).

11. Šimůnek, J., M. Šejna and M.T. van Genuchten, The Hydrus-1D Software Package for Simulating the One-dimensional Movement of Water, Heat, and Multiple Solutes in Variably Saturated Media. Version 4. Beta 1. ICGWMC-TPS-70, International Ground Water Modeling Center, Colorado School of Mines, Golden, CO (2008).

12. van Genuchten, M.T., F.J. Leij and S.R. Yates, The RETC Code for Quantifying the Hydraulic Functions of Unsaturated Soils. U.S. Salinity Laboratory, Department of Agriculture, Agricultural Research Services, Riverside, CA (1991).

13. Brooks, R.H. and A.T. Corey, Hydraulic Properties of Porous Media. Hydrology Papers 3, Colorado State University, Fort Collins, CO (1964).

14. Richards, L.A., Capillary conduction of liquids through porous mediums. Physics, 1(5), 318-333 (1931).

15. Yeh, H.F., C.C. Lee and C.H. Lee, A rainfall-infiltration model for unsaturated soil slope stability. J. Environ. Eng. Manage., 18(4), 261-268 (2008).

16. Huygens, D., T. Ruetting, P. Boeckx, O. van Cleemput, R. Godoy and C. Mueller, Soil nitrogen conservation mechanisms in a pristine south Chilean Nothofagus forest ecosystem. Soil Biol. Biochem., 39(10), 2248-2458 (2007).

17. Olesen, T., B.S. Griffiths, K. Henriksen, P. Moldrup and R. Wheatley, Modeling diffusion and reaction in soils. 5. Nitrogen transformations in organic manure-amended soil. Soil Sci., 162(3), 157-168 (1997).

18. Wendland, F., Modelling the nitrate flow in the ground-water provinces of the "old" federal states of the Federal Republic of Germany. Ecol. Model., 75-76 (Sept.), 385-397 (1994).
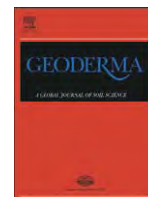
Competitive modeling of sorption and transport of Pb^{2+}, Ni^{2+}, Mn^{2+} AND Zn^{2+} under binary and multi-metal systems in lateritic soil columns

S. Chotpantarat [a,b,*], S.K. Ong [c], C. Sutthirat [b,d], K. Osathaphan [a,e]

[a] Center of Excellence for Environmental and Hazardous Waste Management (EHWM), Chulalongkorn University, 254 Phayathai Road, Bangkok 10330, Thailand
[b] Department of Geology, Faculty of Science, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand
[c] Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, IA 50011, USA
[d] Environmental Research Institute, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand
[e] Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand

ARTICLE INFO

ABSTRACT

Transport of heavy metals from acid mine drainage through soils can impact valuable water resources and have a deleterious effect on their associated ecosystems. The movement of single, binary and multi-metal systems through lateritic soil columns were experimentally determined and then modeled with the HYDRUS-1D using a local equilibrium convection–dispersion (CD_{eq}) model, or chemical nonequilibrium two-site model (TSM) with first order kinetics. The TSM model described the breakthrough curves better than the CD_{eq} model in both binary and multi-metal systems. The $(Q_{max})/(Q_{max}^*)$ ratios were generally greater than unity suggesting that the presence of other metals reduced sorption through competition for sorption sites . Ratios of $(Q_{max})_{Pb}^{2+}/(Q_{max})_{secondary\ metals\ (Mn^{2+},\ Zn^{2+},\ Ni^{2+})}$ (ranging from 0.92 to 1.09) were lower than ratios of $(Q_{max}^*)_{Pb}^{2+}/(Q_{max}^*)_{secondary\ metals\ (Mn^{2+},\ Zn^{2+},\ Ni^{2+})}$ (ranging from 0.94 to 2.80), which indicated the highest sorption affinity of Pb^{2+} was under both binary and multi-metal systems. Furthermore, the fraction of the instantaneous equilibrium site (f) of all metals, particularly for secondary metals, tended to increase with increasing metal concentrations in the system, suggesting that diffusion probably dominates the sorption and transport of heavy metals in the system.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Surface and groundwater pollution are largely caused by human activities, such as mining and smelting, agrochemical application, industrial discharges, energy production and improper waste disposal. The mobility of heavy metals through soils and groundwater is affected by many factors, such as the properties of the heavy metals, physical–chemical properties of the soil, and climatic conditions. Prediction of movement and distribution of heavy metals through the subsurface aquifer require knowledge of the sorption and transport properties of the porous media. Batch sorption experiments have generally been performed to investigate the sorption of two or more metals onto soils (Arias et al., 2006; Covelo et al., 2007; Elliott et al., 1986; Gomes et al., 2001; Jain and Ram, 1996; Serrano et al., 2005). For example, using batch studies for the competitive sorption of Cd and Pb onto four soils, Serrano et al. (2005) showed a higher retention of Pb over Cd in all four soils tested and the interaction between Pb and Cd sorption was found to a function of the soil properties. However, to obtain

transport information under non-equilibrium conditions, a packed soil column with continuous flow is typically used (Miretzky et al., 2006; Pang et al., 2004). To explain the transport of heavy metals in porous media, column experiments have been conducted but most of these studies are focused on a single metal under various flow conditions (Chotpantarat et al., 2011a; Liu et al., 2006; Miretzky et al., 2006; Pang et al., 2004; Strawn and Sparks, 2000; Yolcubal and Akyol, 2007). At typical contaminated sites, such as acid mine drainage sites, the presence of several heavy metals in groundwater is common and they may compete with each other for soil sorption sites, resulting in enhanced transport of heavy metals in the porous media. Several papers (Fonseca et al., 2011; Lafuente et al., 2008; Rodríguez-maroto et al., 2003) have addressed the sorption of heavy metals in multi-metal systems. For example, using columns with calcareous soils to evaluate Cr, Cu, Pb, Ni, Zn and Cd sorption, Lafuente et al. (2008) reported that sorption of Cr, Cu and Pb were higher than those of Ni, Zn and Cd under competitive conditions. Fonseca et al. (2011) reported that for a soil column with loamy sand soil , Cr and Cu were found to be more strongly sorbed due to an increase in the soil pH as compared to Cd, Pb and Zn. Furthermore, in order to predict the transport and distribution of heavy metals more accurately, reliable transport-related parameters of heavy metals in groundwater or subsurface environments need to be evaluated, but many studies to date have focused on the sorption of heavy metals under equilibrium conditions.

* Corresponding author at: Department of Geology, Faculty of Science, Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand. Tel.: +66 831785470; fax: +66 22185464.
E-mail address: csrilert@gmail.com (S. Chotpantarat).

However, some of the issues with multi-metal systems, such as possible competition between heavy metals for sorption sites, mass transfer and non-equilibrium sorption and transport on soils, and particularly soil that consists mainly of clay, are not completely known.

Many computer programs such as to CXTFIT (Toride et al., 1999), HYDRUS-1D (Šimunek et al., 2008), MACRO (Larsbo and Jarvis, 2003; Larsbo and Jarvis, 2005), SIMULAT (Diekkrüger, 1996), and VADOFT (Carsel et al., 1997) have been applied to model the transport of water and solutes. But for steady state conditions, CXTFIT is frequently used to describe tracer breakthrough curves using the analytical solutions for tracer or conservative miscible displacement tests as shown in the following studies: Vanderborght et al. (1997, 2002), Wallach and Parlange (2000), Kamra et al. (2001), Seo and Lee (2005), Yolcubal and Akyol (2007).

In addition, solute transport modeling under transient flow conditions requires a large number of model parameters, which are typically estimated from experimental results. These numerical models (i.e., MACRO, SIMULAT, VADOFT) including HYDRUS-1D, have many options to numerically estimate such parameters. However, HYDRUS-1D has been selected in this study because it has been used in hundreds of studies and is continually improved (Šimunek et al., 1998, 2005, 2008) to implement new modules such as Langmuir two-site model which are not included in MACRO, SIMULAT and VADOFT. HYDRUS-1D is a published program, which can be downloaded as freeware and has similar window interface with CXTFIT, making the programs easy to use in estimating water, conservative and non-conservative solutes.

The objective of this paper was to model the effects of heavy metal concentrations in single, binary and multi-metal systems on the competitive sorption and kinetic mechanisms in lateritic soil column experiments and to explain the competitive mechanisms in terms of the estimated sorption capacities, retardation factors and the fraction of instantaneous equilibrium sorption sites (f). Lateritic soils (consisting of 53.8% clay) were collected from a gold mine site in Thailand and the breakthrough curves (BTCs) from column experiments, as reported by Chotpantarat (2008), were used in the modeling efforts. To this end, HYDRUS-1D (Šimunek et al., 2008), a local convection–dispersion equilibrium (CD_{eq}) model with linear and nonlinear (Langmuir) isotherms and the chemical nonequilibrium two-site (TSM) model, plus CXTFIT (Toride et al., 1999), an analytical solution of the one-dimensional advection–dispersion equilibrium equation which include exchange between a mobile and an immobile region and the use of linear sorption, were used. Information obtained from this study may be used to explain the behavior of multi-metal transport in contaminated sites.

2. Materials and methods

2.1. Column experiments

Column experiments were conducted using lateritic soils obtained from Akara gold mine, Phichit Province, Thailand at a depth of 0–2 m below ground surface. The soil has a bulk and particle density of 1.23 and 2.71 g cm^{-3}, respectively and the percent of sand, silt and clay were 21.8, 24.4 and 53.8, respectively. The pH of the soil was 5.3 while the cation exchange capacity (CEC) was 28.8 cmol kg^{-1}. The organic matter and specific surface area of the soil were 0.16% and 48.69 m^2 g, respectively. Details of the experimental methodology column experiments used here have been reported previously (Chotpantarat, 2008; Chotpantarat et al., 2011b). Briefly, lateritic soils were uniformly packed in acrylic columns with an inner diameter of 2.50 cm and a depth of 10 cm. The soil column was initially saturated with deionized water from the bottom to eliminate entrapped air (Miretzky et al., 2006). After the saturation procedure, a solution of 30 mg L^{-1} of bromide (Br$^-$) was injected from the bottom at a rate of 8 ± 0.5 mL hr^{-1} and the column effluent was collected using a fraction collector at various times. The system was maintained at a constant pH of 5 with NaAc buffer solution. The mixed heavy metal solutions were then injected from the bottom of the column and the effluent collected periodically to monitor the concentrations of the respective heavy metals and pH in the effluent. The metal concentrations were determined by flame atomic absorption spectrophotometry (FAAS). The BTCs, expressed as the relative concentrations (C/Co) versus pore volume (V/Vo), were plotted, where Co is the initial concentration added and Vo is the pore volume of the soil column. The column experiments conducted were (i) single metal systems comprising of 5 mM of Pb^{2+}, Mn^{2+}, Ni^{2+} or Zn^{2+} at pH 5, (ii) binary metal experiments comprising of combinations of Pb^{2+} and Mn^{2+}, Pb^{2+} and Ni^{2+}, and Pb^{2+} and Zn^{2+} at pH 5 with Pb^{2+} concentration fixed at 5 mM and Mn^{2+}, Ni^{2+} and Zn^{2+} concentrations at 3 mM, 5 mM and 10 mM for each column run and (iii) a multi-metal system using all four metals, Pb^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}, together at 5 mM each at pH 5.0.

2.2. Numerical transport modeling of column experiments

The BTCs obtained from the tracer experiments were analyzed with CXTFIT, a nonlinear least squares optimization computer program (Toride et al., 1999) with a number of analytical solutions for one-dimensional solute transport based on the convection–dispersion equation (CDE) and the two-region non-equilibrium model (TRM) for the estimation of hydrodynamic dispersion coefficient (D), including the non-equilibrium parameters.

The CD_{eq} may be written as shown in Eq. (1) below:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial C^*}{\partial t} \pm \left[\frac{\partial C}{\partial t}\right]_{rxn} \tag{1}$$

where C is the concentration of solute in liquid phase (mg L^{-1}); t is the time (hr); D_L is the longitudinal dispersion coefficient (cm^2 hr^{-1}); v_x is the average linear groundwater velocity (cm hr^{-1}); ρ is the bulk density of aquifer (g cm^{-3}); θ is the volumetric moisture content or porosity for saturated media; C^* is the amount of solute sorbed per unit weight of solid (mg g^{-1}) and rxn is the subscript indicating a biological or chemical reaction of the solute (mg L^{-1} hr^{-1}).

Unfortunately, CXTFIT is limited in that it does not have the analytical solutions for the transport of nonlinear sorbing solutes. Therefore, to assess the BTCs for nonlinear sorption of metals in the lateritic soil column experiments, HYDRUS 1D was used (Šimunek et al., 2008).

HYDRUS-1D was applied in both the direct and the inverse mode to assess the experimental BTCs using linear, nonlinear (CD_{eq} model) and rate-limited two-site sorption model (TSM model) as presented by Eq. (2) (Brusseau et al., 1991; Fetter, 1993):

$$\left(1 + \frac{f\rho}{\theta}\left[\frac{Q_{max}b}{(1+bC)^2}\right]\right)\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \frac{\alpha\rho}{\theta}\left((1-f)\frac{Q_{max}bC}{1+bC} - s_2\right) \tag{2}$$

where f (−) is the fraction of equilibrium sites and α (day^{-1}) is a first-order kinetic rate coefficient and S_2 (mg g^{-1} soil) is the solid phase concentration at site 2.

2.3. Parameter estimation

The columns were assumed to be homogeneously packed with the soil and saturated with water while the water flow and solute transport in the soil-filled columns were assumed to be one-dimensional. The hydrodynamic dispersion coefficient (D) of the soil was estimated by curve fitting the bromide BTCs with the nonlinear least-squares parameters optimization method of CXTFIT (Toride et al., 1999). The two-region approach was then applied to examine any physical non-equilibrium processes in the system. The value of D, as obtained from the bromide BTC, was then used to estimate the average soil dispersivity, $\lambda_{avg} = D_{avg}/v$, which was then used to estimate the sorption parameters of metals, as provided by the HYDRUS-1D code version 4.Beta 1 (Šimunek et al.,

2008). In addition, the chemical non-equilibrium two-site model with Langmuir sorption was used to estimate the sorption parameters (Q_{max} and b in the case of Langmuir isotherm) and the non-equilibrium parameters (f and α) for the heavy metal transport. Least square errors were used to determine the appropriateness of the curve fit.

3. Results and discussion

3.1. Metal transport modeling

The average dispersivity, λ_{avg}, obtained from the CXTFIT program for the three bromide column runs, was 1.42 cm, as reported by Chotpantarat (2008), and the results revealed that all the water in

the system was mobile. This value was subsequently used for the modeling of the heavy metal BTCs.

The heavy metal BTCs were fitted using the equilibrium convection–dispersion model (CD_{eq}) and chemical non-equilibrium two-site model of HYDRUS-1D. Since the program was unable to model all the metals at the same time in the binary and multiple heavy metal runs, the interactions between the metals in the system for each heavy metal BTC for the multi-metal column experiments was captured by fitting the BTCs individually. The best fit curves using the various model conditions in HYDRUS-1D are presented in Figs. 1–3 (not including duplicated columns), and the fitted parameters are presented in Tables 1 and 2. For comparison purposes, the experimental data for the Pb^{2+} BTC in a single system were presented along with those for Pb^{2+} in the binary and multi-metal systems in
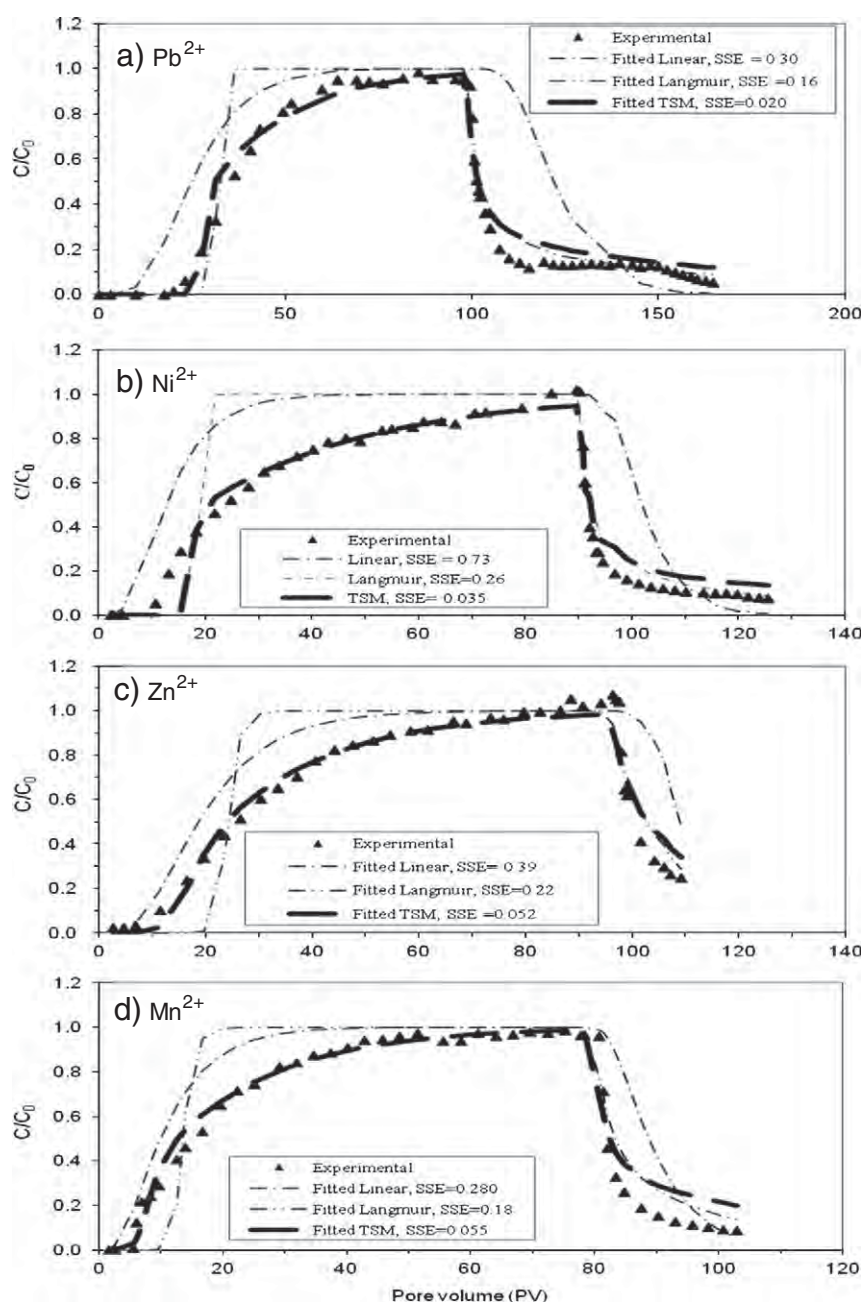

Fig. 1. Heavy metal breakthrough data for lateritic soil at pH 5 showing that for (a) Pb^{2+}, (b) Ni^{2+}, (c) Zn^{2+} and (d) Mn^{2+}. Curves represent the heavy metal concentrations using optimized curve-fitting with the CD_{eq} model with either linear or Langmuir isotherms, and the optimized curve-fitting with the chemical nonequilibrium two-site model (TSM).

Figs. 1–3. Using the same initial concentration (5 mM) for the secondary metals (Ni^{2+}, Zn^{2+} and Mn^{2+}) as the Pb^{2+}, the BTCs for these metals in single systems were plotted as shown in Figs. 2 and 3 to compare the BTCs of the same heavy metals in the binary and multi-metal systems.

3.1.1. Equilibrium convection–dispersion model (CD$_{eq}$)

The CD$_{eq}$ model is based on the local equilibrium assumption (*LEA*), where sorption is assumed to be fast relative to the pore-water velocity. Both linear and nonlinear isotherms (Langmuir) were used in the CD$_{eq}$ model to curve fit the metal BTCs, as shown in Figs. 1–3. Fig. 1 provides the results from modeling of the single metal case for all four metals, while Fig. 2 shows that for the Pb^{2+}–Ni^{2+} binary system. The figures for the other binary metal systems were generally similar, and are not shown here, but discussion on the differences between the theoretical (modeled) and experimentally estimated transport and sorption parameters are highlighted. Fig. 3 illustrates the modeling of the multi-metal system with all four metals at 5 mM in the solution. The estimated parameters derived

from HYDRUS-1D by minimizing the sum of square errors (SSE) revealed that the Langmuir isotherm explained the experimental data better than the linear isotherm (Table 1). With the linear sorption isotherm, the initial breakthrough time of the best fit curve was lower than the experimental data and the number of PVs at which the effluent concentration was equal to that of the influent ($C_e = C_0$) were faster than the experimental BTCs. Moreover, the rising and decreasing limbs derived from the linear model were overestimated when compared with the experimental data (Figs. 1–3).

A characteristic of the experimental BTCs in binary and multi-metal systems was the asymmetrical shape with a sharply rising front and a relatively more dispersed elution portion (Figs. 2 and 3), suggesting nonlinear sorption behavior. The BTCs observed in this study were similar to those reported previously in column studies of Cr(VI) in calcareous Karst soil, where the breakthrough curves of Cr(VI) were asymmetrical with a sharply rising front and a more dispersed portion (Yolcubal and Akyol, 2007). Although the BTCs obtained with the Langmuir isotherm fitted better than those using a linear isotherm, the Langmuir-isotherm-simulated BTCs still showed sharp concentration
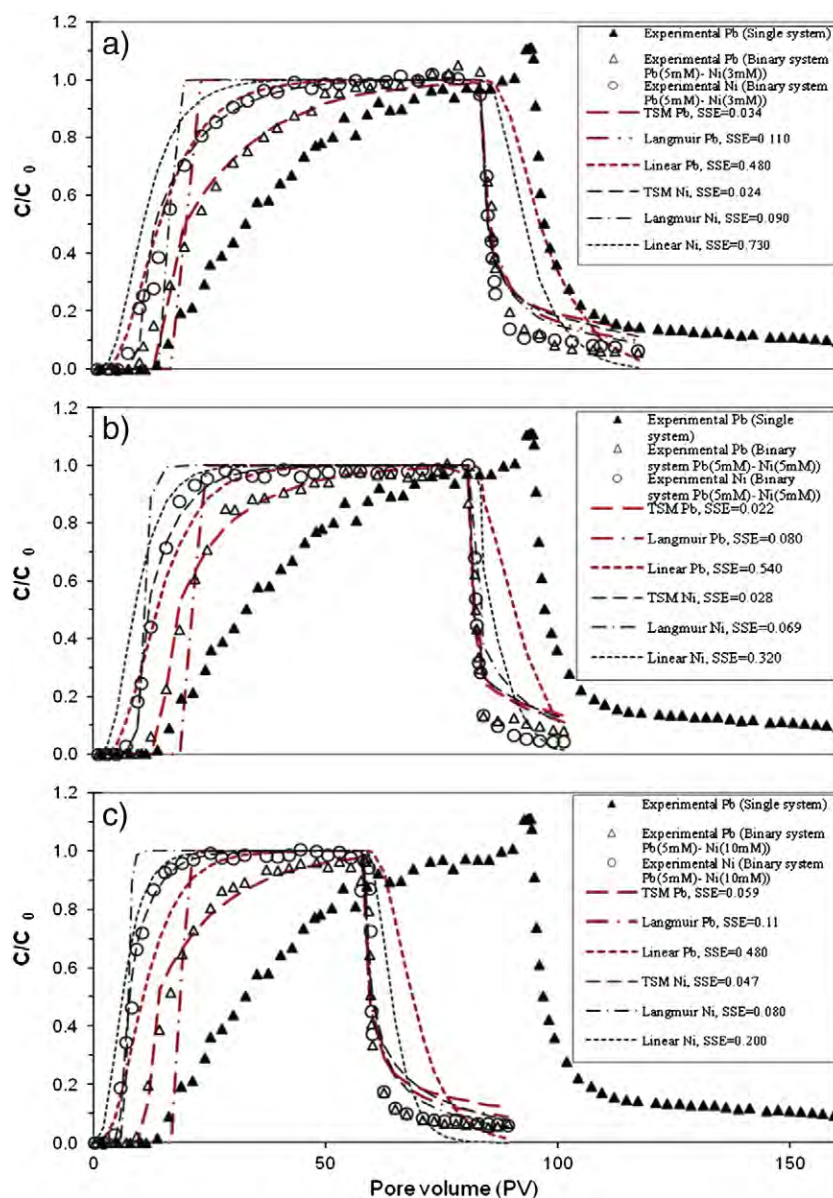

Fig. 2. Heavy metal breakthrough data in a lateritic soil column for single Pb^{2+} (5 mM), and the Pb^{2+}–Ni^{2+} binary metal systems at pH 5, (a) for Pb^{2+} (5 mM)–Ni^{2+} (3 mM) (b) for Pb^{2+} (5 mM)–Ni^{2+} (5 mM), and (c) for Pb^{2+} (5 mM)–Ni^{2+} (10 mM). Curves represent heavy metal concentrations using optimized curve-fitting with the CD$_{eq}$ model with either linear or Langmuir isotherms, and the optimized curve-fitting with the chemical nonequilibrium two-site model (TSM).
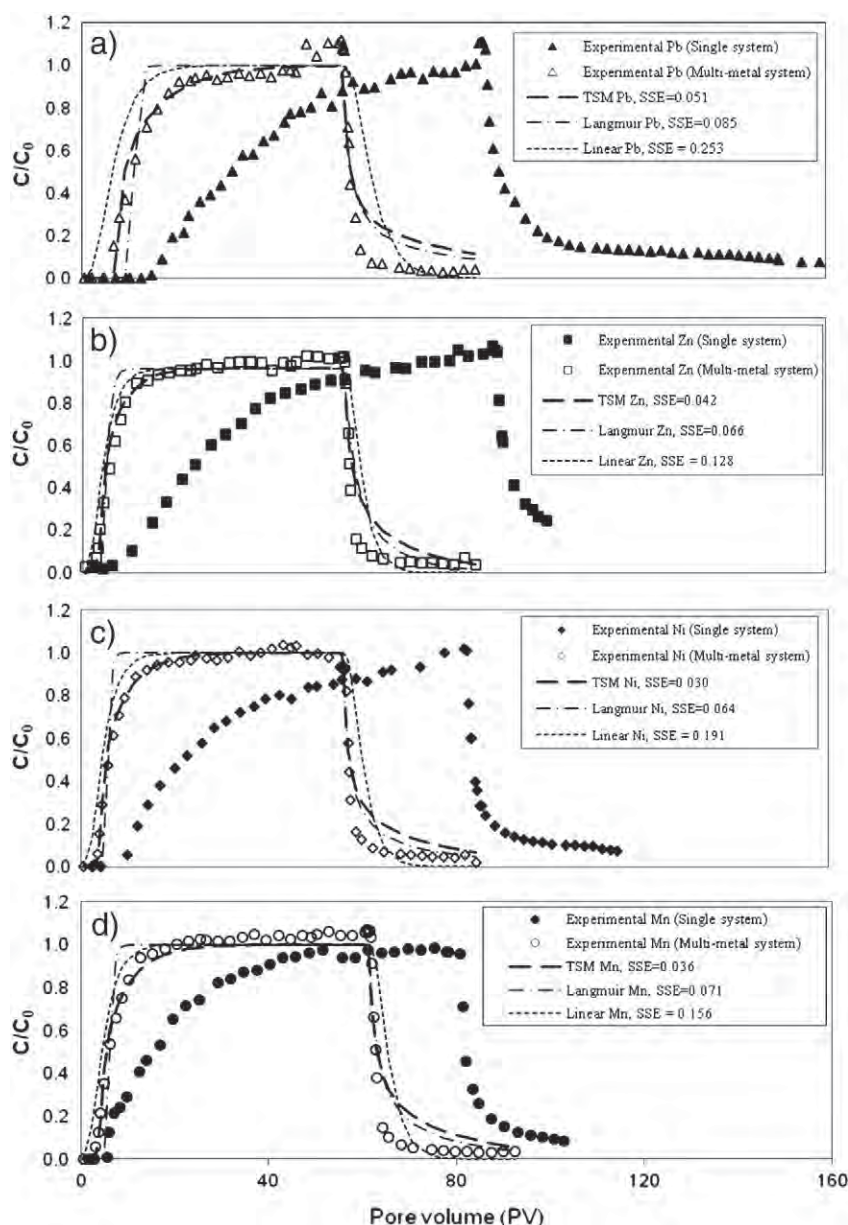
Fig. 3. Heavy metal breakthrough data in lateritic soil column for the multi- metal system (Pb^{2+} 5 mM–Zn^{2+} 5 mM–Ni^{2+} mM–Mn^{2+} 5 mM) at pH 5 and different fits with the equilibrium convection–dispersion model (CD_{eq}) with either linear or Langmuir isotherms and the chemical nonequilibrium two-site model (TSM) were compared with observed data in single and binary system: (a) Pb^{2+}, (b) Zn^{2+}, (c) Ni^{2+} and (d) Mn^{2+}.

fronts, and did not fit well with all the observed experimental data, especially the rising limb portion (Figs. 1–3). In addition, the Langmuir-isotherm-simulated BTCs could not describe the initial breakthrough times well since the curve fits of the model were more than the experimental breakthrough times for metals in single metal systems. As observed by others, the asymmetrical shape of metal BTCs with long tailings may be better described by a non-equilibrium transport model (Brusseau et al., 1991; Pang et al., 2002).

3.1.2. Chemical non-equilibrium two-site model (TSM)

As shown earlier, the CD_{eq} model using either linear or Langmuir sorption isotherms did not fully describe the heavy metal BTCs in lateritic soil (Figs. 1–3). Non-equilibrium sorption-related transport characteristics have been reported for some metals in repacked soil and/or gravel columns (Sparks, 1995; Tsang and Lo, 2006). One of the approaches used to describe non-equilibrium transport was to assume a short, initial fast phase of sorption followed by an extended period of slower sorption (Kookana et al., 1994), which can be modeled using the TSM. When the

metal BTCs were fitted with the TSM, the model described all of the experimentally observed heavy metal BTCs better than the CD_{eq} model with linear or Langmuir sorption isotherms (Figs. 1–3). For example, the SSE derived from fitting the BTC of Pb^{2+} in the Pb^{2+} (5 mM)–Ni^{2+} (3 mM) system at pH 5 were: SSE_{TSM} (0.034)$<SSE_{Langmuir}$ (0.110)$<SSE_{Linear}$ (0.480), which was similar to that reported by others. For example Kookana et al. (1994) observed asymmetrical BTCs for Cd^{2+} in Spodosol and Oxisol soil, which may be due to sorption-related (chemical) non-equilibrium behavior. Likewise, Pang et al. (2002), who evaluated the effects of pore-water velocity on the chemical non-equilibrium of single heavy metal systems through alluvial gravel columns, showed that the BTCs of each of the Cd, Zn and Pb in single metal systems were best fitted using the TSM. According to column studies with different secondary metals in this study, the TSM fitted the rising and the declining limb of the metal BTCs much better than those using the equilibrium assumption, such as the CD_{eq} models (Figs. 1–3). Moreover, applying the *t*-test on the average SSEs obtained from the TSM and the CD_{eq} model with Langmuir isotherm for individual metals in single,

Table 1
Estimated transport parameters for heavy metal breakthrough curves (BTCs) using equilibrium convection–dispersion (CD_{eq}) model with linear and Langmuir isotherm approaches, as generated by HYDRUS-1D.

System	C_0 (mM) 1st metal (Pb^{2+})	2nd metal	$\lambda^{\pm}$ (cm)	Measured v (cm hr^{-1})	Linear $K_d \pm 95\%CI$ (L g^{-1}) 1st	SSE	Langmuir $Q_{max} \pm 95\%CI$ (mM g^{-1}) 1st	$b \pm 95\%CI$ (L mM^{-1}) 1st	SSE	Linear $K_d \pm 95\%CI$ (L g^{-1}) 2nd	SSE	Langmuir $Q_{max} \pm 95\%CI$ (mM g^{-1}) 2nd	$b \pm 95\%CI$ (L mM^{-1}) 2nd	SSE
1 Pb^{2+}-Ni^{2+}	5.05	0	1.42	1.58	15.42±0.04	0.30	0.10±0.01	5.09±1.03	0.16	–	–	–	–	–
2	5.01	0	0.97	1.61	16.04±0.08	0.75	0.11±0.01	6.56±0.84	0.08	–	–	–	–	–
3	0	4.89	1.42	1.58	–	–	–	–	–	8.27±0.01	0.73	0.06±0.02	4.88±1.76	0.26
4	4.86	3.01	1.42	1.74	9.47±0.09	0.48	0.07±0.01	6.58±1.20	0.11	6.69±0.01	0.40	0.03±0.004	7.02±1.23	0.09
5	4.85‡	3.17	1.57	1.78	9.48±0.08	0.52	0.07±0.01	8.33±1.55	0.15	2.92±0.01	0.32	0.04±0.005	14.61±3.05	0.10
6	4.93	5.13	1.42	1.68	8.74±0.01	0.54	0.06±0.01	9.60±1.71	0.08	5.12±0.01	0.32	0.04±0.005	3.62±0.53	0.05
7	`4.88	10.06	1.42	1.59	7.64±0.08	0.48	0.056±0.003	4.58±0.33	0.11	4.11±0.01	0.20	0.06±0.01	1.08±0.29	0.08
8 Pb^{2+}–Zn^{2+}	0.00	4.61	1.42	1.72	–	–	–	–	–	13.02±0.08	0.39	0.09±0.02	1.08±0.29	0.22
9	5.26	2.91	1.42	1.67	8.07±0.01	0.54	0.07±0.02	9.86±1.63	0.11	1.83±0.02	0.31	0.03±0.003	9.83±1.80	0.10
10	5.22	5.36	1.42	1.68	7.59±0.09	0.45	0.06±0.01	10.55±1.91	0.07	1.49±0.02	0.23	0.02±0.01	2.90±1.16	0.07
11	5.41	9.67	1.42	1.62	5.14±0.01	0.40	0.06±0.01	3.91±0.88	0.13	3.09±0.09	0.11	0.07±0.02	1.61±0.18	0.20
12	4.33‡	9.48	1.42	1.55	7.32±0.01	0.67	0.04±0.002	4.97±0.24	0.17	1.67±0.02	0.22	0.06±0.02	0.61±0.17	0.06
13 Pb^{2+}–Mn^{2+}	0	4.81	1.42	1.68	–	–	–	–	–	6.70±0.10	0.28	0.06±0.02	1.16±0.45	0.18
14	5.31	2.73	1.42	1.76	10.95±0.05	0.50	0.09±0.01	8.83±0.90	0.10	2.46±0.01	0.24	0.02±0.004	6.02±1.29	0.08
15	5.14	4.47	1.42	1.55	6.54±0.08	0.33	0.06±0.01	6.52±1.11	0.09	2.66±0.09	0.17	0.03±0.004	4.00±1.16	0.10
16	4.85	8.66	1.42	1.67	5.86±0.10	0.46	0.06±0.01	6.33±0.90	0.10	1.20±0.02	0.20	0.05±0.01	3.37±0.68	0.07
17 Pb^{2+}–Zn^{2+}–Ni^{2+}–Mn^{2+}	4.56	Zn^{2+}=4.73	1.42	1.69	5.24±0.08	0.25	0.04±0.001	4.06±0.13	0.08	3.11±0.08	0.11	0.02±0.01	0.47±0.14	0.07
		Ni^{2+}=5.19								3.21±0.01	0.17	0.03±0.01	2.07±0.47	0.08
		Mn^{2+}=4.38								3.03±0.09	0.14	0.02±0.01	1.00±0.26	0.08

† dispersivity derived from tracer test (Chotpantarat, 2008; Chotpantarat et al., 2011a); $\pm$ average dispersivity derived from average of dispersivity values of 3 tracer columns (Chotpantarat, 2008; Chotpantarat et al., 2011a); ‡Duplicated column (Chotpantarat, 2008; Chotpantarat et al., 2011a).

binary and multi- metal systems, revealed that the curve-fitted results of the TSM were significantly different from the CD_{eq} model (t-test, $P<0.05$), with those values fitted by the TSM being in better agreement with the experimental results.

For the sake of comparison, according to the best fit parameters from the TSM, the maximum sorption capacity of Pb^{2+} in the single system, $(Q_{max})_{Pb}^{2+}$, was higher than those in the binary and multi-metal systems (Fig. 4 and Table 2), $(Q_{max}^*)_{Pb}^{2+}$. This is in agreement with the retardation factors and average sorption capacity of Pb^{2+} in a single metal system over those in a binary or multi-metal system, as already reported (Chotpantarat et al., 2011b). As expected, when metals compete for sorption sites in the binary and multi-metal systems, the maximum sorption capacity (Q_{max}) of individual metal in the binary and multi-metal systems, $(Q_{max}^*)_{Pb}^{2+}$, $(Q_{max}^*)_{Ni}^{2+}$, $(Q_{max}^*)_{Mn}^{2+}$ and $(Q_{max}^*)_{Zn}^{2+}$, is reduced compared to the corresponding value in the single metal systems, $(Q_{max})_{Pb}^{2+}$, $(Q_{max})_{Ni}^{2+}$, $(Q_{max})_{Mn}^{2+}$ and $(Q_{max})_{Zn}^{2+}$. The maximum sorption capacity of Pb^{2+}, $(Q_{max}^*)_{Pb}^{2+}$ was higher than those for the three other secondary metals at the same (5 mM) concentration, regardless of whether the metals were applied in a binary or a multi-metal system. The ratios of $(Q_{max})_{Pb}^{2+}/(Q_{max})_{secondary\ metals}$ $_{(Mn^{2+}, Zn^{2+}, Ni^{2+})}$ ranged from 0.92 to 1.09 and were lower than the ratios of $(Q_{max}^*)_{Pb}^{2+}/(Q_{max}^*)_{secondary\ metals\ (Mn^{2+}, Zn^{2+}, Ni^{2+})}$ that ranged from 0.94 to 2.80. This confirms the higher sorption affinity of Pb^{2+} in

lateritic soil than the other three metals studied (Zn^{2+}, Mn^{2+} and Ni^{2+}) under both binary and multi-metal systems. This result was similar to that found by other researchers using both pure and heterogeneous soils under batch experiments (Adhikari and Singh, 2003; Arias et al., 2006; Fontes and Gomes, 2003; Serrano et al., 2005). However, increasing the secondary metal concentrations resulted in an increase in the maximum sorption capacity of the secondary metals in the binary metal systems.

The $(Q_{max})/(Q_{max}^*)$ ratios were generally greater than unity, suggesting that the simultaneous presence of metals in both binary and multi-metal systems reduced sorption through competition for sorption sites in the solid phases. In addition, it was found that $(Q_{max})_{Zn}^{2+}/(Q_{max}^*)_{Zn}^{2+} > (Q_{max})_{Mn}^{2+}/(Q_{max}^*)_{Mn}^{2+} > (Q_{max})_{Ni}^{2+}/(Q_{max}^*)_{Ni}^{2+} > (Q_{max})_{Pb}^{2+}/(Q_{max}^*)_{Pb}^{2+}$, suggesting that sorption of Zn^{2+}, Mn^{2+} and Ni^{2+} were affected more strongly, in that order, by the simultaneous presence of a competing metal than Pb^{2+} was when the concentrations of the secondary metals were less than 5 mM. In contrast, when the concentrations of secondary metals were higher than that of the Pb^{2+} (5 mM), the $(Q_{max})/(Q_{max}^*)$ ratios of Pb^{2+} were lower than those of the secondary metals due to their higher concentrations. In a similar way, for the multi-metal system, the ratios of $(Q_{max})_{Zn}^{2+}/(Q_{max}^*)_{Zn}^{2+} \sim (Q_{max})_{Mn}^{2+}/(Q_{max}^*)_{Mn}^{2+} \sim (Q_{max})_{Ni}^{2+}/(Q_{max}^*)_{Ni}^{2+} > (Q_{max})_{Pb}^{2+}/(Q_{max}^*)_{Pb}^{2+}$ suggesting that the sorption of Zn^{2+}, Mn^{2+} and Ni^{2+} were affected,

Table 2
Estimated transport parameters for heavymetal breakthrough curves (BTCs) using the chemical nonequilibrium two-site model (TSM) , as generated by HYDRUS-1D.

No	System	C_0 (mM) 1st metal (Pb^{2+})	2nd metal	$\lambda^\pm$ (cm)	Measured v (cm hr^{-1})	1st metal $Q_{max}\pm95\%CI$ (mM g^{-1})	$b\pm95\%CI$ (L mM^{-1})	$f\pm95\%CI$	$\alpha\pm95\%CI$ (hr^{-1})	SSE	2st metal $Q_{max}\pm95\%CI$ (mM g^{-1})	$b\pm95\%CI$ (L mM^{-1})	$f\pm95\%CI$	$\alpha\pm95\%CI$ (hr^{-1})	SSE
1	Pb^{2+}–Ni^{2+}	5.05	0	1.42	1.58	0.12±0.01	3.45±0.46	0.28±0.04	0.012±0.001	0.020	-	-	-	-	-
2		5.01	0	0.97	1.61	0.13±0.02	2.71±0.34	0.43±0.06	0.013±0.005	0.044	-	-	-	-	-
3		0	4.89	1,42	1.58	–	–	–	-	-	0.11±0.02	2.62±0.40	0.25±0.02	0.009±0.001	0.035
4		4.86	3.01	1.42	1.74	0.08±0.01	3.36±0.61	0.38±0.06	0.017±0.003	0.034	0.04±0.01	4.89±0.92	0.35±0.06	0.028±0.004	0.024
5		4.85‡	3.17	1.57	1.78	0.09±0.01	2.87±0.50	0.27±0.04	0.015±0.020	0.024	0.04±0.01	5.49±1.09	0.35±0.06	0.026±0.006	0.036
6		4.93	5.13	1.42	1.68	0.07±0.01	4.91±0.71	0.50±0.06	0.020±0.005	0.022	0.045±0.01	3.54±0.57	0.43±0.10	0.041±0.009	0.028
7		4.88	10.06	1.42	1.59	0.07±0.01	3.43±0.63	0.52±0.07	0.018±0.006	0.059	0.07±0.02	0.40±0.10	0.56±0.12	0.060±0.026	0.047
8	Pb^{2+}–Zn^{2+}	0	4.61	1.42	1.72	–	–	–	-	-	0.13±0.02	0.60±0.11	0.41±0.06	0.016±0.004	0.052
9		5.26	2.91	1.42	1.67	0.07±0.01	3.16±0.82	0.32±0.08	0.022±0.003	0.022	0.03±0.01	4.86±0.92	0.50±0.07	0.029±0.009	0.041
10		5.22	5.36	1.42	1.68	0.07±0.02	4.00±0.66	0.48±0.08	0.025±0.007	0.041	0.04±0.01	2.16±0.50	0.44±0.09	0.044±0.015	0.041
11		5.41	9.67	1.42	1.62	0.06±0.01	1.51±0.36	0.57±0.10	0.028±0.013	0.069	0.07±0.02	0.120±0.07	0.63±0.14	0.055±0.047	0.061
12		4.33‡	9.48	1.42	1.55	0.06±0.02	3.35±1.10	0.37±0.12	0.024±0.008	0.069	0.06±0.01	1.54±0.38	0.52±0.13	0.040±0.021	0.044
13	Pb^{2+}–Mn^{2+}	0	4.81	1.42	1.68	–	–	–	-	-	0.11±0.02	0.87±0.19	0.31±0.05	0.019±0.004	0.055
14		5.31	2.73	1.42	1.76	0.07±0.02	2.63±0.60	0.37±0.08	0.022±0.005	0.058	0.03±0.01	0.96±0.24	0.50±0.07	0.021±0.010	0.076
15		5.14	4.47	1.42	1.55	0.06±0.01	2.70±0.71	0.40±0.10	0.029±0.008	0.041	0.05±0.01	1.75±0.38	0.47±0.08	0.040±0.015	0.037
16		4.85	8.66	1.42	1.67	0.06±0.01	3.90±0.72	0.39±0.08	0.023±0.006	0.049	0.06±0.01	1.99±0.33	0.46±0.07	0.027±0.009	0.039
17	Pb^{2+}–Zn^{2+}–Ni^{2+}–Mn^{2+}	4.56	Zn^{2+} = 4.73	1.42	1.69	0.05±0.01	1.74±0.43	0.49±0.08	0.028±0.011	0.064	0.03±0.01	0.46±0.12	0.61±0.10	0.067±0.051	0.052
			Ni^{2+} = 5.19								0.03±0.01	1.02±0.21	0.47±0.06	0.049±0.018	0.035
			Mn^{2+} = 4.38								0.03±0.01	0.74±0.18	0.52±0.09	0.050±0.023	0.046

† dispersivity derived from tracer test (Chotpantarat, 2008; Chotpantarat et al., 2011a); ± average dispersivity derived from average of dispersivity values of 3 tracer columns (Chotpantarat, 2008; Chotpantarat et al., 2011a); ‡Duplicated column (Chotpantarat, 2008; Chotpantarat et al., 2011a).

in that order, more strongly by the simultaneous presence of a competing metal than was Pb^{2+}. Indeed, the ability of Pb^{2+} to effectively compete for sorption sites on different surfaces has been shown by other researchers in batch sorption systems with Cd^{2+} (Fontes and Gomes, 2003; Rodríguez-maroto et al., 2003) and other metal ions in multi-metal solutions (Fontes and Gomes, 2003; Saha et al., 2002). Moreover, as shown in Fig. 4, which is a plot of the $(Q_{max})_{Pb}^{2+}$ from the TSM versus the concentrations of the secondary metals, an increase in the concentration of the secondary metals in the binary and multi-metal systems resulted in an exponential decrease in the maximum sorption capacity of Pb^{2+}, $(Q_{max})_{Pb}^{2+}$, with respect to the maximum sorption capacity of Pb^{2+} in the single system. For example, in Pb^{2+}–Zn^{2+} system, the maximum sorption capacity of Pb^{2+} (0.12 mM) for 0 mM of Zn^{2+} was statistically different from that of maximum sorption capacity of Pb^{2+} (0.08 mM) in the presence of 3 mM of Zn^{2+}. As the concentration of Zn^{2+} increased above 3 mM, the maximum sorption capacity of Pb^{2+} showed a decreasing trend but was not significantly different from the maximum sorption capacities at higher Zn^{2+} concentrations. This is consistent with the decrease in retardation factors of Pb^{2+}, as affected by the concentration of Zn^{2+}, reported before (Chotpantarat et al., 2011b). Furthermore, with the Langmuir model, the total sorption capacities for single, binary and

multi-metal systems were essentially constant (ranging from 0.10 to 0.13 mM g^{-1}).

The binding energy coefficient varied with metal solutions, the initial concentration of the secondary metals and the total metal concentration (b_{Pb}, b_{Ni}, b_{Mn} and b_{Zn} for the single metal system, and b_{Pb}^*, b_{Ni}^*, b_{Mn}^* and b_{Zn}^* for the binary metal systems, respectively), although all systems showed a greater affinity for Pb^{2+} than for the secondary metal at the same concentration (e.g., 5 mM for Ni^{2+}, Zn^{2+}, and Mn^{2+} for binary metal systems). For example, the results showed that b_{Pb} (3.45±0.46) > b_{Zn} (0.60±0.11) for the single metal system and b^*_{Pb} (4.00±0.66) > b^*_{Zn} (2.16±0.50) for the Pb^{2+}–Zn^{2+} binary metal system, respectively. In addition, the results showed that $b_i < b_i^*$ in all binary metal systems except for that of Pb^{2+} (5 mM)–Ni^{2+} (10 mM) and Pb^{2+} (5 mM)–Zn^{2+} (10 mM), which may be related to the specifically sorbed metals at high energy surfaces with low dissociation constants, indicating that competition for sorption sites promotes the retention of such secondary metals on specific sites. As a result, although the maximum sorption capacity, $(Q_{max}^*)_i$, decreased, the metals were held in the soil matrix more strongly. This result concurs with that reported for the competitive sorption of Cu and Zn (Mesquita and Vierae Silva, 2002), or for Pb and Cd in acid soils (Serrano et al., 2005). In contrast, as the secondary
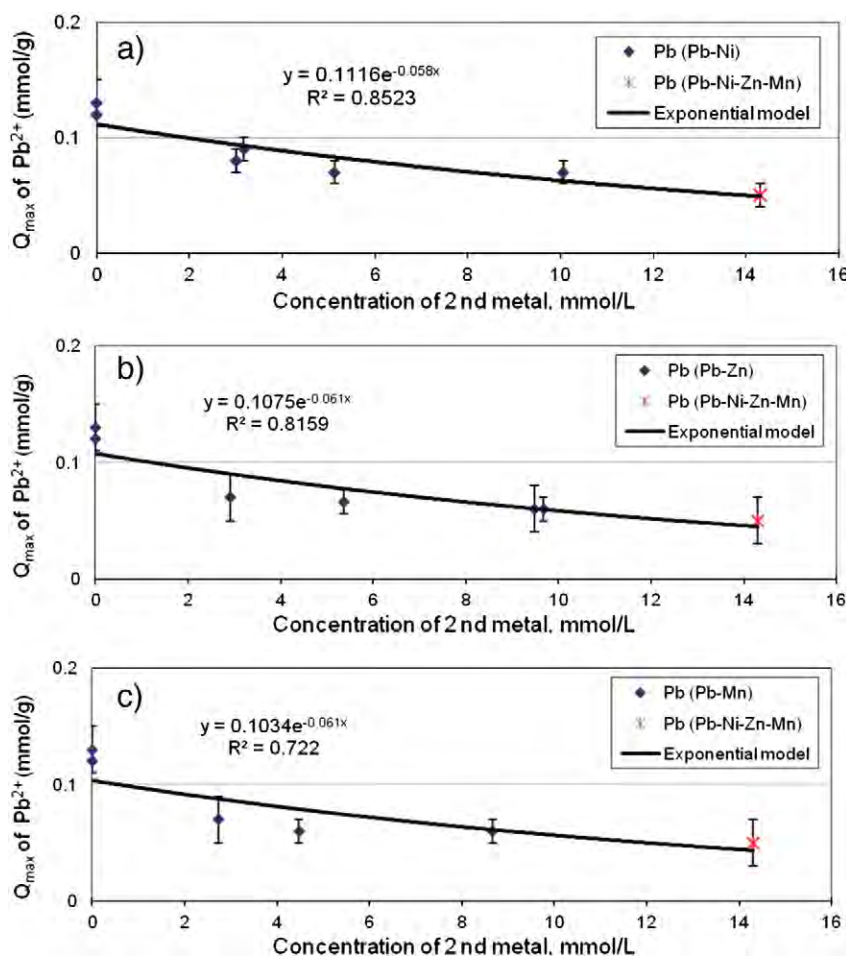
Fig. 4. Maximum sorption capacity, Q_{max}, of Pb^{2+} with increasing initial concentrations of the 2nd metal (a) Ni^{2+}, (b) Zn^{2+} and (c) Mn^{2+} in the binary (5 mM Pb^{2+} and 0–14 mM secondary metal) and multiple metal (all 5 mM) systems.

metal concentration increased to a level higher than that of the Pb^{2+} (5 mM) in the binary and multi-metal systems, the *b* values seemed to be reduced. This could be due to the high metal loads relative to its low binding energy coefficient.

The fraction of the instantaneous equilibrium site (*f*) of all the metals, and particularly for the secondary metals in the binary and multi-metal systems, tends to increase with increasing metal concentrations in the system (Fig. 5, Table 2). For example, the fraction of the instantaneous equilibrium site (*f*) of Ni^{2+} in single system significantly increased from 0.25 ± 0.02 to 0.56 ± 0.12 for Ni^{2+} in Pb^{2+}(5 mM)- Ni^{2+}(10 mM). Since the Peclet number in the systems was low (ranging from 5.85 to 9.37), diffusion probably dominates the sorption and transport of heavy metal in the system. Brusseau et al. (1991) indicated that for a non-equilibrium process caused by diffusion in the micropores or interlayer clay spaces of the soil matrix, *f* was found to be independent of the velocity, *V*. As a result, *f* tends to increase under competitive sorption, potentially from competition for sorption sites in the rapid reaction phase. The higher the concentration in the system the higher is the fraction of occupied instantaneous sorption sites. Consequently, the increased fraction of instantaneous site would imply that metal sorption changes from a non-equilibrium mechanism towards an equilibrium one. For example, in the multi-metal system (Fig. 3), the SSE obtained from the fitted curves of the four metals from the Langmuir model (SSE ranging from 0.070 to 0.080) and the TSM (SSE ranging from 0.035 to 0.064) were more similar in magnitude than those obtained from the binary metal systems (SSE ranging from 0.06 to 0.22 and from 0.040 to 0.76 for the Langmuir model and the TSM, respectively). The gradual change from a non-equilibrium to an

equilibrium behavior is thus likely to be related to the total metal concentration in the system (Fig. 5).

In general, the kinetics of metal sorption on soils follow a two stage time-dependent behavior with an initially fast reaction followed by a much slower reaction. The 1st kinetic rate appears to increase as the secondary metal concentration increases in both binary and multi-metal systems (Table 2), as compared to those in a single metal system. This potentially indicates that the rate limiting stage for heavy metal sorption in lateritic soil is affected by the simultaneous presence of other metals, particularly in the multi-metal system. In accord, Serrano et al. (2005) found that the Cd^{2+} sorption rate for the initial rapid reaction sorption in a binary metal system was higher as compared to that for the single metal system.

The TSM correctly explained the early tailing of the asymmetrical portion of heavy metal BTCs in both the binary and multi-metal systems (Figs. 2 and 3), but slightly overestimated the extended tailing of heavy metals. This was probably due to the fact that either the rate of sorption/desorption could not be described by a first-order rate constant (Connaughton et al., 1993; Selim, 1999) or that more than one type of kinetic rates are needed in addition to the instantaneous sorption sites. Selim (1999) observed that the sorption/desorption behavior of Cu^{2+} for a McLaren soil showed a hysteresis behavior, at high Cu^{2+} concentrations, and so could not be explained with a first-order rate constant. Drillia et al. (2005) found that soil with little organic matter, but with strong sorption hysteresis, could be described by a slower reversible or even an irreversible process that is not included in the TSM. In addition, the extended tailings might be controlled by mass transfer diffusion that is also not accounted for in the TSM (Beigel
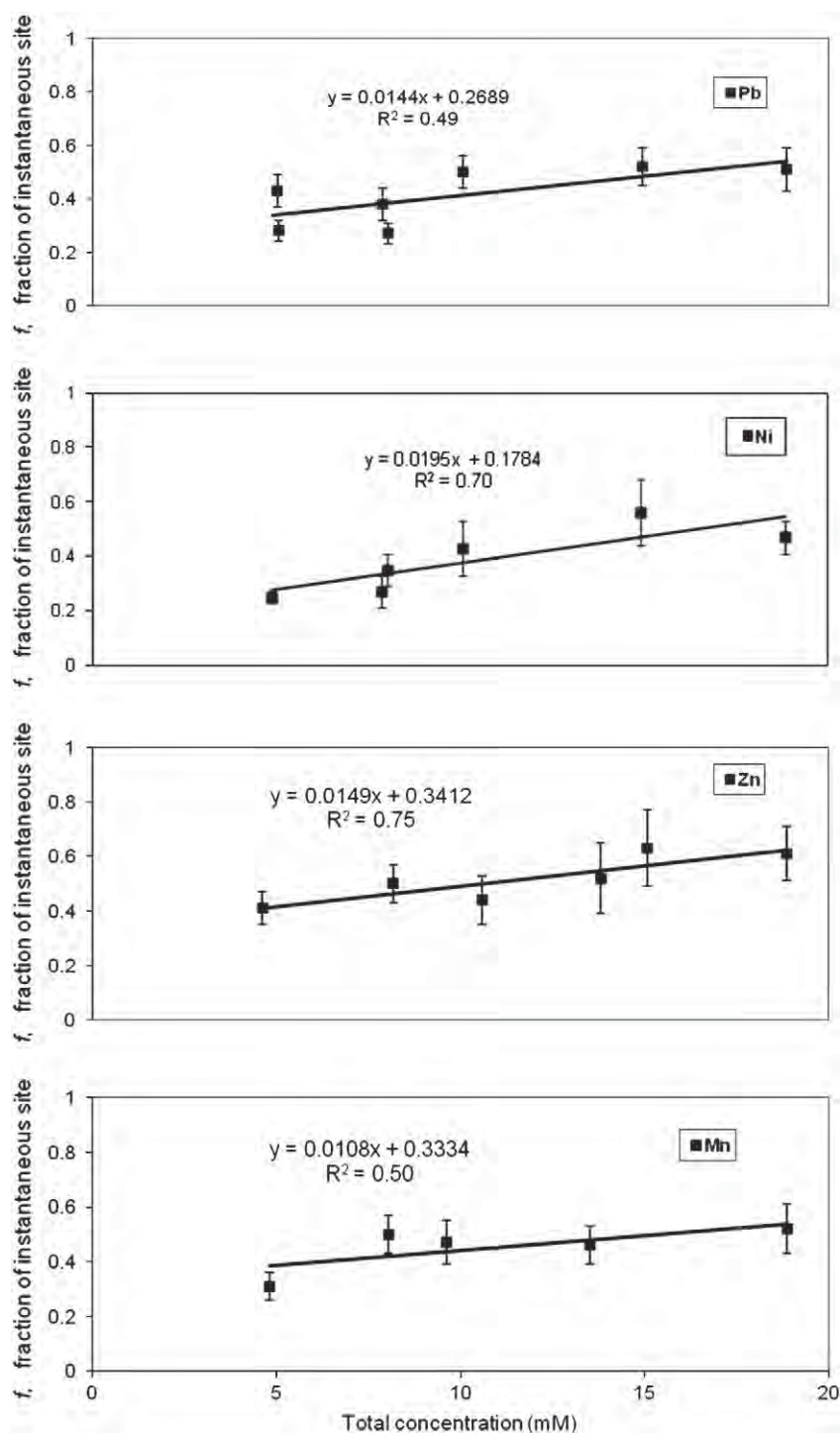
Fig. 5. Effect of total heavy metal concentration in binary and multiple heavy metal systems on the fraction of instantaneous equilibrium sorption sites (f).

and Di Pietro, 1999). Since the column studies do not provide information on hysteresis and/or mass transfer, further separate experimentation is required to more precisely model and predict heavy metal transport through this soil (Seuntjens et al., 2001).

4. Conclusion

The study evaluated the effect of metal concentrations on the sorption and transport mechanisms through a lateritic soil column, as well as estimating the appropriate sorption and transport parameters, for single, binary and multiple metal systems. The use of the CD_{eq} model with either linear or Langmuir isotherms did not describe the rising

and declining limbs of the metal concentrations in single, binary and multiple metal systems, but the TSM with first order kinetics described the BTCs more accurately.

According to the TSM, the maximum sorption capacity of Pb^{2+} was highest in the single system and reduced in the binary and multi-metal systems. The simultaneous presence of other metals in both binary and multi-metal systems reduced sorption through competition for sorption sites on the solid phases. Moreover, the sorption of Mn^{2+}, Zn^{2+} and Ni^{2+} were more strongly affected by the simultaneous presence of a competing metal than Pb^{2+} was. The sorption affinity of Pb^{2+} was higher than the other three heavy metal metals for lateritic soil for all conditions evaluated.

Competition between the metals for sorption sites tended to promote the retention of secondary metals on more specific sorption sites. Furthermore, the fraction of the instantaneous equilibrium sites (f) of all metals, particularly for secondary metals in the binary and multi-metal systems, increases with increasing metal concentrations, which is likely to be because diffusion dominates the sorption and transport of heavy metals. Consequently, the increased fraction of instantaneous sites probably changes the metal sorption from a non-equilibrium to an equilibrium mechanism.

The more complex TSM was found to describe the rising limb and initial declining limb well but could not explain the extended tailing phenomenon. This might be due to the fact that the rate of sorption/desorption from the sorption sites cannot be described by a first-order rate constant. Regardless, the curve-fitted results of the TSM for the individual heavy metals in the binary and multi-metal systems were found to be statistically different from the results obtained with the CD_{eq} model and in better agreement with the experimental results. These results reinforce the necessity of using transport models and proper parameters under competitive and non-equilibrium conditions to predict heavy metal transport more accurately for field conditions and more efficiently in selecting the appropriate strategies in remediation/monitoring the heavy metal contaminated sites.

Acknowledgments

References

Adhikari, R., Singh, M.V., 2003. Adsorption characteristics of lead and cadmium in some soils of India. Geoderma 114, 81–92.

Arias, M., Pérez-Novo, C., López, E., Soto, B., 2006. Competitive adsorption and desorption of copper and zinc in acid soils. Geoderma 133, 151–159.

Beigel, C., Di Pietro, L., 1999. Transport of triticonazole in homogeneous soil columns: influence of nonequilibrium sorption. Soil Science Society of America Journal 63, 1077–1086.

Brusseau, M.L., Larsen, T., Christensen, T.H., 1991. Rate-limited sorption and non-equilibrium transport of organic chemicals in low organic carbon aquifer materials. Water Research 28, 2485–2497.

Carsel, R.F., Imhoff, J.C., Hummel, P.R., Cheplick, M.J., Donigian, A.S., 1997. PRZM-3, a model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones, Users Manual for Release 3.0, 30605. National Exposure Research Laboratory, U.S. Environmental Protection Agency, Athens, GA.

Chotpantarat, S., 2008. Characterization of gold mine tailings and heavy metals leaching and transport in lateritic soil. Ph.D. Dissertation, Chulalongkorn University, Thailand.

Chotpantarat, S., Ong, S.K., Sutthirat, C., Osathaphan, K., 2011a. Effect of pH on transport of Pb^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+} through lateritic soil: column experiments and transport modeling. Journal of Environmental Sciences 23, 640–648.

Chotpantarat, S., Ong, S.K., Sutthirat, C., Osathaphan, K., 2011b. Competitive sorption and transport of Pb^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+} in lateritic soil columns. Journal of Hazardous Materials 190, 391–396.

Connaughton, D.F., Stedinger, J.G., Liou, L.W., Shuler, M.L., 1993. Description of time-varying desorption kinetics: release of naphthalene from contaminated soils. Environmental Science & Technology 27, 2397–2403.

Covelo, E.F., Vega, F.A., Andrade, M.L., 2007. Simultaneous sorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn in acid soils II. Soil ranking and influence of soil characteristics. J. Hazard. Mater. 147, 862–870.

Diekkrüger, B., 1996. SIMULAT—Ein Modellsystem zur Berechnung der Wasser- und Stoffdynamik landwirtschaftlich genutzter Standorte. In: Richter, O., Söndgerath, D., Diekkrüger, B. (Eds.), Sonderforschungsbereich vol. 179, Wasser- und Stoffdynamik in Agrarökosystemen. Institut für Geographie und Geoökologie der Technischen Universität Braunschweig, Braunschweig, pp. 30–47.

Drillia, P., Stamateletou, K., Lyberatos, G., 2005. Fate and mobility of pharmaceuticals in solid matrices. Chemosphere 60, 1034–1044.

Elliott, H.A., Liberati, M.R., Huang, C.P., 1986. Competitive adsorption of heavy metals by soils. Journal of Environmental Quality 15, 214–219.

Fetter, C.W., 1993. Contaminant Hydrogeology. Practice Hall, Upper Saddle River, NJ.

Fonseca, B., Figueiredo, H., Rodrigues, J., Queiroz, A., Tavares, T., 2011. Mobility of Cr, Pb, Cd, Cu and Zn in a loamy soil: a comparative study. Geoderma 164, 232–237.

Fontes, M.P.F., Gomes, P.C., 2003. Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils. Applied Geochemistry 18, 795–804.

Gomes, P.C., Fomtes, M.P.F., Silva, A.G.D., Mendonça, E.D.S., Netto, A.R., 2001. Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Science Society of America Journal 65, 1115–1121.

Jain, C.K., Ram, D., 1996. Adsorption of lead and zinc on bed sediments of the river Kali. Water Research 31, 154–162.

Kamra, S.K., Lennartz, B., van Genuchten, M.Th., Widmoser, P., 2001. Evaluating non-equilibrium solute transport in small soil columns. Journal of Contaminant Hydrology 48 (3–4), 189–212.

Kookana, R.S., Naidu, R., Tiller, K.G., 1994. Sorption non-equilibrium during cadmium transport through soils. Australian Journal of Soil Research 32, 635–651.

Lafuente, A.L., González, C., Quintana, J.R., Vázquez, A., Romero, A., 2008. Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region. Geoderma 145, 238–244.

Larsbo, M., Jarvis, N.J., 2003. MACRO 5.0, a Model of Water Flow and Solute Transport in Macroporous Soil. Technical description. Emergo 2003, 6. Swedish Univ. of Agricult. Sci., Dept. of Soil Sci., Uppsala, Sweden. (48 pp.).

Larsbo, M., Jarvis, N.J., 2005. Simulating solute transport in a structured field soil: uncertainty in parameter identification and predictions. Journal of Environmental Quality 34 (2), 621–634.

Liu, C., Chang, T., Wang, M., Huang, C., 2006. Transport of cadmium, nickel, and zinc in Taoyuan red soil using one-dimensional convective–dispersive model. Geoderma 131, 181–189.

Mesquita, M.E., Vierae Silva, J.M., 2002. Preliminary study of pH effect in the application of Langmuir and Freundlich isotherms to Cu–Zn competitive adsorption. Geoderma 106, 219–234.

Miretzky, P., Muñoz, C., Carrillo-Chávez, A., 2006. Experimental Zn(II) retention in a sandy soil by very small columns. Chemosphere 65, 2082–2089.

Pang, L., Close, M., Schneider, D., Stanton, G., 2002. Effect of pore-water velocity on chemical nonequilibrium transport of Cd, Zn, and Pb in alluvial gravel columns. Journal of Contaminant Hydrology 57, 241–258.

Pang, L., Close, M., Greenfield, H., Stanton, G., 2004. Adsorption and transport of cadmium and rhodamine WT in pumice sand columns. New Zealand Journal of Marine and Freshwater Research 38, 367–378.

Rodríguez-maroto, J.M., García-delgado, R.A., Gómez-lahoz, C., Vereda-alonso, C., García-herruzo, F., Muñoz, M.P.P., 2003. Competitive retention of lead and cadmium on an agricultural soil. Environmental Monitoring and Assessment 89, 165–177.

Saha, U.K., Taniguchi, S., Sakurai, K., 2002. Simultaneous adsorption of cadmium, zinc, and lead on hydroxyalumium and hydroxyaluminosilicate-montmorillinite complexes. Soil Science Society of America Journal 66, 1125–1131.

Selim, H.M., 1999. Modeling the kinetics of heavy metals reactivity in soils. In: Selim, H.M. (Ed.).

Seo, Y., Lee, J., 2005. Characterizing preferential flow of nitrate and phosphate in soil using time domain reflectometry. Soil Science 170 (1), 47–54.

Serrano, S., Garrido, F., Campbell, C.G., García-Gonzalez, M.T., 2005. Competitive sorption of cadmium and lead in acid soils of Central Spain. Geoderma 124, 91–104.

Seuntjens, P., Tirez, K., Simůnek, J., van Genuchten, M.Th., Cornelis, C., Geuzens, P., 2001. Aging effects on cadmium transport in undisturbed contaminated sandy soil columns. Journal of Environmental Quality 30, 1040–1050.

Šimunek, J., Sejna, M., van Genuchten, M.Th., 1998. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated porous media. Version 2.0, IGWMC-TPS-70. International Ground Water Modeling Center, Colorado School of Mines, Golden Colorado. (202 pp.).

Šimunek, J., van Genuchten, M.Th, Sejna, M., 2005. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated porous media: Version 3.0 Hydrus-1D Software Series 1. Department of Environmental Sciences, University of California Riverside, Riverside, CA. (270 pp.).

Šimunek, J., Šejna, M., van Genuchten, M.T., 2008. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably saturated media, Version 4 Beta 1. ICGWMC-TPS-70. International Ground Water Modeling Center, Colorado School of Mines, Golden, Colorado.

Sparks, D.L., 1995. Environmental soil chemistry. Academic Press, San Diego, CA.

Strawn, D.G., Sparks, D.L., 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb (II) sorption and desorption in soil. Soil Science Society of America Journal 64, 144–156.

Toride, N., Leij, F.J., van Genuchten, M.T., 1999. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.1. U.S. Salinity Laboratory. Agricultural Research Service US Department of Agriculture, Riverside, California.

Tsang, D.C.W., Lo, I.M., 2006. Competitive Cu and Cd sorption and transport in soils: a combined batch kinetics, column, and sequential extraction study. Environmental Science & Technology 40, 6655–6661.

Vanderborght, J., Gähwiller, P., Flühler, H., 2002. Identification of transport processes in soil cores using fluorescent tracers. Soil Science Society of America Journal 66, 774–787.

Vanderborght, J., Mallants, D., Vanclooster, M., Feyen, J., 1997. Parameter uncertainty in the mobile–immobile solute transport model. Journal of Hydrology 190 (1–2), 75–101.

Wallach, R., Parlange, J.Y., 2000. Applying the boundary layer concept to model transport of dissolved chemicals in preferential flow paths. Water Resources Research 36 (10), 2845–2851.

Yolcubal, I., Akyol, N.H., 2007. Retention and transport of hexavalent chromium in calcareous karst soils. Turkish Journal of Earth Science 16, 363–379.

ORIGINAL PAPER

Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in Ubon Ratchathani province, Thailand

**Pokkate Wongsasuluk · Srilert Chotpantarat ·
Wattasit Siriwong · Mark Robson**

Abstract Most local people in the agricultural areas of Hua-ruea sub-district, Ubon Ratchathani province (Thailand), generally consume shallow groundwater from farm wells. This study aimed to assess the health risk related to heavy metal contamination in that groundwater. Samples were randomly collected from 12 wells twice in each of the rainy and the dry seasons and were analyzed by inductive coupled plasma spectrometry-mass spectrometry (ICP-MS). The concentration of detected metals in each well and the overall mean were below the acceptable groundwater standard limits for As, Cd, Cr, Cu, Hg, Ni and Zn, but Pb levels were higher in four wells with an overall average Pb concentration of 16.66 ± 18.52 µg/l. Exposure questionnaires, completed by face-to-face interviews with 100 local people who drink groundwater from farm wells, were used to evaluate the hazard quotients (HQs) and hazard indices (HIs). The HQs for non-carcinogenic risk for As, Cu, Zn and Pb, with a range of 0.004–2.901, 0.053–54.818, 0.003–6.399 and 0.007–26.80, respectively, and the HI values (range from 0.10 to 88.21) exceeded acceptable limits in 58 % of the wells. The HI results were higher than one for groundwater wells located in intensively cultivated chili fields. The highest cancer risk found was 2.6×10^{-6} for As in well no. 11. This

P. Wongsasuluk
International Postgraduate Programs in Environmental
Management, Graduate School, Chulalongkorn
University, Bangkok 10330, Thailand
e-mail: pokkate_wong@hotmail.com

P. Wongsasuluk · S. Chotpantarat
Center of Excellence on Hazardous Substance
Management (HSM), Chulalongkorn University,
Bangkok 10330, Thailand

S. Chotpantarat (✉)
Department of Geology, Faculty of Science,
Chulalongkorn University, Bangkok 10330, Thailand
e-mail: csrilert@gmail.com

W. Siriwong · M. Robson
Thai Fogarty ITREOH Center, Chulalongkorn University,
Bangkok 10330, Thailand
e-mail: wattasit.s@chula.ac.th

M. Robson
e-mail: robson@aesop.rutgers.edu

W. Siriwong
College of Public Health Science, Chulalongkorn
University, Bangkok 10330, Thailand

M. Robson
New Jersey Agricultural Experiment Station, Rutgers
University, New Brunswick, NJ, USA

M. Robson
School of Environmental and Biological Sciences,
Rutgers University, New Brunswick, NJ, USA

Springer

study suggested that people living in warmer climates are more susceptible to and at greater risk of groundwater contamination because of their increased daily drinking water intake. This may lead to an increased number of cases of non-carcinogenic and carcinogenic health defects among local people exposed to heavy metals by drinking the groundwater.

Introduction

Heavy metal contamination is potentially a significant problem in several community and agricultural areas (Vodela et al. 1997) because agrochemicals, including plant nutrients and fertilizers, can lead to dramatic increases in the concentrations of heavy metals in the water and soil (Rattan et al. 2005). These heavy metals have the potential to reach levels in the soil and then in the surface and groundwater that are adverse to human health (Rashed 2010; Chotpantarat et al. 2011; Chotpantarat and Sutthirat 2011; Taboada-Castro et al. 2012). Heavy metals can initially accumulate above natural levels in agricultural soils over time from the continual application of commercial agrochemicals that contain several potentially toxic heavy metals. Their subsequent migration and availability once leached from agricultural soils is influenced by several factors, such as the water pH, redox potential, and type and quality of the soil. One of the more important environmental issues today is the level of groundwater contamination with heavy metals and metalloids, including arsenic (As) and cadmium (Cd), because of their strong toxicity at even low concentrations (Marcovecchio et al. 2007). These heavy metals and metalloids can be dispersed and accumulated in plants and animals and so taken into and accumulated within higher trophic levels including within the human food chain. In order to quantitatively assess the potential risk, human health risk assessments are used to determine whether exposure to a chemical, at any dose, could cause an increase in the incidence of an adverse effect on human health (Wcislo et al. 2002).

From the past to the present, people living in many agricultural areas have commonly consumed groundwater from shallow groundwater wells (Jaipieam et al. 2009). This is also the case for the residents of the Hua-ruea sub-district, Muang district, Ubon Ratchathani province, in Thailand (Fig. 1). Hua-ruea subdistrict, covering an area of approximately 36 km^2, is an agricultural region with a high density of farms that have used fertilizers for the last 30 years for planting chili and rice. This area has a large percentage of cultivated area and produces various agricultural products, such as rice, cassava, chili and rubber trees (Norkaew et al. 2010). The census population in 2011 was approximately 6,000; most people are farmers whose homes are located on their farm. Their incomes are obtained from hiring out as workers on other farms and/or selling their products, chiefly from chili farming (Taneepanichskul et al. 2010). The residents commonly consume shallow groundwater from wells drilled in the unconfined aquifer on their farms, but they are unaware of the risk of heavy metal contamination in shallow groundwater and the associated adverse health effects. Moreover, most of the shallow groundwater samples in this area have been previously reported to be acidic normally (Srithongdee et al. 2010), under which condition the efficiency of leaching of most species of accumulated heavy metals from the soil through the subsurface environment is increased (Suesat 2010). Furthermore, the As concentrations in groundwater in the central west region of Chaco Province, northern Argentina, where the economy is based on exploitation of agriculture and livestock, were high enough that human health was likely to be adversely affected by drinking the groundwater, so people in this area should be concerned about groundwater contamination levels.

The potential toxicity of contaminants is strongly determined by the composition of the elements involved. The known adverse health effects of heavy metals, such as allergies, hyperpigmentation and induction of cancer caused by As and Cd, for example, result from their absorption in the gastrointestinal system. Once absorbed, they target the liver, placenta, kidneys, lungs, brain and bones (PCD 2000). Longterm ingestion of low As concentrations in drinking water can lead to bladder, lung and prostate cancer (Carlson-Lynch et al. 1994; Mushak and Crocetti 1995; Nakadaira et al. 2000). Evaluation of the effects of nickel (Ni) on normal rat kidney cells revealed that Ni induced oxidative stress, DNA strand breaks and apoptosis even at concentrations as low as 10 μM (Chang-Yu et al. 2010). Furthermore, investigation into the effect of frequent exposure to heavy metals at
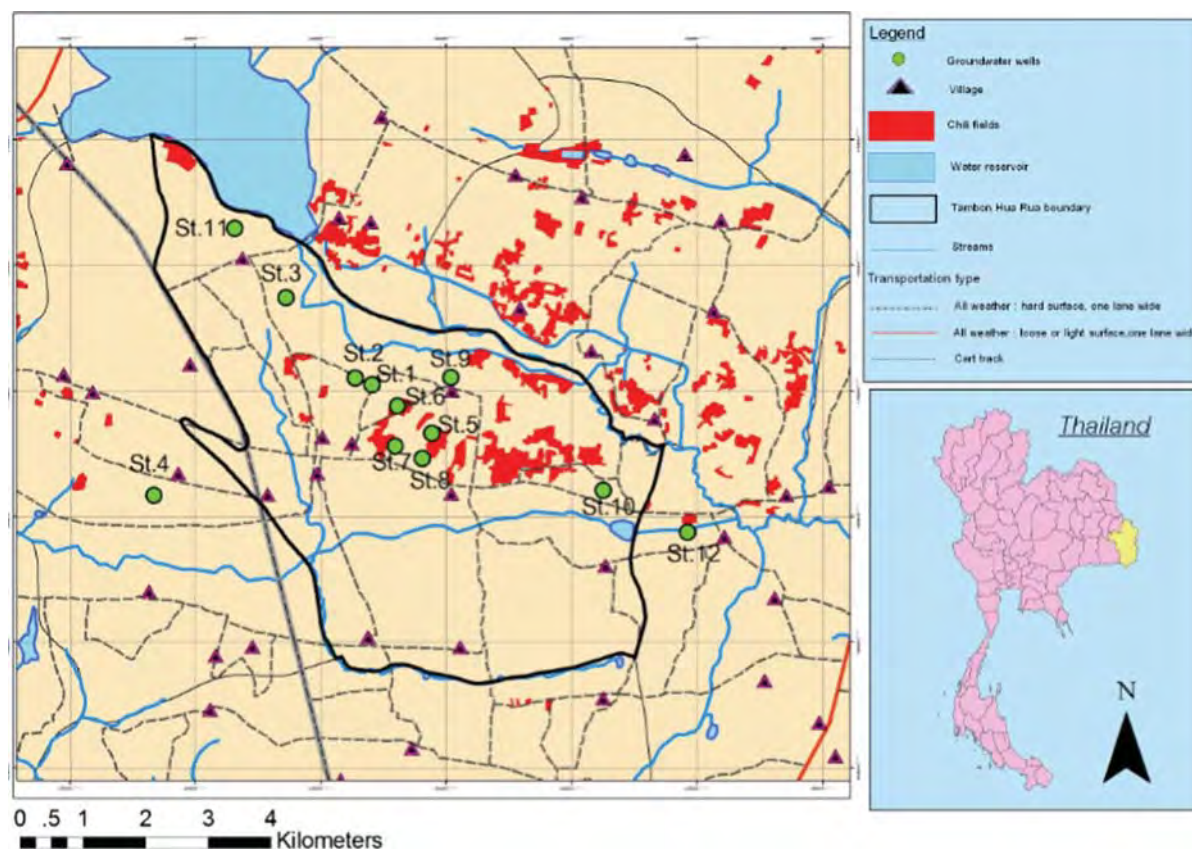
Fig. 1 The study area in Muang district, Ubonratchathani province, Thailand, showing the location of the 12 sampled water wells (stations; ST1–ST12)

low concentrations via intake of traditional medicine in Korea suggested that the daily intake or exposure to lead (Pb) and cadmium via oriental medicine might have effects to human health (Kim et al. 2009).

Therefore, investigation of the contamination levels and dispersion patterns of heavy metals in shallow groundwater around agricultural areas in the Hua-ruea sub-district, Muang district, Ubon Ratchathani province, Thailand, is needed to assess non-carcinogenic and carcinogenic health risks for the residents exposed to such heavy metals through groundwater drinking pathways.

Materials and methods

Study site

Hua-ruea sub-district, located in Muang district, Ubon Ratchathani province in northeastern Thailand, covers

36 km^2 (Fig. 1), and the land use in most areas is agricultural. The census population in 2011 was approximately 6,000.

Sampling and analytical methods

Water was collected from 12 shallow groundwater wells located in unconfined aquifers and distributed in the vicinity of agricultural land use in the study area (Fig. 1). The wells were sampled four times a year, twice each in the rainy and dry seasons, to check for variability in the heavy metal concentrations. Groundwater sampling was performed in June and August 2010 for the rainy season, and in November 2010 and January 2011 for the dry season.

Shallow groundwater samples were collected 10–15 m below the ground surface. The initial 5–10 min of pumped water was discarded, and thereafter samples were collected in thoroughly rinsed polyethylene bottles. The pH and electrical

conductivity (EC) of the freshly collected non-filtered samples were measured in situ using a pH and EC meter, respectively. For each sample, one part was acidified with 65 % (v/v) HNO_3 to pH <2 to dissolve all the heavy metals and to prevent crystallization or precipitation and adsorption of trace metals to the container surfaces prior to analysis. All water samples were then kept at 4 °C in sealed containers (to prevent evaporation) and transported back to the laboratory prior to analyzing the concentrations of As, Cd, chromium (Cr), copper (Cu), Pb, mercury (Hg), Ni and Zinc (Zn) by inductively coupled plasma spectrometry-mass spectrometry (ICP-MS) (Perkin-Elmer SCIEX, ELAN 6000). Heavy metals were selected for toxicological evaluation if they were detected in most of the groundwater samples in the preliminary survey.

Analytical performance

The calibration graph, using the mixed standards of metal ions, was obtained from a total heavy metal concentration of 0.1, 0.5, 1.0, 2.5, 5 and 10 μg/l by ICP-MS. Correlation coefficients of the obtained standard curves were greater than 0.99. The field blanks were prepared in the field under the same conditions as field samples and were sent with test groundwater samples for analysis. Quality control, in terms of inter- and intra-observer variation, was controlled by using the same standard laboratory (Department of Chemical, Faculty of Science, Mahidol University) to analyze the heavy metal residues; the samples were analyzed by a single researcher. The laboratory has been assessed and accredited for this analytical chemical technique according to the AOAC Peer-Verified Methods Program's recommendation (1998). The limits of detection (LODs), defined as the lowest concentration level that can be determined to be statistically different from a blank (99 % confidence), of each heavy metal ion during the rainy and dry seasons were As (0.22 and 0.17 μg/l), Cd (0.13 and 0.18 μg/l), Cr (0.14 and 0.44 μg/l), Cu (0.70 and 0.09 μg/l), Hg (0.05 and 0.07 μg/l), Pb (0.80 and 0.65 μg/l), Ni (0.14 and 0.38 μg/l) and Zn (4.3 and 1.7 μg/l), respectively.

Questionnaires

This study focused on the local people who consume shallow groundwater in Hua-ruea sub-district, Muang district, Ubon Ratchathani province. A preliminary investigation identified residents who principally drink water from groundwater wells in the study area and so excluded those who drink water from other sources, such as tap or bottled water. In addition, residents younger than 15 years were excluded since they typically drink bottled or tap water at school. From this preselected set of residents, 100 were randomly chosen; an even distribution of participants across the study area was ensured. Face-to-face interviews were then carried out with these 100 participants from August 2010 to January 2011. They were then asked to complete the questionnaires. The age range was 15 to 90 years.

The interview questionnaire study consisted of two parts. The first part ascertained the general information and personal background of the participants, such as their name, age, body weight, gender, education level and occupation. The second part focused on their groundwater consumption behavior, such as intake rate, frequency and quantity of consumption.

Risk assessment

The obtained exposure data were summarized using simple descriptive statistics including range, average and standard deviation. Risk assessment is a function of the hazard and exposure and is defined as the processes of estimating the probability of occurrence of any given probable magnitude of adverse health effects over a specified time period. The health risk assessment of each potentially toxic metal is usually based on the quantification of the risk level and is expressed in terms of a carcinogenic or a non-carcinogenic health risk. The two principal toxicity risk factors evaluated are the slope factor (SF) for carcinogen risk characterization and the reference dose (RfD) for non-carcinogen risk characterization (Lim et al. 2008). The toxicity indices of each potentially toxic metal are shown in Table 1 (USEPA IRIS 2011). The estimations of the magnitude, frequency and duration of human exposure to each potentially toxic metal in the environment are typically reported as average daily dose (ADD) (USEPA 1992; Siriwong 2006), as shown in Eq. (1);

$$ADD = (C \times IR \times EF \times ED)/(BW \times AT), \qquad (1)$$

where ADD is the exposure duration (mg/kg-day), C is the concentration (mg/l), IR is the intake rate (l/day),

Table 1 The toxicity responses (dose response) to heavy metals as the oral reference dose (RfD) and oral slope factor (SF) (USEPA IRIS 2011)

Heavy metals	Oral RfD (mg/kg/day)	Oral SF (mg/kg-day)$^{-1}$
As	3×10^{-4}	1.50
Cd	5.0×10^{-4}	n.d.
Cr	3.0×10^{-3}	n.d.
Cu	4×10^{-2}	n.d.
Hg	3.0×10^{-4}	n.d.
Pb	3.5×10^{-3}	n.d.
Ni	2.0×10^{-2}	n.d.
Zn	0.3	n.d.

n.d. = not determined

EF is the exposure frequency (day/year), ED is the exposure duration (year), BW is the body weight (kg), and AT is the average time (day).

The input parameters in ADD formulas are shown in Table 2.

Risk characterization is the final step of health risk assessment. The health risk from groundwater consumption was assessed in relation to its chronic (non-carcinogenic) as well as carcinogenic effects, based on the calculation of ADD estimates and defined toxicity values for each potentially toxic metal according to the following relationships. The non-carcinogen risk was calculated as the hazard quotient (HQ), as shown in Eq. (2);

$$HQ = ADD/RfD, \tag{2}$$

where ADD and RfD are in mg/kg-day.

Table 2 Input parameters to characterize the ADD value (exposure parameters)

Exposure parameters	Description	Unit	Value
C	Contamination concentration in groundwater	mg/l	
IR	Ingestion rate per unit time	l/day	3.45 ± 2.0
EF	Exposure frequency	Days/year	365
ED	Exposure duration	Years	42
BW	Body weight	Kg	60 ± 12
AT	Average time	Days	25,550 days (70 years)

If the value of HQ exceeds 1, there is an unacceptable risk of adverse non-carcinogenic effects on health, while if the HQ is less than 1, it is at an acceptable level (USEPA 2001). For the risk assessment of a mixture of chemicals, the individual HQs are combined to form the hazard index (HI), where an HI >1 means an unacceptable risk of non-carcinogenic effects on health, while HI <1 means an acceptable level of risk (ECETOC 2001).

The carcinogenic risk can be calculated as the product of ADD (mg/kg-day) times the SF (mg/kg/day). An acceptable level is $\leq 1 \times 10^{-6}$, which means on average the probability is that approximately 1 person per 1,000,000 will develop cancer as a consequence of the exposure (Lim et al. 2008), while values $\leq 1 \times 10^{-6}$ are acceptable risk levels.

Results

Face-to-face interviews

For the calculation of the human health risk assessment, face-to-face interviews were conducted with 100 randomly selected people from a preselected local set of inhabitants who drink water from groundwater wells in the study area (see "Materials and methods" section). The participants represented only local residents who consume groundwater from farm wells and excluded those who consume drinking water from other sources, including tap water. Participants were distributed evenly over the study area. Questionnaires were used to collect personal information and evaluate the daily rate of groundwater consumption. The data and exposure parameters from the questionnaires are summarized as follows.

The group comprised 55 females and 45 males with an average age of 42 ± 16 (mean $\pm$ SD) years (41 ± 17 years for males and 43 ± 14 years for females). The average weight of participants was 60 ± 12 kg (range of 30–94 kg). The level of most participants was the elementary school level or below (61 %), with only a few having graduated at the level of a diploma (2 %) or bachelor's degree (2 %). In addition, most of the participants were farmers ($\sim$80 %). The average groundwater consumption of the hundred surveyed people was high at 3.45 ± 2.0 l/day/person. For calculation of the risk assessment, the average groundwater consumption rate was taken as

3.45 l/day. The 95 percentile calculation was excluded in this study because very few participants drink approximately 10 l/day. Although the normal standard consumption rate of adult people ranged from 1.5 to 2.0 l/day/person (USEPA 1980), the local people in this study drank considerably more (on average 1.7- to 2.3-fold more). This is because they work on their farm from sunrise to sunset in very hot weather during the day.

Properties of shallow groundwater and wells

(1) pH

The pH of the shallow groundwater varied slightly within each well (except at station 11, which varied a lot) and ranged across the 12 wells from 3.69 to 7.90 with an average pH of 4.72 $\pm$ 1.00 (mean $\pm$ SD). The greater pH variability (from pH 6.59 to 7.90) at station (well) 11 might be caused by seasonal contamination (Patriquin et al. 1993).

(2) Groundwater level

With respect to the groundwater levels of the 12 shallow groundwater wells, they varied from 112.1 to 132.6 m above mean sea level (amsl) with an average groundwater level of 124.6 $\pm$ 5.2 m amsl. The direction of flow of the groundwater in this area was from the reservoir in the north to the south and southeastern parts (Fig. 1). The depth from the ground surface to the groundwater level (well depth) ranged from 2.04 to 4.38 m (average 2.85 $\pm$ 0.79 m) across the year.

(3) Conductivity

The EC is used to estimate the amount of dissolved minerals. In the study, the EC of the shallow groundwater at each of the 12 sites was more variable, ranging from 58.9 to 1,162.3 μS/cm (average 232.4 $\pm$ 39.4 μS/cm), although excluding the highest EC of well no. 11, the range of the remaining 11 wells was lower at 58.9–276.5 μS/cm (average 147.9 $\pm$ 24.7 μS/cm) and the lowest from well no. 9.

(4) Concentration of heavy metals

The total concentrations of potentially toxic metals in groundwater are presented in Table 3 along with the drinking groundwater standards of the US Environmental Protection Agency (USEPA 2012), World Health Organization (WHO 2011) and the Pollution Control Department (PCD 2000, 2004). The annual average concentration of As for the whole year from 12 wells in the shallow groundwater ranged from 0.25 $\pm$ 0.11 to 6.44 $\pm$ 3.17 μg/l (mean $\pm$ SD derived from four measurements in each well, two each in the rainy and dry seasons) with an average concentration of 1.06 $\pm$ 1.74 μg/l, although well no. 11 had a 5.23- to 34.72-fold higher As concentration (8.68 $\pm$ 0.42 μg/l in the rainy season (not shown in Table 3) than all the other wells. Thus, the range for the other 11 wells excluding well no. 11 was considerably lower at 0.25–1.66 μg/l with an average concentration (mean $\pm$ SD) of 0.57 $\pm$ 0.42 μg/l (Table 3; Fig. 2a). Average concentrations of As appeared higher during the rainy season (1.52 $\pm$ 2.37 μg/l) than during the dry season (0.60 $\pm$ 1.14 μg/l), suggesting that As might be desorbed and leached from contaminated soils into shallow groundwater (Buchhamer et al. 2012). All 12 wells at this site had AS levels lower than the acceptable limit according to drinking water standards (USEPA 2012; PCD 2000; WHO 2011).

The concentrations of Pb in the shallow groundwater ranged from 0.95 $\pm$ 0.42 to 66.85 $\pm$ 36.35 μg/l with an average concentration (mean $\pm$ SD) of 16.66 $\pm$ 18.52 μg/l. The highest concentration of Pb (92.55 $\pm$ 26.09 μg/l) in the rainy season (not shown in Table 3) was observed in well no. 7, which is situated in an area of intensive agricultural activity (Table 3; Fig. 2b). This is higher than the permissible standards for drinking water (USEPA 2012; PCD 2000; WHO 2011). The average concentration of Pb during the rainy season and dry season was 18.6 $\pm$ 25.4 and 14.7 $\pm$ 4.4 μg/l, respectively. The concentrations of Cd, Cr, Cu, Hg, Ni and Zn in the 12 shallow groundwater sites in this study area were lower than all the drinking water standards and so according to these criteria were acceptable (Table 3).

Human health risk assessment

As mentioned above, the concentrations of Cd, Cr, Cu, Hg, Ni and Zn in the 12 shallow groundwater sites in this study area were lower than all the drinking water standards and so were acceptable (Table 3). Accordingly, the human health risk assessment of Cd, Cr, Cu, Hg and Ni showed HQ values suggesting an acceptable level of non-carcinogenic adverse health risk (Table 4). This is consistent with the absence of any reports of a significant non-carcinogenic risk from

Table 3 The average annual concentration of heavy metals (µg/L) in the water from shallow groundwater wells located in the vicinity of agricultural areas at Hua-ruea sub-district, Muang District, Ubon Ratchathani Province, Thailand

Heavy metal concentrations (µg/L) in each well (station number)[a]

Metals	1	2	3	4	5	6	7	8
As	0.69 ± 0.16	0.43 ± 0.36	0.56 ± 0.33	0.30 ± 0.19	0.25 ± 0.11	0.89 ± 0.36	0.59 ± 0.59	1.66 ± 1.98
Cd	0.14 ± 0.01	0.18 ± 0.06	0.14 ± 0.01	0.13 ± 0.00	0.15 ± 0.02	0.21 ± 0.06	0.23 ± 0.12	0.13 ± 0.00
Cr	0.48 ± 0.05	0.30 ± 0.21	2.14 ± 2.40	0.29 ± 0.21	0.30 ± 0.21	0.35 ± 0.13	0.35 ± 0.13	0.69 ± 0.35
Cu	76.1 ± 87.3	33.7 ± 23.5	11.6 ± 0.8	18.7 ± 9.7	10.0 ± 1.2	35.8 ± 12.6	323 ± 384	140 ± 9
Pb	23.1 ± 1.7	11.3 ± 2.5	8.26 ± 1.75	7.74 ± 1.76	9.56 ± 2.47	28.1 ± 5.6	66.9 ± 36.4	28.1 ± 4.4
Hg	0.51 ± 0.64	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01
Ni	7.46 ± 2.02	4.48 ± 0.35	6.22 ± 0.10	5.72 ± 0.11	4.38 ± 1.60	15.6 ± 4.6	12.7 ± 0.1	4.75 ± 0.67
Zn	66.6 ± 27.3	43.5 ± 18.1	20.1 ± 1.0	18.9 ± 5.6	16.0 ± 8.5	51.9 ± 1.4	302 ± 293	173 ± 81

	Heavy metal concentrations (µg/L) in each well (station number)[a]					Drinking groundwater standard (µg/L)		
Metals	9	10	11	12	Average ± SD	USEPA (2012)	PCD (2000)	WHO (2011)
As	0.28 ± 0.16	0.27 ± 0.13	6.44 ± 3.17	0.36 ± 0.28	1.06 ± 1.74	10	10	10
Cd	0.13 ± 0.00	0.13 ± 0.00	0.13 ± 0.00	0.13 ± 0.00	0.15 ± 0.03	5	3	3
Cr	0.35 ± 0.13	0.29 ± 0.21	0.61 ± 0.24	0.79 ± 0.49	0.58 ± 0.52	100	50	50
Cu	12.2 ± 15.9	32.4 ± 17.1	14.9 ± 1.8	13.8 ± 3.5	60.3 ± 91.0	1,300	1,000	2,000
Pb	0.95 ± 0.42	12.8 ± 1.0	2.06 ± 0.82	1.05 ± 0.33	16.7 ± 18.5	15	10	10
Hg	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.10 ± 0.13	2	1	6
Ni	2.57 ± 1.85	7.71 ± 1.92	0.65 ± 0.37	1.34 ± 0.43	6.13 ± 4.38	Not mentioned	20	70
Zn	6.94 ± 5.73	31.9 ± 2.6	17.5 ± 6.6	12.4 ± 2.3	63.4 ± 87.8	5,000	5,000	Not mentioned

[a] For locations of each water well (Station) see Fig. 1. Data are shown as the mean ± 1 SD for 1 year and are derived from four readings, two each in the rainy and dry seasons

these heavy metals by oral exposure, with the reported risks coming from exposure via inhalation. However, in contrast, note that Cu showed HQ values indicating an unacceptable non-carcinogenic health risk at three wells (see below) despite being at acceptable water levels at these wells.

However, unacceptable HQs were found for Pb, Zn and As at some of the wells. Four sites (sites 1, 6, 7 and 8) had an unacceptable non-carcinogenic health risk level for Pb (HQs of 3.20, 4.74, 26.80 and 4.74, respectively), although the other eight sites had no significant non-carcinogenic health risk from Pb, with HQ values ranging from 0.007 to 0.99 (Table 4; Fig. 3). For Cu, the HQ values at wells 1, 7 and 8 were also at unacceptable levels at 3.041, 54.818, and 6.399, respectively (Table 4). For Zn, although ten of the sites had no significant non-carcinogenic health risk with HQ values ranging from 0.003 to 0.310, two sites (sites 7 and 8) had unacceptable non-carcinogenic health risk levels with HQ values of 2.097 and 6.399, respectively. The highest obtained HQ values for Cu,

Pb and Zn were from a well that was situated in an area of intensive agricultural use (no. 7). In addition, As presented unacceptable health risk levels for both non-carcinogenic and carcinogenic risks. For the non-carcinogenic risk, the HQ value of As ranged from 0.004 to 0.193 at 11 of the 12 wells, but at one (no. 11) had an HQ value of 2.901 (Table 4), representing an unacceptable health risk (Table 4; Fig. 4a). Furthermore, the cancer risk was acceptable for all wells except for no. 11 (Fig. 4b), where three people in a million might develop cancer (cancer risk = 2.6×10^{-6}).

The distribution of the non-carcinogenic risk relates to the high concentrations of Cu, Zn and Pb, which were relatively high at the center of the study area in a region with higher intensity chili farming than in the surrounding areas.

The human health risk assessment of As was higher than the acceptable level, although the concentration of As in the shallow groundwater was lower than the groundwater drinking standard. Likewise, the same
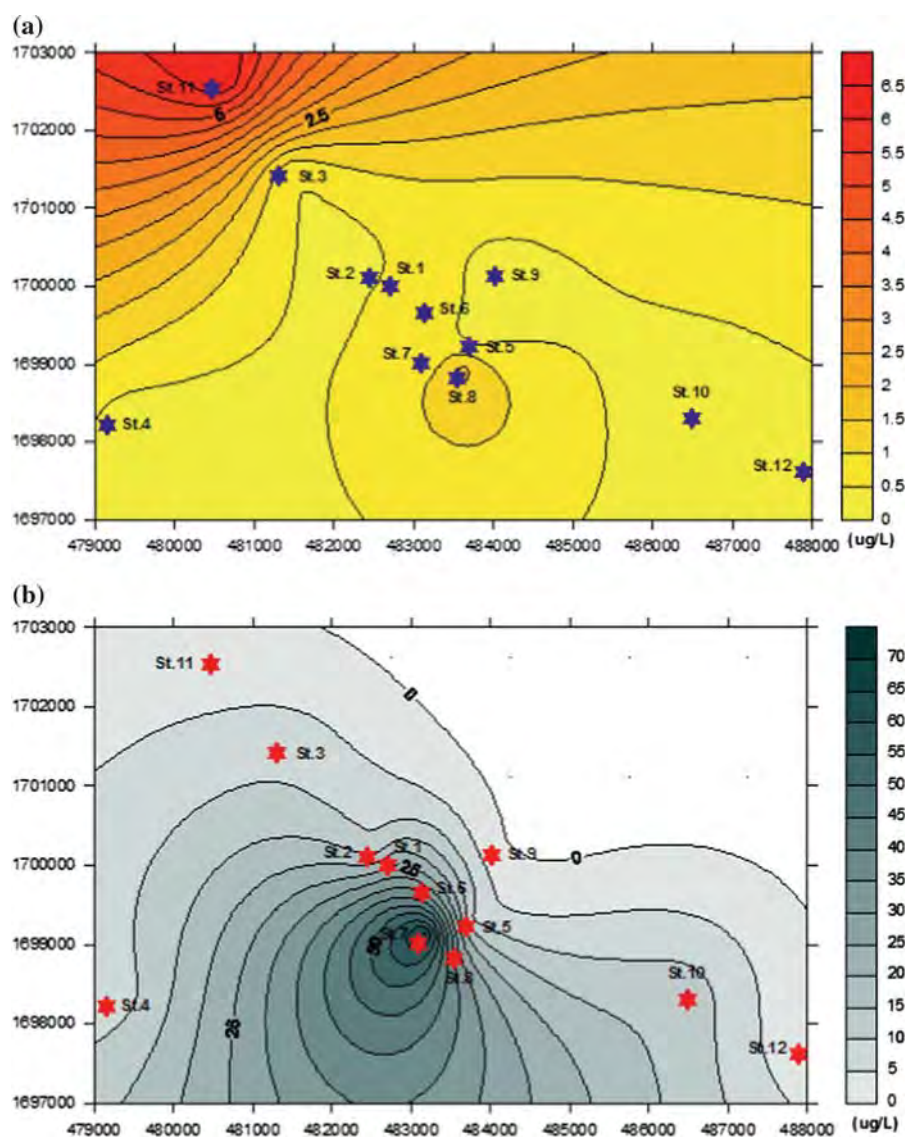
Fig. 2 Distribution map of the average (**a**) As and (**b**) Pb concentrations (µg/l) over the dry and rainy seasons and the locations of the 12 drinking water wells (ST1–ST12)

pattern was seen for Zn, in that unacceptable non-cancer health risks were observed at two sites where the Zn concentration in the water was within the acceptable limit (Table 4). Although a low intake level of Zn is required by humans and Zn is of relatively low toxicity compared with other heavy metals, a high intake rate of Zn causes both acute (such as stomach cramps, nausea and vomiting) and chronic (such as anemia and pancreas damage) adverse health effects (Natural Healing Site 2010). In addition, the human health risk characterization of Pb at four sites

was higher than the acceptable level, but conforms to the observation that the concentrations at these sites were higher than the drinking water standard (Fig. 3).

According to the HQ values, the HI of all the heavy metal ions (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) ranged from 0.10 to 88.21 and the HI of wells 1, 2, 6, 7, 8 10 and 11 were higher than 1 (HI = 6.66, 1.52, 5.92, 88.21, 17.41, 1.68 and 3.07, respectively) for the non-carcinogenic adverse health effects. Therefore, if we take into consideration the additive effect of potentially toxic metals, then the oral HI results raise

Table 4 Non-carcinogenic risk (hazard quotient, HQ) of heavy metals in shallow groundwater from the 12 wells (stations) at Hua-ruea sub-district, Muang District, Ubon Ratchathani Province, Thailand

Metals	Non-cancer health risk (HQ) from heavy metals in the water at each shallow groundwater site (station number)[a]											
	1	2	3	4	5	6	7	8	9	10	11	12
As	0.033	0.013	0.22	0.006	0.004	0.055	0.024	0.193	0.005	0.005	**2.901**	0.009
Cd	1.00E-03	1.00E-03	1.00E-03	1.00E-03	1.00E-03	2.00E-03	2.00E-03	1.00E-03	1.00E-03	1.00E-03	1.00E-03	1.00E-03
Cr	2.00E-03	1.00E-03	3.20E-02	1.00E-03	1.00E-03	1.00E-03	1.00E-03	3.00E-03	1.00E-03	1.00E-03	3.00E-03	4.00E-03
Cu	**3.041**	0.595	0.071	0.184	0.053	0.674	**54.818**	**10.355**	0.078	0.552	0.117	0.100
Pb	**3.20**	0.76	0.409	0.359	0.548	**4.74**	**26.80**	**4.74**	0.054	0.99	0.025	0.007
Hg	1.80E-02	3.00E-04	3.00E-04	3.00E-04	3.00E-04	3.00E-04	3.00E-04	3.00E-04	3.00E-04	3.00E-04	3.00E-04	3.00E-04
Ni	5.80E-02	2.10E-02	4.10E-02	3.40E-02	2.00E-02	0.26	0.17	2.40E-02	6.90E-03	6.20E-02	4.40E-04	1.90E-03
Zn	0.310	0.132	0.028	0.025	0.018	0.188	**6.40**	**2.10**	0.003	0.071	0.021	0.011

[a] For locations of each well, (Station) see Fig. 1. Bold type indicates above the acceptable risk level

concern about the non-carcinogenic adverse health effects of drinking groundwater in this area.

Discussion

Properties of shallow groundwater and wells

The groundwater pH found in this study agrees with the results of Srithongdee et al. (2010) who previously reported that the pH of water from ten shallow groundwater wells in this area ranged from 3.68 to 4.88, which is too acidic for drinking, and that increasing water acidity was positively correlated with increasing nitrate concentrations. Although this acidification of the water is consistent with the long-term application of high levels of fertilizers, as reported in another study by Jeyaruba and Thushyan-thy (2009), Srithongdee et al. (2010) reported that the pesticide concentrations in the groundwater were generally less than the LOD. Eriksson (1990) and Patriquin et al. (1993) found that the application of ammoniacal fertilizers may cause the acidification of soil since nitrate is formed from them by microbial nitrification. As such, the low pH of groundwater in this area may have resulted from the heavy and continuous application of fertilizers over a long period.

The water level varied only slightly between the seasons and sites across the 12 sites, and this variation when present was likely to be due to the occurrence of a tropical storm in October–November 2010. Sri-thongdee et al. (2010) reported that increasing nitrate concentrations were positively correlated with increasing electrical conductivity (EC). The EC at each site reflects the level of dissolved chemicals (especially salts) in the groundwater in this area. Thus, the higher the EC, the higher the levels of dissolved chemicals in the groundwater sample.

The concentration of other metals during the rainy season was not much higher than those during the dry season, which might reflect their release into the pore water and percolation into the shallow groundwater. Furthermore, Suesat (2010) investigated fractionation of four heavy metals (i.e., As, Cu, Pb and Zn) in soils in this agricultural area and found that the sum of As, Cu, Pb and Zn associated with the first fraction (the exchangeable fraction) ranged from 0.07 to 0.33 mg/kg (corresponding to 4–10 % of the total As level),

Fig. 3 Non-carcinogenic risk map for lead (Pb) at the study area and the locations of the 12 drinking water wells (ST1–ST12)
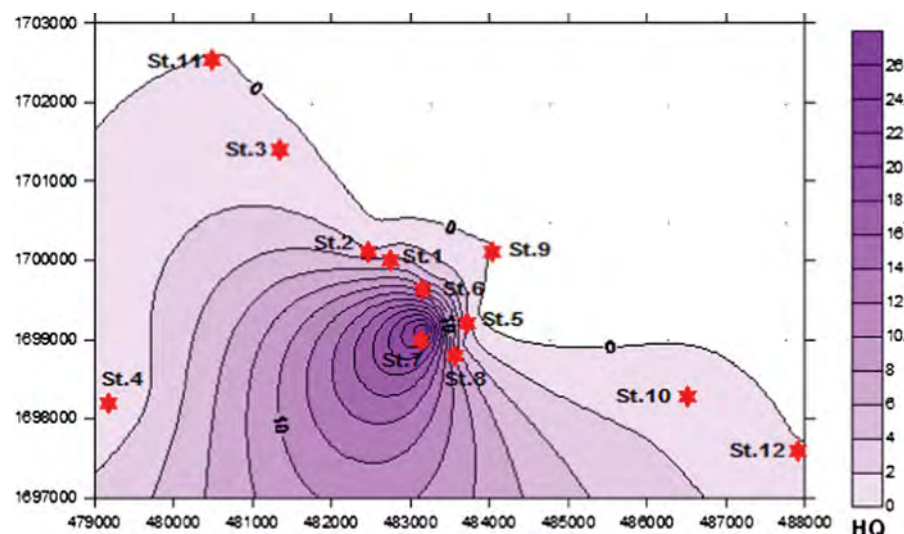

4.39–11.75 mg/kg (corresponding to 18–50 % of the total Cu level), 0.11–0.28 mg/kg (corresponding to 1.3–5 % of the total Pb level) and 70.66–110.20 mg/kg (corresponding to 55–74 % of the total Zn level), respectively. These findings indicated that the elevated Cu and Zn levels in this fraction may be caused by anthropogenic inputs, which are relatively weakly bound forms, including the adsorptive and exchangeable, and those bound to carbonates. This consequently increases their migration and bioavailability in soils and the subsurface environment (Gibbs 1977). The Cu and Zn levels associated with the exchangeable fraction were quite high and extremely important since they showed the mobility potential of metals that can easily migrate through ion-exchange processes (Filgueiras et al. 2002). Moreover, more than 50 % of the amounts of these four metals was associated with the first three fractions (exchangeable, carbonate and reducible), which are easily released following changes in environmental conditions, such as the redox potential, ionic strength, pH, salinity, etc. The metal concentrations of each fraction were in accord with those in the shallow groundwater.

The much higher concentration of As at well station 11 than in the other wells in this study correlates with the alkaline pH value of the shallow groundwater. Moreover, the previously reported highly positive significant correlation between the As concentration and pH ($r = 0.942$, $n = 48$) during the wet season (Wongsasuluk 2010) suggests that As

might be released into pore water by desorption processes that are increased by alkaline pH (Buchhamer et al. 2012). This result is in accord with the study of Takeno (2005) who reported that As in the form of H_2AsO_3 would dissolve in water at a high pH value, and so the pH of the water affects the As concentration. In addition, Claesson and Fagerberg (2003) reported that as the pH of the groundwater at Santiago del Estero in Argentina increased (pH 6.4–9.3), so did the As concentrations. In aquatic systems, inorganic As is primarily present in two oxidation states, arsenate (As^{5+}) and arsenite (As^{3+}) (ATSDR 2000). Although both forms generally occur together, As^{5+} predominates under oxidizing conditions, and As^{3+} predominates under reducing conditions (Stumm and Morgan 1996). All the wells in this area are normally under oxidizing conditions because they are located in an unconfined aquifer, which is directly exposed to the atmosphere, and this is especially true for well 11 because it is located in the recharge area. Thus, the higher pH of the water in well 11 (range from pH 6.59–7.90 in the rainy season and from pH 6.34–7.25 in the dry season compared to pH 3.83–5.85 for the other 11 wells) combined with the oxidizing environment and alkaline pH would tend more to releasing As into the groundwater.

In addition, Nassef et al. (2006) reported that Pb levels in the groundwater of agricultural areas at Sadat were higher than the drinking water standard, ranging between 0.11 and 24.9 µg/l (average of 3.31 µg/l),

Fig. 4 **a** Non-carcinogenic and **b** carcinogenic risk map of arsenic (As) at the study area and the locations of the 12 drinking water wells (ST1–ST12)
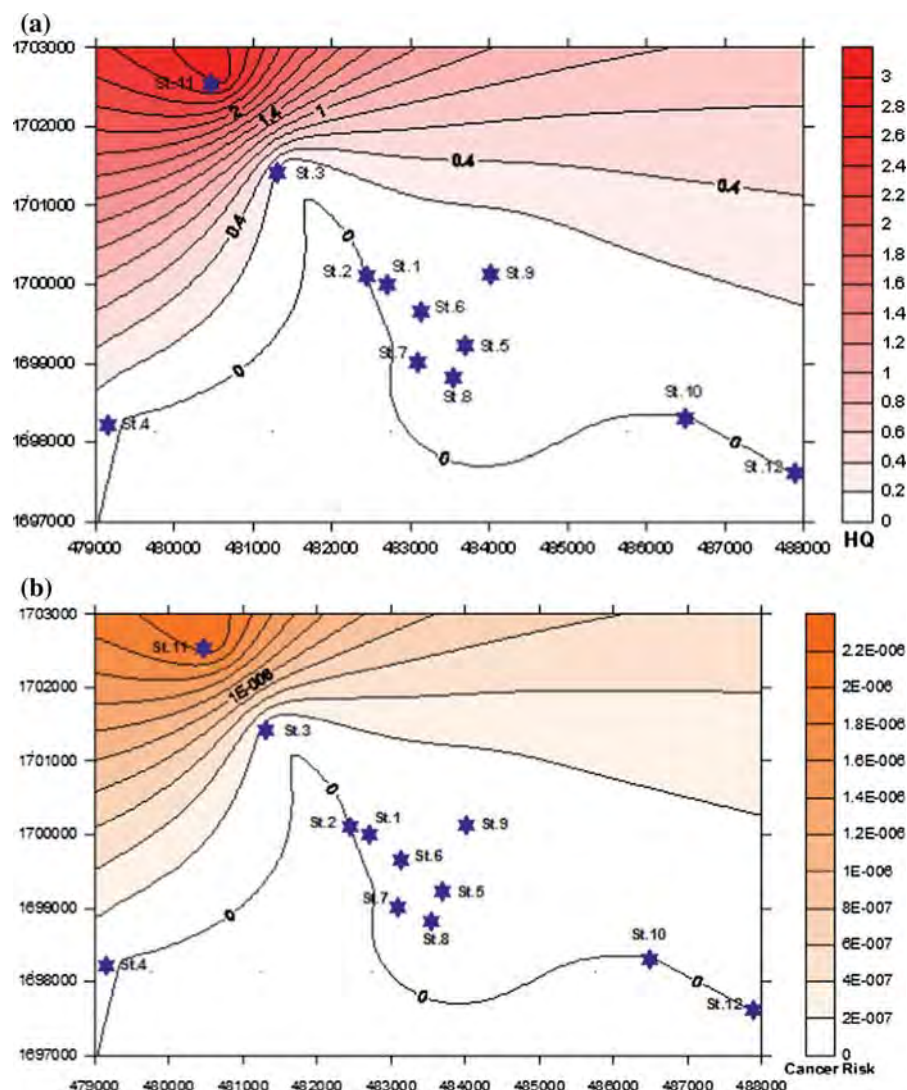
whereas those in a residential area ranged from 0.38 to 0.82 µg/l (average of 0.56 µg/l). Thus, the higher amount of Pb in agricultural areas may well originate from agricultural activities. Moreover, the heavy metal pollution levels in paddy fields in Wenling City, China, were reported to show that the accumulation of Cd, Cu, Pb, Ni and Zn was due to agricultural chemicals causing Cd, Cu, Pb, Ni, and Zn contamination in the paddy fields. In particular, high concentrations of Cd, Cu, Pb and Zn in some areas may be due to industrialization and agriculture development (Keli Zhao et al. 2010).

In this study, the concentrations of each heavy metal had a similar pattern in that a higher concentration was found in the central, intensively agricultural areas.

Moreover, the distribution of heavy metals in the groundwater in this study site conformed to the groundwater hydraulic gradient (hydraulic gradient = Δgroundwater level/Δdistance between wells). This is lower in the middle of the study area, indicating that the flow of groundwater in the middle was low compared to that of the adjacent areas. Dilution in aquifers can be described by the volumetric flow rate per unit perpendicular to the groundwater flow related to the hydraulic gradient. As a result, by dilution, the heavy metal concentrations in the water at wells located in the central area would be higher than those in the wells in the surrounding areas (Debernardi et al. 2008).

Evaluation of the heavy metals in drinking groundwater in Dakahlyia Governorate, Egypt, in areas that

were mainly used for agriculture found that the incorrect overuseage of large amounts of phosphate fertilizers might have led to the relatively high concentrations of Cd and Ni in the groundwater (Mandour and Azab 2011). Excess fertilizer that is not used by the plants then percolates into the soil with the irrigation water. Consequently, they reach the groundwater wherever the permeability of the soil permits.

Human health risk assessment

Within Slovakia, Rapant and Krcmová (2007) reported that the cancer risk caused by As in groundwater reached as high as $>10^{-4}$, or more than 100 people in a million. Saipan and Ruangwises (2009) showed that the population of Ronphibun, Thailand, might experience adverse health impacts since the cancinogenic risk and non-carcinogenic health risk indices were ascertained to be 1.26×10^{-3} and 6.98, respectively.

In addition, the local people living in the study area of this report, which is located in a tropical zone, generally had to work on their farms under relatively high temperatures and humidity with strong sunlight exposure; consequently, their physical requirement for water was quite high. They drank water at an average rate of 3.45 ± 2.0 l/day compared to the usual average of 2 l/day (USEPA 1980). People in countries with colder weather than in Thailand would be expected to have a lower water intake rate, such as the 1.5 l/day average level reported in Korea (Lim et al. 2008). Thus, the human health risk assessment depends not only on the heavy metal concentration in the water, but also on the water consumption rate. In accordance, Peplow and Edmonds (2004) found that the average risk of cancer from exposure to As from abandoned mines was approximately twofold higher for adults engaged in occupations with high sunlight exposure. Pokkamthanam et al. (2011) found that As in water consumed by Bandlaguda adults may cause both adverse non-carcinogenic and carcinogenic health risks because the mean water consumption is quite high (4.5 ± 2.4 l/day) because of the physically demanding work and the water requirements caused by participants' occupations, such as factory workers, laborers, welders, carpenters and farmers. Therefore, farmers in tropical countries should be made more aware of heavy metals contamination, even at low concentrations, because of their high intake rate.

Conclusions

This study evaluated the human health risk from heavy metals in the drinking water from 12 shallow groundwater wells in Hua-ruea sub-district, Muang district, Ubon Ratchathani province, Thailand. The concentrations of Cd, Cr, Cu, Hg, Ni and Zn in the 12 shallow groundwater sites in this study area were lower than all the drinking water standards and so according to these criteria were acceptable. However, the average concentrations of Pb were all higher than allowed according to the drinking water standard. In addition, As concentrations in one well (no. 11) had a 5.23- to 34.72-fold higher As concentration than all the other wells.

Unacceptable non-cancer health risk levels were found at 1, 3, 2 and 4 of the 12 tested wells for As, Cu, Zn and Pb, respectively, but not for the other heavy metals; an unacceptable cancer risk was found at one site for As (station 11). However, these heavy metal concentrations in the groundwater were within acceptable limits, revealing the importance of the actual consumption rates in estimating health risk factors. Furthermore, the HIs of groundwater at wells 1, 2, 6, 7, 8, 10 and 11 were higher than 1 for adverse non-carcinogenic health effects. These wells are all located in intensively cultivated chili fields.

The results of this study can be used beneficially and applied to managing and communicating about risk with the local people who generally drink shallow groundwater as well as to preventing adverse health risks from groundwater contamination. Local people drinking from groundwater wells, especially in intensively cultivated chili fields, should be educated about the potential adverse effects of drinking directly from shallow groundwater wells. In order to reduce the estimated carcinogenic risk and non-carcinogenic HQs, they should be advised to treat their water or find alternative sources for drinking. Local authorities should be made aware of such health risks and provide potable water facilities. This study could be used as a database for groundwater drinking standards, which should be revised for tropical countries to reflect the higher water intake rates. In general, this study adds to the results of others that illustrate the greater need for risk awareness and communication about heavy metal contamination of shallow groundwaters, especially in agricultural areas in tropical zones.

References

Agency for Toxic Substances and Disease Registry. (2000). Toxicological profile for arsenic (update). Atlanta, Georgia.

AOAC Peer-Verified Methods Program. (1998). Manual on policies and procedures, Arlington, Va., USA. http://www.aoac.org/vmeth/PVM.pdf. Accessed 04/10/2013.

Buchhamer, E. E., Blanes, P. S., Osicka, R. M., & Giménez, M. C. (2012). Environmental risk assessment of arsenic and fluoride in the Chaco province, Argentina: Research advances. *Journal of Toxicology and Environmental Health, Part A, 75*, 1437–1450.

Carlson-Lynch, H., Beck, B. D., & Boardman, P. D. (1994). Arsenic risk assessment. *Environmental Health Perspectives, 102*(4), 354–356.

Chang-Yu, C., Tsu-Kung, L., Yi-Chuang, C., Yi-Fen, W., Huey-Wen, S., Kuan-Hua, L., et al. (2010). Nickel(II)-induced oxidative stress, apoptosis, G2/M arrest, and genotoxicity in normal rat kidney cells. *Journal of Toxicology and Environmental Health, Part A, 73*, 529–539.

Chotpantarat, S., & Sutthirat, C. (2011). Different sorption approaches and leachate fluxes affecting on Mn^{2+} transport through lateritic aquifer. *American Journal of Environmental Science, 7*(1), 65–72.

Chotpantarat, S., Ong, S. K., Sutthirat, C., & Osathaphan, K. (2011). Effect of pH on transport of Pb^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+} through lateritic soil: Column experiments and transport modeling. *Journal of Environmental Sciences, 23*(4), 640–648.

Claesson, M., & Fagerberg, J. (2003). Arsenic in groundwater of Santiago del Estero—source, mobility pattern and remediation with natural materials. Master Thesis, Dept. of Land and Wat Res. Eng., KTH, Stockholm, Sweden, TRITA-LWRLEXL-03-05, p. 59.

Debernardi, L., De Luca, D. A., & Lasagna, M. (2008). Correlation between nitrate concentration in groundwater and parameters affecting aquifer intrinsic vulnerability. *Environmental Geology, 54*, 1081–1090.

Eriksson, J. E. (1990). Effect of nitrogen-containing fertilizers on solubility and plant uptake of cadmium. *Water, Air, and Soil pollution, 49*, 355–368.

European Centre for Ecotoxicology of Chemicals. (2001). Aquatic toxicity of mixtures. Technical report 80, Brussels, Belgium.

Filgueiras, A. V., Lavilla, I., & Bendicho, C. (2002). Chemical sequential extraction for metal partitioning in environmental solid samples. *Journal of Environmental Monitoring, 4*, 823–857.

Gibbs, R. J. (1977). Transport phases of transition metals in the Amazon and Yukon Rivers. *Geological Society of American Bulletin, 88*, 829–843.

Jaipieam, S., Visuthismajarn, P., Sutheravut, P., Siriwong, W., Thoumsang, S., Borjan, M., et al. (2009). Organophosphate pesticide residues in drinking water from artesian wells and health risk assessment of agricultural communities, Thailand. *Human Ecological Risk Assessment, 15*, 1304–1316.

Jeyaruba, T., & Thushyanthy, M. (2009). The effect of agriculture on quality of groundwater. *Middle-East Journal of Scientific Research, 4*(2), 110–114.

Kim, H. K., Yoon, E. K., Jang, J., Hwang, M., Kim, J. Y., Ha, J. H., et al. (2009). Assessment of heavy metal exposure via the intake of oriental medicines in Korea. *Journal of Toxicology and Environmental Health, Part A, 72*, 1336–1342.

Lim, H. S., Lee, J. S., Chon, H. T., & Sager, M. (2008). Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea. *Journal of Geochemical Exploration, 96*, 223–230.

Mandour, R. A., & Azab, Y. A. (2011). Toxic levels of some heavy metals in drinking groundwater in Dakahlyia Governorate, Egypt in the year 2010. *International Journal of Occupational and Environmental Medicine, 2*(2), 112–117.

Marcovecchio, J. E., Botte, S. E., & Freije, R. H. (2007). Heavy metals, major metals, trace elements. In L. M. Nollet (Ed.), *Handbook of water analysis* (2nd ed., pp. 275–311). London: CRC Press.

Mushak, P., & Crocetti, A. F. (1995). Risk and revisionism in arsenic cancer risk assessment. *Environmental Health Perspectives, 103*(7–8), 6834–6839.

Nakadaira, H., Nakamura, K., Mutoh, K., Yamamoto, M., & Katoh, K. (2000). Arsenic residues in well water 36 y after endemic arsenic poisoning. *Archives of Environmental Health, 55*(5), 364.

Nassef, M., Hannigan, R., Sayed, K. A. E., & Tahawy, M. S. E. (2006). Determination of some heavy metals in the environment of Sadat Industrial City. In: *Proceedings of the 2nd Environmental Physics Conference*, Alexandria, Egypt.

Natural Healing Site. (2010). Heavy metal toxicity. http://www.tuberose.com/Heavy_Metal_Toxicity.html. Accessed August 15, 2010.

Norkaew, S., Siriwong, W., Siripattanakul, S., & Mark, R. (2010). Knowledge, attitude, and practice (KAP) of using personal protective equipment (PPE) for chilli-growing farmers in Huarua Sub-District, Mueang District, Ubonrachathani Province, Thailand. *Journal of Health Research, 24*(2), 93–100.

Patriquin, D. G., Blaikie, H., Patriquin, M. J., & Yang, C. (1993). On-farm measurement of pH, electrical conductivity and nitrate in soil extracts for monitoring coupling and decoupling of nutrient cycles. *Biological Agriculture & Horticulture, 9*, 231–272.

Peplow, D., & Edmonds, R. (2004). Health risks associated with contamination of groundwater by abandoned mines near Twisp in Okanogan County, Washington, USA. *Environmental Geochemistry and Health, 26*, 69–79.

Pokkamthanam, A. S., Riederer, A. M., & Anchala, R. (2011). Risk assessment of ingestion of arsenic-contaminated water among adults in Bandlaguda, India. *Blacksmith Institute Journal of Health & Pollution, 1*, 8–15.

PCD, Pollution Control Department. (2000). Groundwater standards for drinking proposes. Manual inspection of contaminated groundwater standards for drinking proposes. Manual inspection of contaminated groundwater from waste disposal facilities, Ministry of Natural Resources and Environment.

PCD, Pollution Control Department. (2004). Ministry of Natural Resources and Environment. Drinking water standards. http://www.pcd.go.th/info_serv/en_reg_std_water01.html#s1. Accessed January 20, 2012.

Rapant, S., & Krčmová, K. (2007). Health risk assessment maps for arsenic groundwater content: Application of national geochemical databases. *Environmental Geochemistry and Health, 29*, 131–141.

Rashed, M. N. (2010). Monitoring of contaminated toxic and heavy metals from mine tailings through age accumulation in soil and some wild plants at Southeast Egypt. *Journal of Hazardous Materials, 178*(1–3), 739–746.

Rattan, R. K., Datta, S. P., Chhonkar, P. K., Suribabu, K., & Singh, A. K. (2005). Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. *Agricultural Ecosystems and Environment, 109*, 310–322.

Saipan, P., & Ruangwises, S. (2009). Health risk assessment of inorganic arsenic intake of Ronphibun residents via duplicate diet study. *Journal of the Medical Association of Thailand, 92*(6), 849–856.

Siriwong, W. (2006). Organophosphate pesticide residues in aquatic ecosystem and health risk assessment of local agriculture community. Doctor dissertation Program in Environmental Management (Interdisciplinary Programs), Graduate School Chulalongkorn University, Thailand.

Srithongdee, T., Chotpantarat, S., Siriwong W., & Siripattanakul, S. (2010). Nitrate and pesticide contamination of shallow groundwater under chilli field of Hua Rua, Ubon Ratchathani Province. In: Proceedings of the APRC-2010, Ubon Ratchathani, Thailand.

Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry* (3rd ed.). NY: Wiley.

Suesat, S. (2010). Distribution and potential mobility of heavy metals in soil and shallow groundwater aquifer in an agricultural area: A case study of Hua Rua Area, Changwat Ubon Ratchathani. Bachelor's degree report, Geology, Faculty of Science, Chulalongkorn University, Thailand.

Taboada-Castro, M., Diéguez-Villar, A., Luz Rodríguez-Blanco, M., & Teresa Taboada-Castro, M. (2012). Agricultural impact of dissolved trace elements in runoff water from an experimental catchment with hand-use changes. *Communications in Soil Science and Plant Analysis, 43*, 81–87.

Takeno, N. (2005). Atlas of Eh-pH diagrams. Intercomparison of Thermodynamic Databases, National Institute of Advanced Industrial Science and Technology Research Center for Deep Geological Environments: Geological Survey of Japan Open File Report No. 419.

Taneepanichskul, N., Siriwong, W., Siripattanakul, S., Pongpanich, S., & Robson, M. G. (2010). Risk assessment of Chlorpyrifos (organophosphate pesticide) associated with dermal exposure in chilli-growing farmers at Ubon Rachathani Province, Thailand. *Journal of Health Research, 24*(2), 149–156.

USEPA (US Environmental Protection Agency). (1980). Water quality criteria documents; availability. 45 Federal Register, 45(231), 79318–79.

USEPA (US Environmental Protection Agency). (1992). Definitions and general principles for exposure assessment. Guidelines for exposure assessment. Washington, D.C.: Office of Pesticide Programs, USA.

USEPA (US Environmental Protection Agency). (2001). Baseline human health risk assessment Vasquez Boulevard and I-70 superfund site, Denver CO. http://www.epa.gov/region8/superfund/sites/VB-170-Risk.pdf. Accessed 01/20/2011.

USEPA (US Environmental Protection Agency). (2012). Ground water and drinking water. http://www.water.epa.gov/drink/index.cfm. Accessed 01/15/2011.

USEPA IRIS (US Environmental Protection Agency's Integrated Risk Information System). (2011). http://www.epa.gov/iris/. Accessed 01/15/2011.

Vodela, J. K., Renden, J. A., Lenz, S. D., McElhenney, W. H., & Kemppainen, B. W. (1997). Drinking water contaminants. *Poultry Science, 76*, 1474–1492.

Wcislo, E., Ioven, D., Kucharski, R., & Szdzui, J. (2002). Human health risk assessment case study: An abandoned metal smelter site in Poland. *Chemosphere, 47*, 507–515.

WHO (World Health Organization). (2011). Guidelines for drinking-water quality (4th ed.). http://www.whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf. Accessed 01/15/2011.

Wongsasuluk, P. (2010). Human health risk assessment associated with heavy metals in drinking shallow groundwater wells at Ubon Ratchathani Province, Thailand. Master thesis. Chulalongkorn University, Thailand.

Zhao, K., Liu, X., Xu, J., & Selim, H. M. (2010). Heavy metal contaminations in a soil–rice system: Identification of spatial dependence in relation to soil properties of paddy fields. *Journal of Hazardous Materials, 181*, 778–787.