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Regards

Editors

Arsenic pollution in groundwater in the Red River Delta

Tong Ngoc Thanh MSc.[1]

Abstract

The Red River Delta is located in northern Vietnam and has an area of 17,000km^2. The delta is underlain by un-consolidated formations and Neocene sediments. It is one of the most developed economic areas of Vietnam. The economic development is closely linked to the use of the groundwater resources. Today the extraction of groundwater has become significant but is not always strictly controlled. This causes the lowering of the groundwater table, saline intrusion and pollution including arsenic pollution. Efforts to establish some knowledge of the arsenic levels in the Red River delta plain have started. However, to solve this problem from a regional perspective, the collaboration and support as well as exchange of experience of experts and international organizations is needed.

Introduction

Groundwater pollution, especially arsenic (As) pollution is harmful for human health if water is used for domestic purposes. In May 2001 the conference "Geology and Health" was held in Bangkok-Thailand. Reports at this conference show that in Bangladesh, China and India as well as in Cambodia, Myanmar, Pakistan, Thailand and Laos there are regions where groundwater is polluted by As.

In Vietnam during mineral exploration, areas with high As concentrations have also been discovered. In the Red River delta, in the Mekong River Delta and on the Thai Nguyen Plateau, levels of As have been investigated by the National Groundwater Monitoring Network. With sponsorship from UNICEF and in collaboration with the National University, the Northern Hydro-geological Engineering Geological Division (NHEGD) investigated As levels in groundwater in the Red River Delta. High As concentrations have been detected in some regions. The Red River delta plain is underlain by quaternary sediments. The development of the delta plain is related to a series of marine transgressions and regressions, as well as to tectonic activities. The sediments are mainly riverbed facies of widely varying thickness. Two main aquifers are recognized.

The Holocene inter-granular aquifer (qh)

This is the shallowest aquifer, distributed rather widely from the center of the plain to the sea, but there is only a narrow strip along the Red River. The thickness of this aquifer varies. It is 10-20m to 30-40m in the center of the plain from Nam Dinh-Thai Binh to the sea. In the plain margins, the aquifer is only 1.5-3m. The average thickness is 13.6m. This aquifer has high water potential with a hydraulic conductivity ranging from 95 to 1788 m^3 d^{-1}. The average hydraulic conductivity is from 300-500 m^3 day^{-1}.

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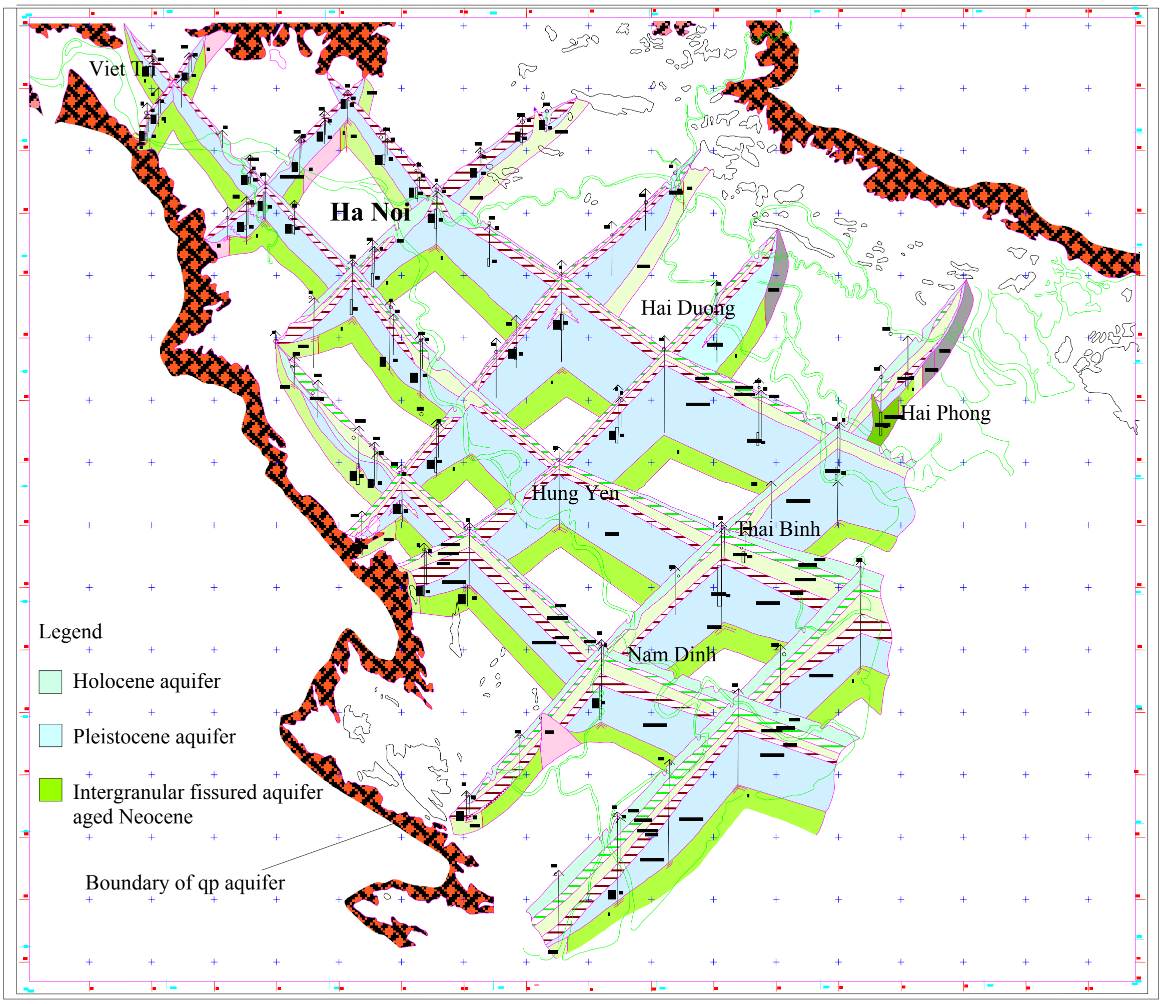
Figure 1. Hydro-geological structure of the Red River delta plain



From the peak of the plain to Hanoi the water is 'fresh' with a TDS ranging from 0.189 to 0.445g l^{-1} and predominance of calcium-magnesium bicarbonate. From Hanoi to Cam Giang, An Thi and Khoai Chau the water is still fresh but due to a decreasing permeability, the hydraulic gradient and the shallow water table the TDS is increasing. The water type is dominated by HCO_3-Ca → HCO_3-Ca-Na → HCO_3-Cl-Ca-Na → Cl-HCO_3-Ca-Na. From Hung Yen and Hai Duong to the sea the water changes from fresh to saline although not completely and areas of fresh water still exist. The water type in the fresh areas is now dominated by HCO_3-Ca → HCO_3-Cl-Na and Cl-HCO_3- Na. There is a transition zone with a TDS of 1-6 g l^{-1}, where the water type is HCO_3-Cl-Na → Cl-HCO_3-Na. In the saline area the TDS is high, up to 3g l^{-1} or more. This aquifer is sufficient for small-scale water supply.

The Pleistocene inter-granular aquifer (qp)

This is the main aquifer it is distributed widely under the Red River Delta but it is exposed only in the margins of the plain (Figure.1).The qp aquifer is composed of two layers the upper layer consisting of medium to coarse sand mixed with gravel and lower layer composed of cobbles and pebbles mixed with sand. A clay layer separates the two, but this clay separation is not always there, and as a consequence the two sub-aquifers have the same water level.

The thickness of the qp aquifer varies widely from several meters in the northwest margin to approximately 100m in the centre and the southeast (Figure 1.). The upper level has good water potential with hydraulic conductivity ranging from 48 to 756m^3 d^{-1}. In comparison, the lower section of the qp aquifer has a better potential for water, with hydraulic conductivity ranging from 700 to 2000m^3 d^{-1}. Most of the production wells draw from the lower section of the qp aquifer.

The Pleistocene aquifer has sufficient potential for large-scale water supply. In recent times, the groundwater abstraction in Hanoi, Hai Duong, Hung Yen, Vinh Yen, Phuc Yen towns and Kien An-Hai Phong, Hai Hau, Nghia Hung-Nam Dinh provinces totals over 1,000,000 m^3 d^{-1}.

The negative effects of groundwater pumping

Currently groundwater is abstracted in Vietnam in general and in the Red River Delta in particular in the following manner.

1. *Public exploitation wells:* These wells are managed by special public organizations (Clean Water Business Companies). The construction of these wells is based on the results of water exploration programs carried out by competent organizations. These wells operate within urban areas and industrial zones. Total water abstraction volume is approximately 500, 00 m^3 d^{-1} and in the Hanoi area is approximately 400,000 m^3 d^{-1}.

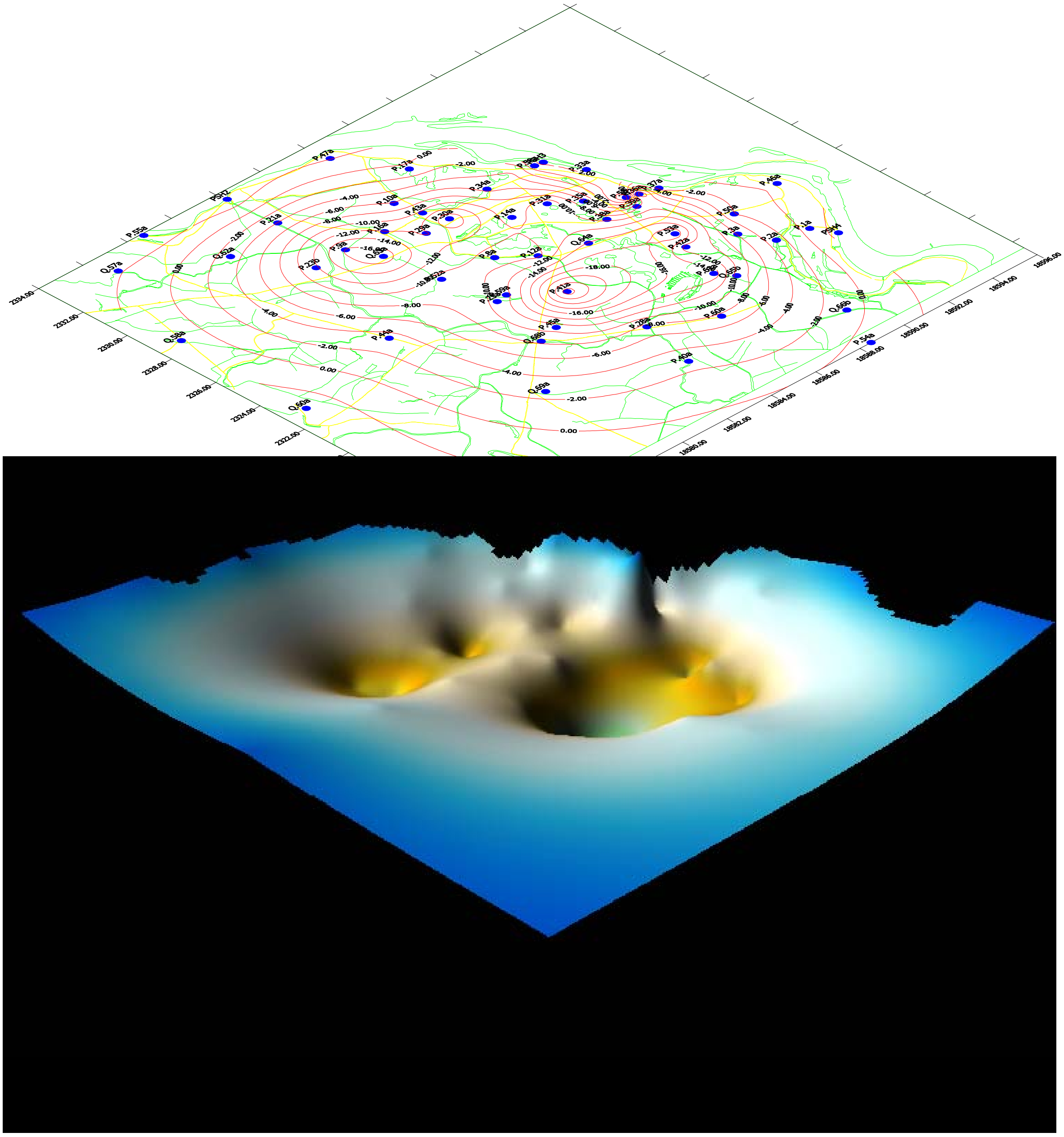
2. *Private Wells:* These wells are exploited by other organizations such as hospitals, schools, enterprises and factories. These wells are built without investigation, and without permits from a competent organization. Total abstraction from private wells is currently estimated as 250,000 m^3 d^{-1}.

3. *UNICEF wells:* In rural areas people use groundwater from dug wells or from UNICEF sponsored small, shallow wells. In the beginning each house had its own well. Now this water supply system has improved and in some communities there is a public water supply system served by one or more big wells. Total production from these wells is of the order of 400,000 – 500,000 m^3 d^{-1}.

Groundwater pumping has negative impacts on the environment in general and on the groundwater environment in particular. The impacts are degradation of water resources, salt intrusion and pollution. The degradation of water sources includes the lowering of the water table and the enlarging of the cone of depression. Research indicates that cones of depression have formed in Hanoi, in Vinh Yen, in Hai Phong, in Nam Dinh and in Thai Binh.

The cone of depression in the Hanoi area has been investigated from 1992 to present. The results indicate that the size of the area that has been affected by heavy abstraction and where the water level is below 0m is 269.34km^2 (2001 Data). Within this area there is a core that has been strongly affected and where the water level is below -8m. This central core of depression now covers an area of 97.84km^2, and expands at the rate of 4.2km^2 yr^{-1}. In addition a very strongly affected area with water levels below -14m occupies 28.61km^2. This deepest part of the cone is expanding at the rate of 2.3km^2 yr^{-1}.

Figure 2. Map showing the cone of depression south of Hanoi (August 2001 Data)



<0m: 263.57 km^2

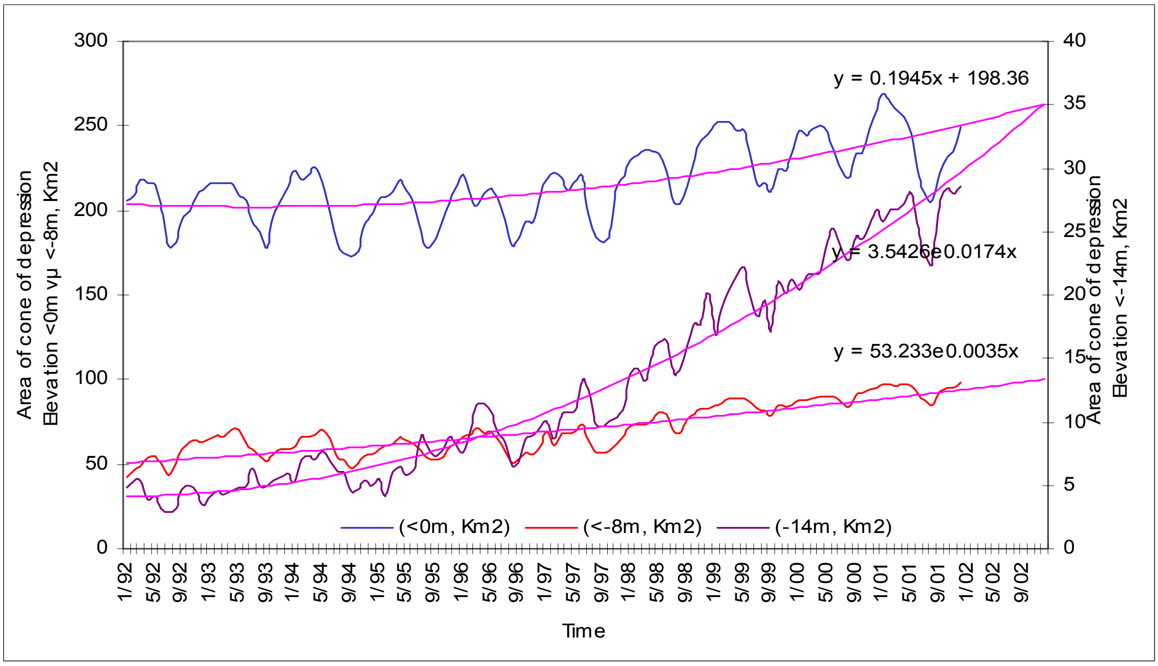
<-8m: 96.90 km^2

<-14m: 26.69 km^2

P.41 Observation well

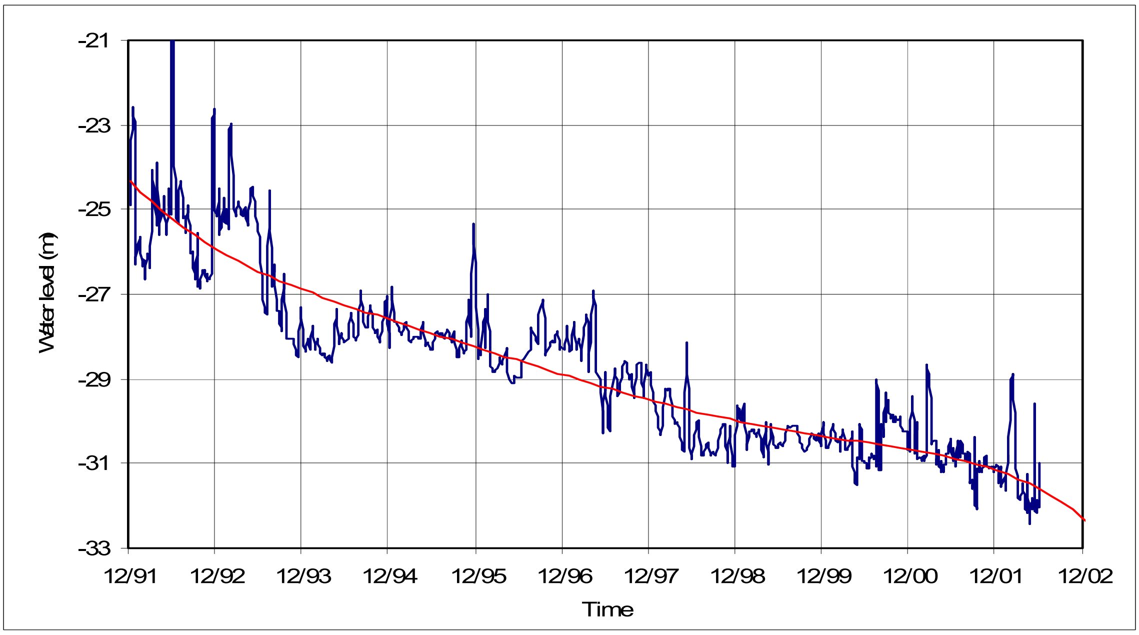
2 Water level of qp aquifer

Figure 3. Graph for the size of the cone of depression south of Hanoi, 1992 – 2001



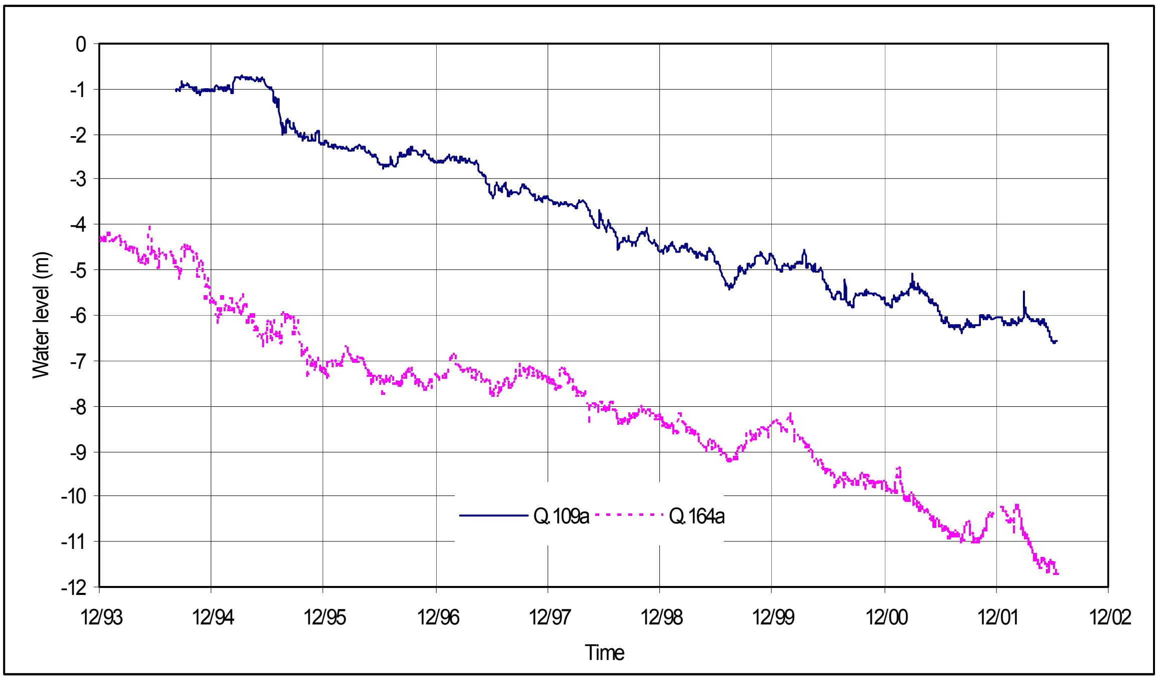
In addition to the constant expansion of the area affected by heavy abstraction and an enlargement of the cone of depression (Figure 3.), the general water level is also lowered. In Hanoi, the water level measured in observation well P41a on the Ha Dinh well field in 2002 was 32.43m (Figure 4), this was 1.22m deeper than in the same period in 2001.

Figure 4. Lowering of water level in observation well P41a – Hanoi area (1991-2002)



Moreover, in Hai Hau, in observation well Q109a (Figure 5), the deepest water level in 2002 was 6.60m. This is 0.44m deeper than in the same period in 2001. In addition, in Kien An-Hai Phong, in observation well Q164a (Figure 6), the deepest water level is 11.73m, 0.94m deeper than in the same period in 2001.

Figure 5. Lowering of water level in the observation well Q.109a in Hai Hau, Nam Dinh and observation well Q164a in Kien, An-Hai Phong (1993-2002)



On the whole the water level in the Pleistocene aquifer has been declining. This, mainly recent, lowering of the water level has led to several forms of pollution and to saline intrusion into the aquifer.

Arsenic levels in the Red River Delta plain

The presence of an As problem was recognized during geology-hydrogeology surveys and in mapping and surveying for minerals in Vietnam in general and in the Red River Delta plain in particular. Arsenic is detected in mining areas, ore outcrops and in areas where industrial wastes contains As. Arsenic occurs naturally in areas mineralized with sulfide minerals and gold and in areas of volcanic activities. The main As liberating mechanism is weathering. The main areas in Vietnam of As concentration are in Pia Oac, Ngan Son, Pac Lang, Chay River, North Tam Dao, Cho Don-Cho Dien, Dao Vien-Chiem Hoa-Na Hang-Tung and Bac Me.

Arsenic also occurs in metamorphic intrusive volcanic formations containing arsenopyrite, pyrite and gold such as in the Hien River, Binh Gia, east of the Chay River, in Nam Xe-Tam Duong, in the downstream part of the Da River. Arsenic concentration in gold ore in the basalts of the Vien-nam formation in Doi Bu (Hoa Binh) is 50-204 mg kg^{-1}. In sandstone, siltstone and in the siliceous shale of the Than Sa formation in a mineralized zone of sulfur-gold-quartz in Khau Au-La Hien (Bac Can, Thai Nguyen) AS concentration is 13.2 mg kg^{-1} and in the ore is 1292-1442 mg kg^{-1}.

Further, in the sericite shale and clay shale of the Coc Xo formation in the zinc-lead ore area of Cho Don (Bac Can) As content is 97.8 mg kg^{-1} with As concentration in the ore ranging from 8.205-261.824 mg kg^{-1}. According to Dang Van Can, 2000 As in water of the ore zone in Lang Vai (Dam Hong) is 0.73mg l^{-1}. In Bo Sinh-Moc Chau District, Son La Province the As level in springs of the right side of the Ma river is 0.43-1.13 mg l^{-1}. Do Tuyet, 1998 reports As concentrations in karst water at Tay Bac of 2.8mg l^{-1} in Tra commune, 2.67mg l^{-1} in Chieng hamlet, 2.29mg l^{-1} in Ngan commune and 3.14mg l^{-1} in Chieng Bui.

In the Red River Delta plain, the industrial zones discharge waste containing As. In the Viet Tri industrial zone the As concentration in groundwater is higher than the Internationally accepted standard limitation with a maximum value of 0.32 mg l^{-1}. In Thuong Dinh industrial zone, Hanoi area, As in wastewater is 0.145-0.346mg l^{-1}, higher than the standard limitation (Nguyen Van Duc, 2001). This wastewater is not treated.

In 1999 with sponsorship from UNICEF, the As level has been studied in 7 provinces of the Red River Delta plain. A total of 1228 samples were taken and analyzed. The results showed that 740 out of 1228 have an As concentration <0.01 mg l^{-1}, 1075 samples have an As concentration <0.05 mg l^{-1} and 153 samples have an As concentration >0.05 mg l^{-1} with a maximum value of 0.6 mg l^{-1}.

Since 2001, the Northern Hydro-geological Engineering Geological Division has been studying As levels in groundwater in the Red River delta plain. Samples are taken twice per year, stored and preserved in accordance with ISO 11969 and Vietnamese standard-TCVN 6626. The results show that out of a total of 34 samples, 17 samples have >0.001mg l^{-1} of As, 5 samples have >0.05mg l^{-1}. The maximum value is 0.428 mg As l^{-1} (Q58a-Dan Phuong-HaTay). In 2002, 18 samples out of 85 samples (21%) having a higher concentration than the standard limitation. Fourteen of these samples are from the qp aquifer with As concentrations of 0.067 mg l^{-1} (Q88b-Ha Nam) and 0.406 mg l^{-1} (Q58a-Ha Tay). The remaining samples are from the qh aquifer with values of 0.088 mg l^{-1} (Q85a-Ha Nam) and 0.440mg l^{-1} (Q56-Ha Tay).

Table 1.Arsenic and other heavy metals in the Red River Delta plain in 2002

No	Element	Vietnamese Standard (mg l^{-1})	Season	No. of samples	Number of samples having higher concentration than Vietnamese Std.			
					Number	%	mg l^{-1} Min	mg l^{-1} Max
1	As	0.05 (TCVN 5944 -1995)	Dry	43	9	20.9	0.067	0.440
			Rainy	42	9	21.0	0.080	0.364
2	Mn	0.1 (TCVN 5944-1995)	Dry	43	36	83.7	0.11	2.99
			Rainy	42	36	85.7	0.12	1.59
3	Be	0.0002 (BKHCNMT-1993)	Dry	43	39	90.7	0.0002	0.0064
			Rainy	42	9	21.4	0.0002	0.0090
4	Ni	0.02 (WHO 1984)	Dry	43	12	27.9	0.020	0.092
			Rainy	42	0	-	-	-
5	Cr	0.05 (TCVN 5944-1995)	Dry	43	0	-	-	-
			Rainy	42	2	4.8	0.055	0.066
6	Cd	0. 01 (TCVN 5944-1995)	Dry	43	0	-	-	-
			Rainy	42	2	4.8	0.0110	0.0173

In 2001-2002, UNICEF Hanoi collaborated with the Northern Hydro-Geological Engineering Geological Division and the University for Natural Science/National University to sample and analyze environmental parameters, including some heavy metals. The study areas are Hanoi city and some provinces including Thai Binh, Nam Dinh and Ninh Binh. The results are presented in Table 2 and Figures 6 and 7.

Hanoi City:

- North of the Red River and Duong River, 8 out of 112 samples in Dong Anh district had an As concentration higher than the Vietnamese Standard of 0.05 mg l^{-1}.

Gia Lam area:

- *qh aquifer:* In the dry season 8 samples (40%) had a higher As concentration than the Vietnamese Standard. In contrast, in the rainy season only 2 samples exceeded the Vietnamese As Standard.
- *qp aquifer*: In dry season 13 samples had a higher As concentration than the Vietnamese Standard and in the rainy season just 2 samples.

Tu Liem area:

- *qh aquifer*: In the dry season 8 samples (14.5%) had a higher As concentration than the Vietnamese Standard and in the rainy season just 1 sample.
- *qp aquifer:* In comparison with the qh aquifer, in the dry season 9 samples taken from the qp aquifer contained As at concentrations exceeding the Vietnamese Standard. In the rainy season this decreases to just 3 samples.

Thanh Tri area:

- *qh aquifer*: In the dry season 43 samples (59.7%) exceeded the Vietnamese Standard for As in drinking water. In the wet season, this decreases to 29 samples (40.3%).
- *qp aquifer*: In the dry season 13 samples (54.2%) exceeded the Vietnamese As Standard. This declined to 9 samples (39.1%) in the rainy season.

Urbanized area of Hanoi:

- *qh aquifer*: In the dry season and rainy season 18 samples (38.3%) and 12 samples (26.1%) had As concentrations exceeding the Vietnamese standard.
- *qp aquifer*: In the dry season 17 samples (39.5%) contained As at concentrations exceeding 0.05 mg l^{-1}. In the rainy season this decreased to 8 samples (19.0%).

Nam Dinh province:

- The total number of samples collected was 125 of which 11 samples had an As concentration higher than the Vietnamese standard. These samples were located mainly north of My Loc, Xuan Truong and Nam Dinh city.

Ninh Binh province:

- Eight out of a total number of samples of 75 had an As concentration exceeding 0.05 mg l^{-1}. These samples were concentrated southeast of Ninh Binh town and the centre of Kim Son.

Thai Binh province:

- Out of 125 samples collected only 1 sample contained As at a concentration >0.05 mg l^{-1} (Vietnamese Standard).

Some possible mechanisms causing arsenic pollution in groundwater

The Red River delta plain is composed of fine unconsolidated sediments such as clay, peat and organic matter, and it is in these materials that heavy metals and As concentrate and are retained. The results for As in soils in 4 wells in Hanoi as reported by the University for Natural Science/National University and the Northern Hydro Geological Engineering Geological Division showed that the maximum value ranges from 6-33.0 mg kg^{-1} and that soil As correlates well with iron concentration. Arsenic may be absorbed by iron Oxy-hydroxide in areas of heavy groundwater pumping. During the disintegration of organic matter in peat, a large amount of methane is formed. Methane combines with As forming a methyl-As compound that dissolves in groundwater. In the Hanoi area, As sources can be clay and peat layers at depths of 0-40m. In addition, human activities including urban areas, factories and residential areas in the Red River Delta plain contribute untreated waste and wastewater which discharges into the drainage system. Also agricultural activities introduce fertilizers and pesticides containing As. The above-mentioned are the main reasons for groundwater pollution. However, the strong groundwater abstraction is the main factor causing pollution, especially in the centre of the well fields. The lowering of the water level causes an increase in the velocity of groundwater flow, and increasing percolation of water

Some methods to mitigate arsenic in groundwater

- Continued investigation into the degree of As pollution and the scale of distribution of As in vulnerable areas of the Red River Delta plain and vicinity.
- Assessment of water sources free of As for water supply as part of integrated groundwater management.
- Treatment of waste from industrial, domestic and agricultural activities.
- Investigate and implement appropriate technologies and treatment models for protect community health from elevated levels of As in groundwater.
- Intensive collaboration between national and international organizations to exchange information and experiences.

Table 2. Arsenic and other metals in groundwater of the Hanoi area compared with TCVN 5501-1991

Criteria / Study area	Number of samples	Arsenic ($mg\ l^{-1}$)		Manganese ($mg\ l^{-1}$)		Iron ($mg\ l^{-1}$)		Ammonia ($mg\ l^{-1}$)	
		>0.05	%	>0.1	%	>0.3	%	> 3	%
A. Upper aquifer (qh)									
I. In dry season									
North area	66	4	6.1	44	66.7	27	36.4	2	3.0
Gia Lam area	20	8	40	19	95.0	12	60	3	15.0
Tu Liem area	55	8	14.5	46	83.6	40	72.7	10	18.2
Thanh Tri area	72	43	59.7	59	81.9	66	91.7	56	77.8
Urban area	47	18	38.3	44	93.6	41	87.23	17	36.2
II. In rainy season									
Gia Lam area	19	2	10.5	17	89.5	11	57.9	0	0
Tu Liem area	55	1	1.8	45	81.8	34	61.8	1	1.8
Thanh Tri area	72	29	40.3	58	80.6	57	79.2	27	37.5
Urban area	46	12	26.1	41	89.1	38	82.6	7	15.2
B. Lower aquifer (qp)									
I. In dry season									
North area	46	4	8.7	33	71.7	33	71.7	3	6.5
Gia Lam area	72	13	18.1	67	93.1	51	70.8	21	29.2
Tu Liem area	25	9	36.0	22	88.0	25	100	9	36.0
Thanh Tri area	24	13	54.2	22	91.7	23	95.8	18	75
Urban area	43	17	39.5	40	93.0	42	97.7	12	27.9
II. In rainy season									
Gia Lam area	72	2	2.8	60	83.3	43	59.7	3	4.2
Tu Liem area	25	3	12.0	18	72.0	21	84.0	0	0
Thanh Tri area	23	9	39.1	19	82.6	22	95.7	8	34.8
Urban area	42	8	19.0	36	85.7	39	92.9	3	7.1

Figure 6. Map of As pollution in the qp aquifer within the Hanoi area

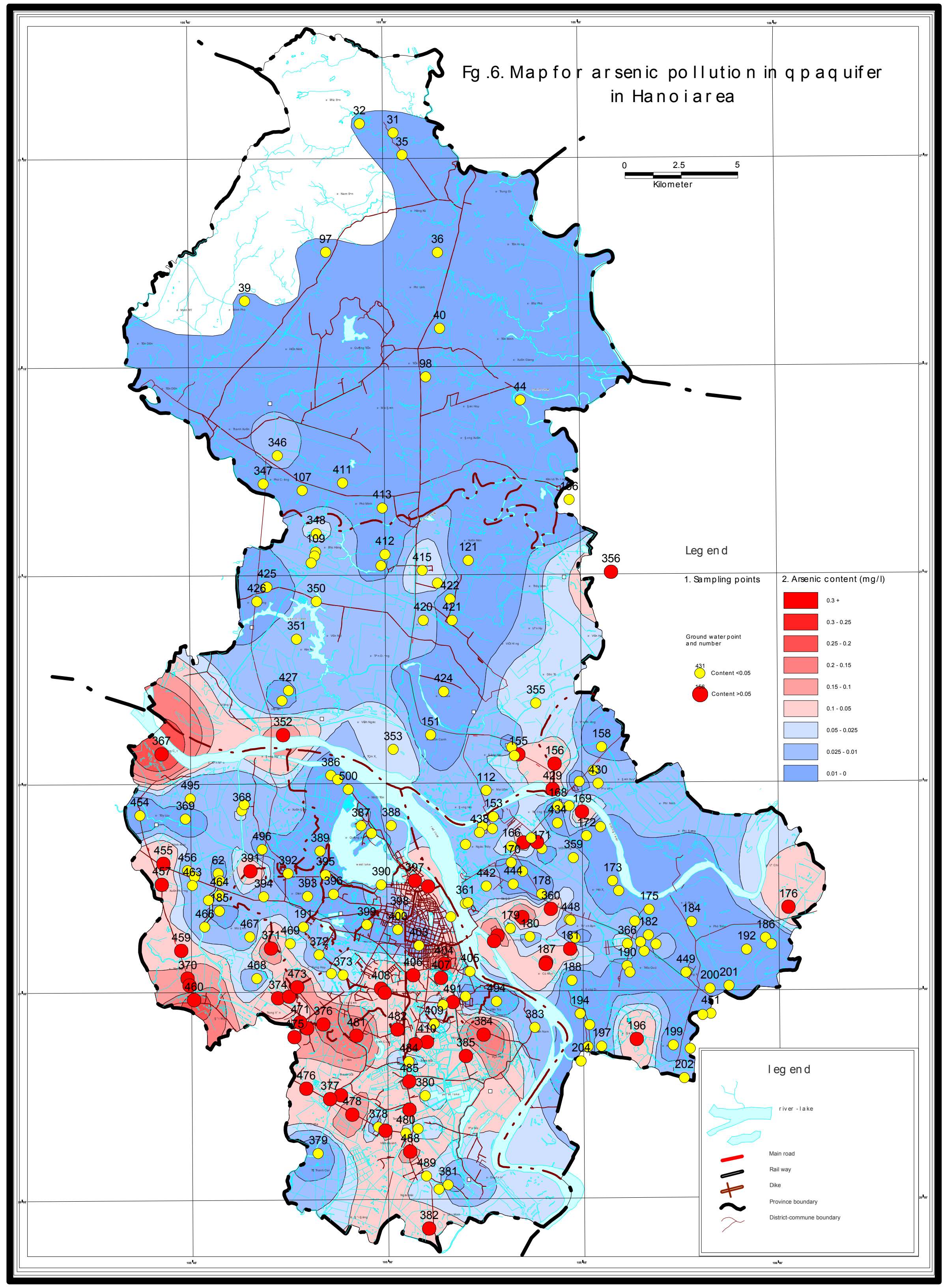
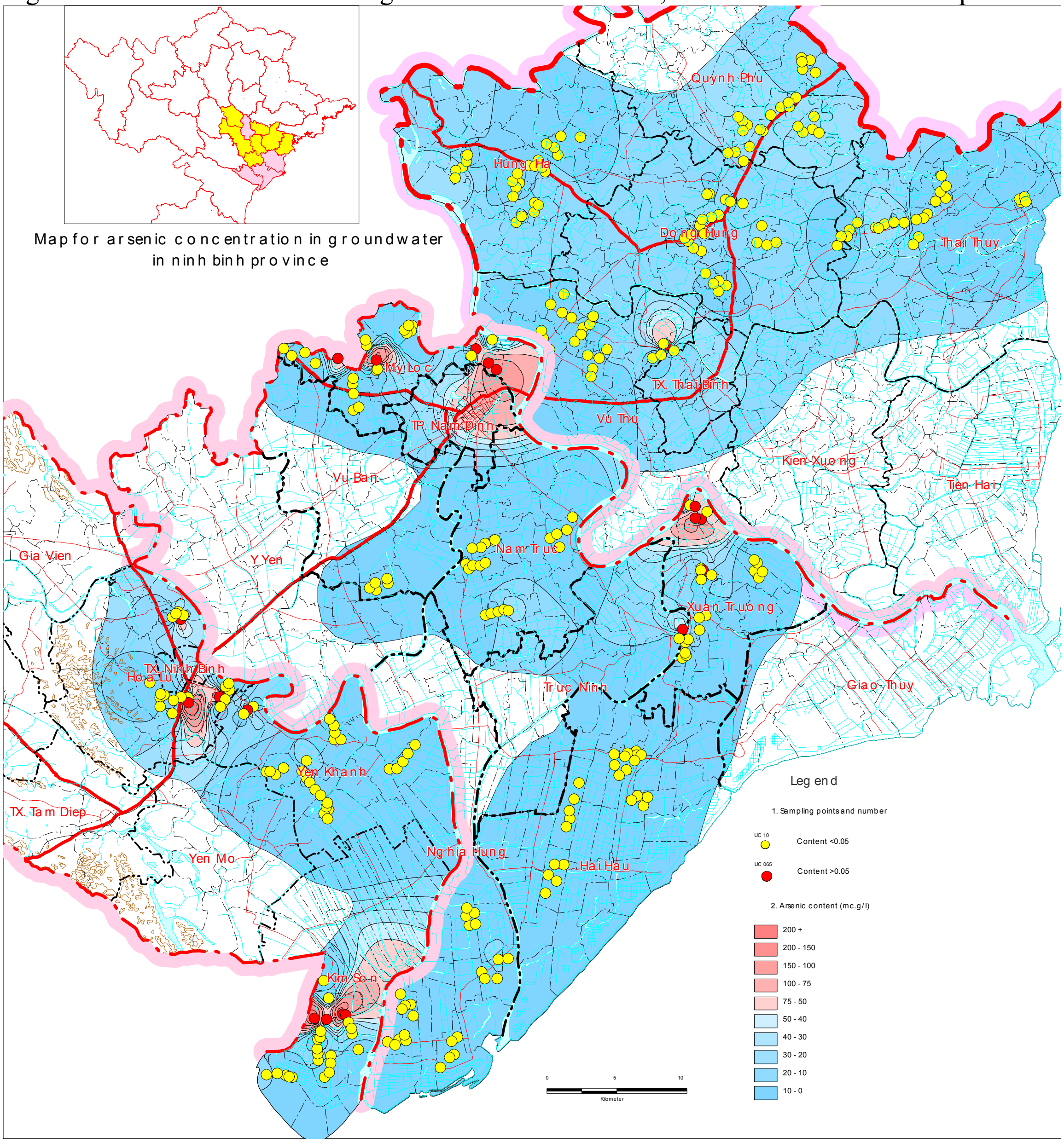


Figure 7. Arsenic concentration in groundwater in Thai Binh, Nam Dinh and Ninh Binh provinces



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Arsenic Removal Technologies for Drinking Water in Vietnam

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Abstract

Severe and widespread contamination by arsenic (As) in groundwater and drinking water has been recently revealed in rural and sub-urban areas of the Vietnamese capital of Hanoi with similar magnitudes as observed in Bangladesh and West Bengal, India. This fact has prompted the need to develop simple, rapid and low-cost techniques for lowering As concentrations in supplied water. In the present study, laboratory and field tests were conducted to assess the suitability of using oxidation processes by activated hypochlorite in water treatment plants in Hanoi city and naturally occurring minerals as sorbents in household-based systems to reduce As concentrations in drinking water. Sorption experiments indicated that co-precipitation of arsenate [As(V)] in ferric hydroxide is much more efficient than of arsenite [As(III)]. With Fe concentrations of 5 mg l^{-1}, As(V) can be efficiently lowered from concentrations of 0.5 mg l^{-1} levels to lower than the Vietnam standard of 0.05 mg l^{-1}. Activated hypochlorite was additionally introduced after the aeration tank in the conventional water treatment process that is currently used in the water treatment plants of Hanoi city. This modified process was able to lower arsenic concentrations below the standard level with relatively low Fe concentration (5 mg l^{-1}). Investigations on pilot scale equipment indicated that the removal efficiency of As in this system was much higher than that in laboratory experiments. To reduce As concentrations to levels lower than the Vietnamese standard level of 0.05 mg l^{-1}, initial Fe/As concentration ratios used in the pilot system and laboratory experiment were 16 and 50, respectively. Laterite and limonite, which are naturally and widely occurring minerals in Vietnam, can be used as potential sorbents for As removal in smaller scale water treatment systems. The sorption capacities of laterite and limonite for As(V) were estimated to be 1100 and 900 mg kg^{-1}, respectively. Initial results of field tests indicated that As concentrations decreased to levels <0.05 mg l^{-1}. The household system based on an adsorption column packed with these minerals seemed to be a suitable technique for small-scale groundwater remediation in rural and sub-urban areas.

Keywords: *Arsenic Removal; Co-precipitation; Sorption; Chlorine Oxidation; Naturally occurring minerals; Laterite; Limonite.*

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Introduction

Arsenic (As) contamination in drinking water and groundwater has increasingly been recognized in recent years and now has become a worldwide problem. Severe contamination has been reported for a decade in Bangladesh and West Bengal, India, where millions of people are consuming As-poisoned groundwater (Nickson *et al.*, 1998). Serious arsenicosis has been observed for a large population in these areas (Chowdhury *et al.*, 2000). Arsenic problems have also been observed in developed nations. In the United States, the Environmental Protection Agency has recently decided to lower the maximum contamination level for As in drinking water from 50 μg l^{-1} to 10 μg l^{-1}. The increasing awareness of As toxicity and the regulatory changes have prompted considerable attention towards developing suitable methods for lowering As levels in drinking water.

Natural occurring contamination by As has been also observed in the Red River delta of northern Vietnam. A recent comprehensive survey has revealed elevated As concentrations over a large rural and sub-urban area of the Vietnamese capital (Berg *et al.*, 2001). In four districts of the rural Hanoi area, As concentrations in about 48% of the investigated groundwater exceeded the Vietnam guideline of 50 μg l^{-1}, and hence, point to a high risk of chronic arsenic poisoning. This fact has prompted the need to investigate suitable methods for lowering/removing As concentrations in drinking water with rapid, simple and low-cost techniques.

A number of recent studies have proposed the use of zerovalent iron filings as filter medium for removing arsenite [As(III)] and arsenate [As(V)] from groundwater (Su and Plus, 2001a, 2001b; Farrell *et al.*, 2001). The process is based on the adsorption and co-precipitation of As(III) and As(V) onto Fe(III) oxides (Melitas *et al.*, 2002). Adsorption capacity of As in the form of arsenite and arsenate onto various ferric clay minerals has been well investigated (Farpuhar *et al.*, 2002). In Bangladesh, several efforts have been made to develop household filtration systems with effective low-cost technologies. Co-precipitation with ferric chloride is an effective and economic technique for removing As from water, because iron hydroxides formed from ferric salt have a high sorption capacity for arsenate (Meng *et al.*, 2001). However, the applicability of such methods depends largely on the geological characteristics of the groundwater. For example, in Bangladesh, elevated concentrations of phosphate and silicate may enhance the mobility of As(V) in soils contaminated with arsenate (Peryea and Kammereck, 1997, Hug et al., 2001). In addition, recent studies have suggested that silicate may disturb the removal of As(III) and As(V) by co-precipitation with ferric chloride (Meng *et al.*, 2000).

In Vietnam, recent investigations showed that the current As contamination in the Red River delta area has been as serious as observed in Bangladesh and West Bengal (Berg *et al.*, 2001). Furthermore, the chemical composition of groundwater in Vietnam is similar to that in Bangladesh. The present study investigated the applicability of a simple and economic technique for removing As in groundwater during the treatment process in water treatment plants of urban Hanoi. Furthermore, this paper evaluates laterite and limonite, which occur very widely in Vietnam, as potential sorbents for As. The sorption kinetics of these minerals for As(III) and As(V) were investigated and their applicability in household adsorption and filtration system for As removal was assessed.

Materials and Methods

Experiments for As removal by adsorption onto Fe hydroxide and oxidation by hypochlorite.

Raw groundwater samples were collected from water supplies of Hanoi city. Appropriate Fe(II) chloride amounts were added and the pH was maintained at 7.0 ± 0.2. Fe(II) was oxidized to Fe(III) by air purging until Fe(II) could not be detected by the orthophenantroline method. As(III) and As(V) in the form of AsO_3^{3-} and AsO_4^{3-} at concentrations of 0.5 mg l^{-1} were added. Solutions were stirred gently for 10 min. and allowed to settle for 15 min for precipitation.

The precipitate was discarded and the solution was analyzed for As and Fe concentrations. Chlorine in the form of hypochlorite was added to a series of Fe(II) solutions with concentrations of 1, 5, 10, 15, 20, 25 and 30 mg l^{-1} and As constant concentration of 0.5 mg l^{-1}. For As analysis, an on-line hydride generation device coupled with Atomic Absorption Spectroscopy (HVG-AAS) (Shimadzu, Kyoto, Japan) was used. Further details for chemical analysis of As can be found in Berg *et al.*, 2001.

Sorption capacity of laterite and limonite for As(III) and As(V)

Laterite and limonite were first treated (see below) and then subjected to determination of their chemical composition as well as naturally occurring As contents (Table 3). Arsenic possibly present in these minerals was removed by washing in an alkali solution (10M NaOH) and by heating to 900 °C for 2 hours. Isothermal sorption experiments were carried out using treated laterite and limonite as sorbents, with initial As(III) and As(V) concentrations of 2, 5, 10, 20, 30, 40, 50 and 100 mg l^{-1} and under atmospheric pressure and 28 °C . The suspensions were centrifuged and the supernatant solutions were filtered through 0.45 μm membrane filters prior to As determination.

The treated laterite and limonite were packed into an adsorption column and applied as filtration device in a household water treatment system. Raw groundwater was pumped through the column. Raw groundwater and filtered water samples were collected periodically (3 - 4 times a week) and were analyzed for total As concentrations.

Results and Discussion

Removal of arsenic in the form of arsenite

In anoxic groundwater, arsenic is present in the form of arsenite (products of H_3AsO_3) due to the reducing conditions. After aeration in the Hanoi water treatment plants, most Fe(II) is oxidized to Fe(III). After Fe is completely oxidized, the dissolved oxygen increases and then facilitates the oxidation of As(III). In treated water of the water treatment plants, As(V) concentration after aeration varied substantially with a

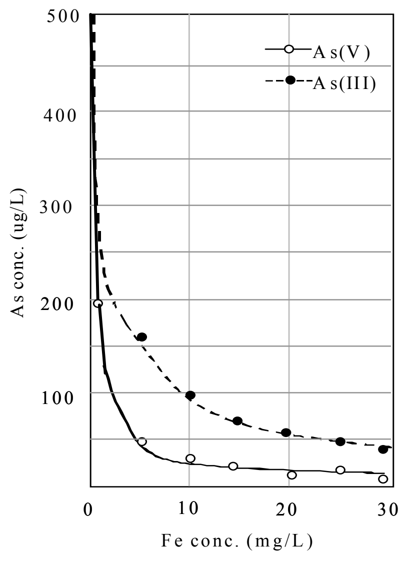


Figure 1. Removal ability of precipitated iron (oxy) hydroxides for As (III) and As (V)

maximum level of about 20 % of total As concentration. However, the co-precipitation and the mechanism of sorption is much more efficient for As(V) as compared to As(III). To clarify this the sorption capacity of As(III) and As(V) onto iron (III) hydroxide under the conditions of the water treatment plants in Hanoi was investigated.

Figure 1 shows the As sorption capacity of Fe(III) hydroxide in the sorption experiment. Fe(II) concentrations of 1, 5, 10, 15, 20, 25 and 30 mg l^{-1} were used and the As(III) concentration was kept constant at 0.5 mg l^{-1}. The sorption of As(III) increased with increasing Fe(II) concentration. As shown in Figure 1, to reduce the As concentration to below the Vietnamese Standard (0.05 mg l^{-1}), a minimum Fe(II) concentration of 25 mg l^{-1} was required. If this technique is applied for water treatment plants in Hanoi, it is difficult to reduce As concentrations to the WHO standard (0.01 mg l^{-1}). Therefore, the possibility of lowering As concentrations in supplied water in the form of As(V) have been further investigated.

Removal of arsenic in the form of arsenate

In this experiment, As(III) was oxidized to As(V) using hypochlorite. In the water treatment plant, the active chlorine solution was added in excess (0.5 mg l^{-1}) for complete oxidation of As(III) to As(V). The sorption isotherm for As(V) onto iron (III) hydroxide showed that the adsorption capacity for As(V) is much more efficient than that of As(III) (Figure 1). For example, with a relatively low Fe concentration of 5 mg l^{-1}, the As concentration can be substantially reduced to a level below 0.05 mg l^{-1}. If treated water contains As concentrations <0.5 mg l^{-1}, the required Fe concentration for lowering such As levels should be > 5 mg l^{-1}.

Influence of chlorine concentrations in lowering As concentrations

In this experiment, chlorine concentrations ranging from 0.25 to 1.25 mg l^{-1} were used and the initial As(III) concentration was kept constant at 0.5 mg l^{-1}. The capacity for total inorganic As removal (%) was examined with Fe concentrations of 1, 5, 15 and 25 mg l^{-1} (Figure 2). Interestingly, the removal efficiency remained constant at more than 80 % for relatively high concentrations of Fe. However, for lower Fe concentrations, the removal efficiency curve had a maximum and the efficiency decreased thereafter with increasing chlorine concentrations (Figure 2). This phenomenon may be due to the oxidation of other compounds or/and the formation of other Fe species (Meng *et al*., 2000). Fortunately, the Fe(II) concentration in groundwater of the Red River Delta is quite high (average 15 - 20 mg l^{-1}). The effect of other compounds such as silicate and phosphate was not investigated in this study.

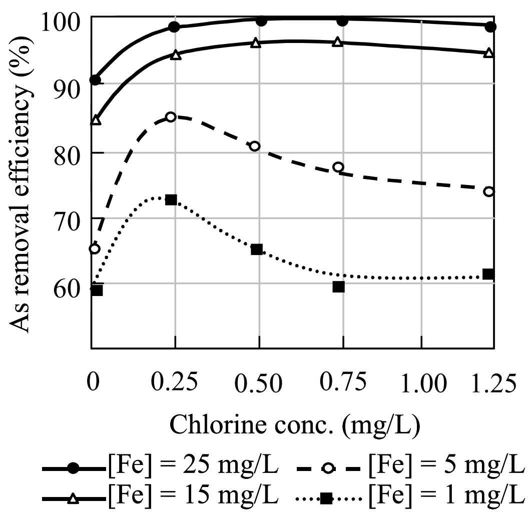
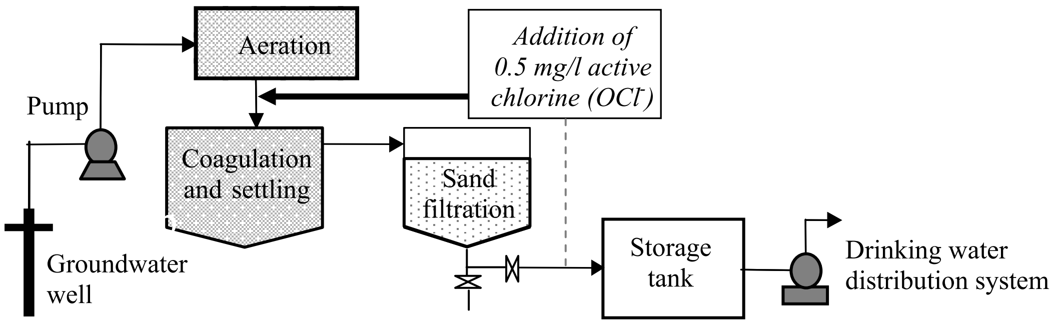


Figure 2. Influence of active chlorine concentrations on As removal efficiency.

Treatment of As in urban Hanoi water treatment plants using hypochlorite.

Based on the efficiency of As removal in the form of As(V), it was proposed to add hypochlorite right after the aeration step in the conventional process for water treatment in the urban Hanoi water treatment plants (Figure 3). After aeration, Fe(II) was fully oxidized to Fe(III), and As(III) was oxidized to As(V). The removal of As(V) was efficient and the hypochlorite can also act for water sanitation purposes. It is therefore suggested that this process can be applied for lowering As concentrations in the city water treatment plants. In this process, the added amount of ClO^- depends on the chemical composition of the groundwater and the fact that the residue must be of 0.5 mg l^{-1} chlorine.

Figure 3. Proposed schematic diagram for additional oxidation by active chlorine in the water treatment process of the urban Hanoi water treatment plants

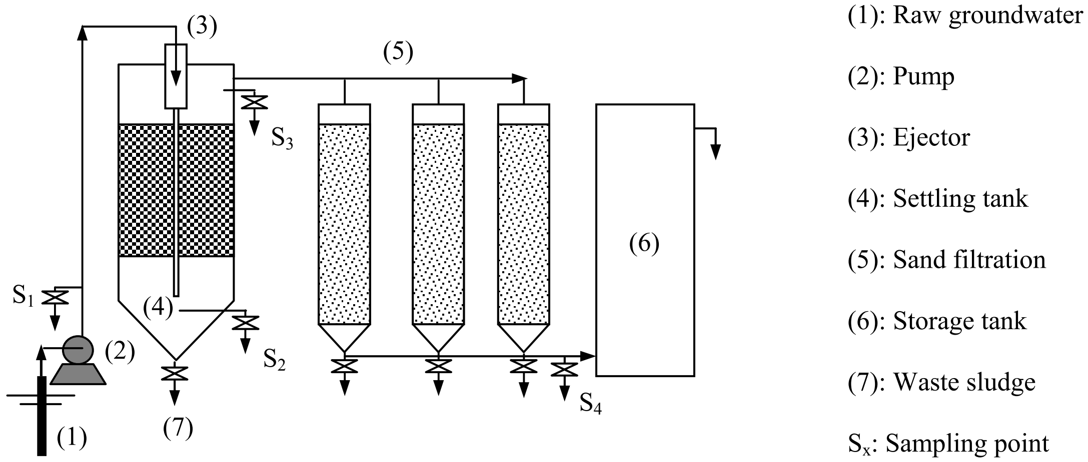


To further investigate the suitability of this method for As removal in water, the removal efficiency on the pilot equipment for groundwater treatment that is currently installed in one city water treatment plant was also tested (Figure 4). Groundwater is pumped from a 40m deep well (1) to an ejector (3) placed in a pre-filtration tank (4). The oxidation of Fe(II) to Fe(III), precipitation of iron(oxy)hydroxides and co-precipitation of As(V) takes place in this tank. After coagulation and pre-filtration, the water is transferred through the sand filtration system (5) and finally to the reservoir (6) (Figure 4). In order to evaluate the quality of the raw groundwater, samples were taken and were analyzed for total Fe, As, phosphate, soluble silicate concentrations, dissolved oxygen and pH continuously for 2 weeks. The composition of the groundwater before treatment in the pilot plant is presented in Table 1.

Table 1. Composition of groundwater before the pilot water treatment system

Composition	Total Fe (mg l^{-1})	Total As (µg l^{-1})	DO (mg l^{-1})	pH	PO_4^{3-} (mg l^{-1})	Soluble Si (mg l^{-1})
Level	25.5	20.1	1.2	6.8	0.12	4.36

Figure 4. Schematic diagram of the water treatment pilot system installed in a city water treatment plant



Because the initial Fe(II) concentration is quite high, Fe(II) was not added into the pilot system. To assess the ability of As removal, As(III) was introduced in the form of AsO_3^{3-} with a series of concentrations from 0.15 to 1.7 mg l^{-1}. The results are presented in Table 2 and Figure 5.

Figure 5. As concentrations in the inlet and outlet of the pilot equipment as an indication of As removal

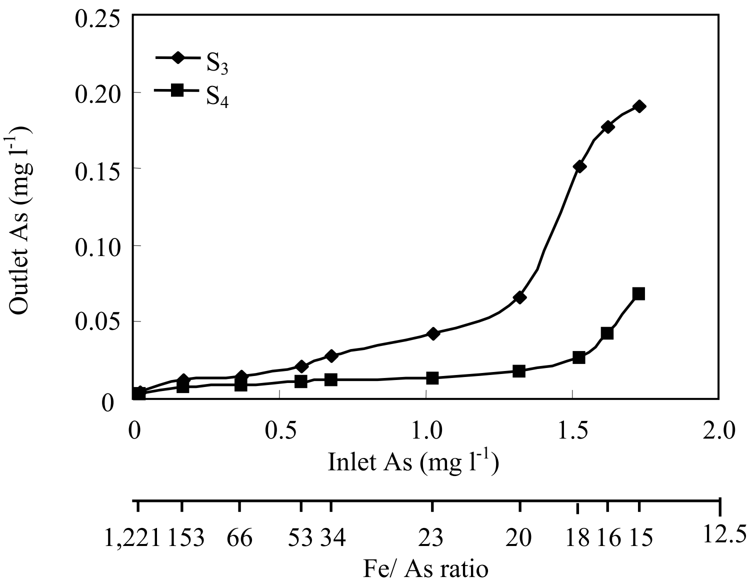


Table 2. Arsenic removal efficiency at different sampling points in the pilot water treatment system (Ref. Figure 4)

Spiked As ($mg\ l^{-1}$)	Fe/ As ratio	As ($mg\ l^{-1}$) and Fe ($mg\ l^{-1}$) at sampling points							
		S_1		S_2		S_3		S_4	
		Fe	As	Fe	As	Fe	As	Fe	As
0.00	1,221	25.64	0.021	22.36	0.020	1.42	0.004	0.53	0.003
0.15	153	26.54	0.173	-	-	2.86	0.012	0.32	0.008
0.35	66	24.56	0.372	-	-	2.61	0.015	0.11	0.009
0.55	53	30.41	0.574	-	-	1.34	0.021	0.43	0.011
0.65	34	23.32	0.677	-	-	1.86	0.028	0.08	0.012
1.00	23	23.43	1.024	-	-	1.67	0.043	0.12	0.014
1.30	20	26.52	1.319	-	-	2.06	0.066	0.01	0.018
1.50	18	27.04	1.522	-	-	4.32	0.151	0.01	0.027
1.60	16	26.02	1.621	-	-	4.22	0.177	0.08	0.043
1.70	15	26.05	1.725	-	-	3.75	0.191	0.21	0.068

It is clear that for As concentrations in the pre-filtration tank (sampling site S_2) that is based on the co-precipitation of As(V) onto ferric hydroxide with initial Fe concentration of around 25 $mg\ l^{-1}$, only about 1.3 $mg\ l^{-1}$ As in groundwater could be removed, with an initial concentration ratio of Fe/As = 20. After the sand filtration, As was continuously removed and the efficiency of As removal in the whole pilot system was increased (with initial Fe/As concentration ratio of 16).

Household sorption and filtration system

In Vietnam, private wells have been used for a long period of time in rural and sub-urban areas. In 1990s, UNICEF's pumped tube well systems have been widely developed and used throughout the country. The UNICEF wells have played a very important role and are the main source of water supply for many people in Vietnam, when surface water was contaminated. However, as mentioned above, recent findings of the unexpected severe As pollution in groundwater raised a serious concern that millions of people living in rural and sub-urban areas are consuming As-enriched groundwater and are at risk for As poisoning (Berg *et al.*, 2001). Due to the lack of knowledge and education, the risk of As exposure for people in rural areas may be more serious. In this study therefore the applicability of naturally occurring iron minerals having a high sorption capacity for some inorganic ions, including As(III) and As(V) was also investigated. Such minerals, namely laterite and limonite, are abundant in Vietnam (Ha Tay, Vinh Phu Province in Northern Vietnam) and are often relatively clean. It was anticipated that these minerals could be used as potential sorbents for a household sorption and filtration system to lower arsenic concentrations in tube wells.

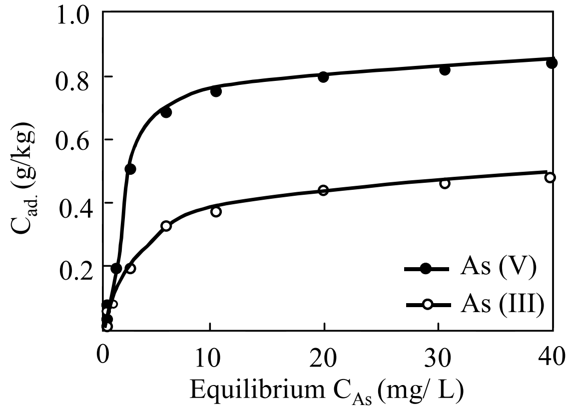


Figure 6. Sorption isotherm of As (III) and As (V) onto limonite (initial As conc. = 500 μg l^{-1})

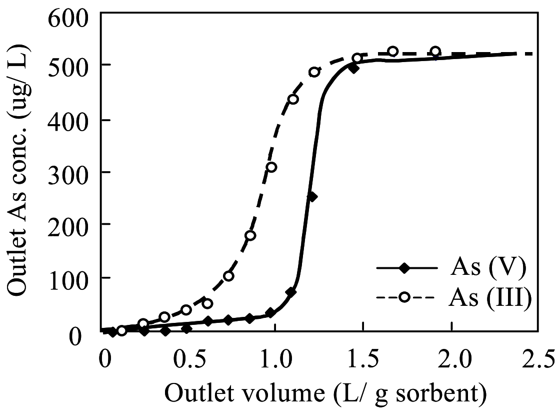


Figure 7. Breakthrough curves of sorption of As(III) and As (V) for limonite (initial con. = 500 μg l^{-1})

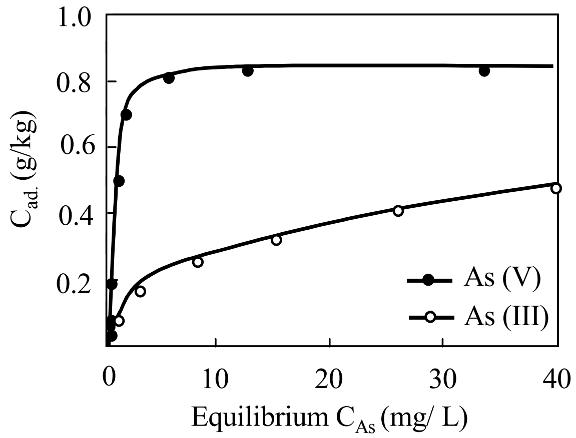


Figure 8. Sorption isotherm of As(III) and As(V) onto laterite (initial conc. = 500 μg l^{-1})

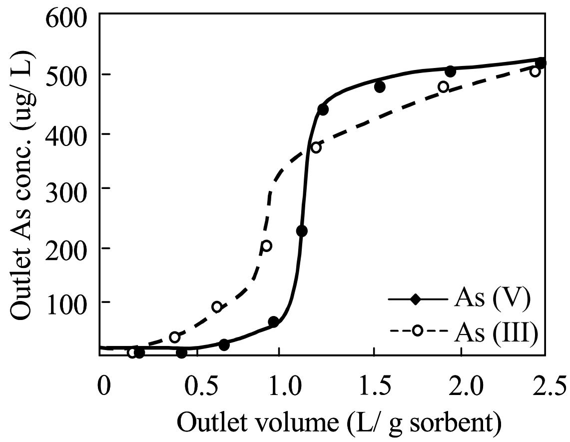


Figure 9. Breakthrough curves of sorption of As(III) and As(V) for laterite (initial conc. = 500 μg l^{-1})

Table 3. Laterite and limonite composition and As content

Material	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	As_2O_3 (mg kg^{-1})		
						Initial	After washing by alkali solution	After heating at 900°
Laterite	40.96	14.38	32.14	0.14	0.18	41.83	33.77	5.36
Limonite	11.25	4.12	84.24	0.25	0.16	16.25	14.27	1.29

Laterite and limonite minerals were collected, treated, sieved and subjected to determination of composition as well as naturally occurring As contents. The results of the analysis of laterite and limonite compositions and As contents in these minerals is shown in Table 3. Sorption isotherms and breakthrough curves of limonite and laterite are shown in Figures 6 and 7 and Figures 8 and 9, respectively. A Langmuir sorption isotherm was able to describe the sorption kinetics of As(III) and As(V) onto laterite and limonite. It is clear that the sorption capacity of As(V) is apparently higher than that of As(III), suggesting the suitability of using these materials to remove As in the form of As(V) from groundwater.

Based on the sorption isotherm, the sorption capacity of limonite for As(III) and As(V) was calculated as 500 and 900 mg kg^{-1}, respectively. For laterite, the sorption capacity was slightly higher [600 mg kg^{-1} for As(III) and 1100 mg kg^{-1} for As(V)], suggesting a more effective sorption ability of this mineral for lowering As concentrations in groundwater using household-based filtration and adsorption system. Further, the arsenic concentrations before and after the sorption column were also tested. The initial results show that this system was able to reduce As concentrations below the Vietnam Standard of 0.05 mg l^{-1}. In addition, manganese was also efficiently removed and there was no contamination by sorbent-originated elements. Further investigations are necessary to provide detailed information on the efficiency and capacity of arsenic removal of this household water treatment system.

Conclusions

The preliminary investigations into suitable techniques for lowering As concentrations in water treatment plants of Hanoi city and household adsorption and filtration systems for rural and sub-urban areas indicates that As can be efficiently removed from drinking water in the form of arsenate. In the water treatment plants, hypochlorite (NaClO) for oxidizing As(III) to As(V) was added to the conventional process applied in the plants. With a Fe concentration of 5 mg l^{-1}, As concentrations can be lowered to a level below the Vietnam Standard from an initial concentration of 0.5 mg l^{-1}. The investigation of the pilot scale equipment indicates that removal of As in this system is more effective than that in the laboratory experiments. For smaller scale water treatment systems in rural and sub-urban areas, naturally occurring minerals such as laterite and limonite, can be used as potential sorbents for As in adsorption and filtration columns. The relatively high sorption capacity for arsenite and arsenate of these minerals suggests the suitability of using them in household-based water treatment systems.

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Drinking Water Quality in Cambodia

Country Report
Prepared by the Ministry of Rural Development Department of Rural Water Supply

Introduction

The quality of drinking water is important to human health and to provide a safe drinking water supply is one of the main objectives of Cambodian National Policy. Therefore, to gain a better understanding of levels of drinking water quality, the Royal Government of Cambodia initiated a survey in 2000 to identify potential human health threats from low quality drinking water throughout a significant portion of Cambodia. With the WPRO's financial and technical support and UNICEF, the government agencies, responsible for water resources and water supply management in the country collectively assessed the water quality in drinking water supply.

Country Profile

Cambodia is located in Southeast Asia between latitudes 10° and 15° N. and longitudes 102° and 108° E. The country covers an area of 181,035 km². Cambodia is bordered by Vietnam in the east and southeast, the Lao PDR in the north and by Thailand in the north and northwest. To the southwest the country has a seacoast on the Gulf of Thailand.

The central plain comprises 75% of the land area and lies between 10 to 30 meters above sea level. The Central Plain is drained by the Mekong river, the Tonle Sap River and by the Bassac and a number of smaller tributaries. The main feature of the Central Plain is the Tonle Sap Lake, the Great Lake. The Lake has an average surface area of 8,155 km² and an average storage volume estimated at 15.9 billion m³. It constitutes the largest single storage and source of inland fresh water. The central plain is surrounded by a sandstone mountain range in the north where it forms the border with Thailand, by granite mountains in the southwest and south and a basaltic plateau in the northeast of the country.

The temperature across the country ranges from a mean daily minimum of 19° C in January to a mean daily maximum of 35° C in April. The mean annual relative humidity values range from 75% to 80%.

Cambodia belongs to the Asian tropical monsoon zone with two main seasons in the year, a dry and a rainy season. The dry season starts from the end of November and ends in April, while the rainy season lasts from May to November. In the rainy season winds with moisture from the Gulf of Thailand provide rain irregularly as far as 200 km inland. During this season riverside areas in the central plain are inundated.

Cambodia is divided administratively into 20 provinces and 4 municipalities. Agriculture, fisheries and timber dominate the economy. According to the 1998 census, Cambodia had a total population of 11.4 million, of which more than 81% live in rural areas.

Brief History

The roots of Khmer culture lie in the flooded plains of the Mekong basin and between the first and eight centuries the independent village-based societies were united a under more centralized authority to form tributary polities. From the ninth to thirteenth centuries the Empire of Angkor ruled over the whole region. However, Khmer state power waned from the fifteenth century and in the nineteenth century it fell to the neighboring powers and subsequently came under European colonial rule. Prince Sihanouk was put on the throne by the French colonial rulers in 1941. King Sihanouk led the nation to independence in 1953. Unfortunately the young and newly independent nation was forced into a regional war by the major powers and suffered the turmoil of a prolonged civil war. The Cambodian people strived and gained peace back with the help of international communities in October 1991, through the Paris Accords. Under the supervision of the UN, Cambodian people and the Royal Government have established the Kingdom of Cambodia and the Royal Government of Cambodia in 1993. Cambodia is a constitutional monarchy. The constitution vests exclusive legislative power in the National Assembly and government is through sectoral ministries and provincial administrations.

Water Resources

In Cambodia, both surface water and groundwater are used for drinking water. The Mekong River and the Tonle Sap Lake are the predominant sources of surface water, with the Mekong serving the east and the Great Lake serving the more westerly populations. The river system provides abundant and good quality drinking water. Applying the WHO standards, these resources require only basic treatment including disinfection. Provincial towns generally have access to surface water from the river systems in unlimited quantities.

Like other tropical countries, surface waters in Cambodia are affected by the seasonal conditions. During the flood season the Mekong's flood-flow enters into the flood plain on both sides of the main channels through many side channels and over the banks.

The Great Lake (Tonle Sap) represents a vast natural storage; it covers an area, which increases from 2,500 km^2 in the dry season to 13,000 km^2 by the end of the rainy season. Recharge of suspended matter follows accordingly and circulation of chemical discharges from industry and of pesticides and fertilizers from agriculture is also a rainy season occurrence.

In most areas groundwater is also available in large quantities throughout the year. Groundwater is generally suitable for public supply after disinfection and without any other treatment. Fine sediment can be a problem in some places, and the use of groundwater can be environmentally sensitive. Many areas exist where groundwater is relied upon because of the shortage of surface water in the dry season.

Groundwater use remains more popular in rural areas and some in smaller urban centers. More than 81% of the population is rural, and close to 60% of this group use groundwater. In contrast, only 15% of Phnom Penh consumes well water. Hand dug wells (or open wells) are widely used throughout the country, but the trend towards drilled wells with hand pumps will continue as the rural development efforts succeed.

Water Supply Status

Construction of water supply and sanitation facilities has been ongoing in Cambodia since the late 1970s. In the period between 1979 and 1994 activities mainly focused on the provision of emergency water supply facilities in areas where security conditions were favorable. In the early 1990s, as security improved and political stability was restored, the water supply sector's focus began to shift from emergency relief to long-term development. During the course of the past 20 years significant results have been achieved in a number of areas, including the water supply sector. According to the 1999 Socio-Economic Survey, 54.3% of the total population has access to safe water supply services as illustrated below.

Source %	Cambodia %	Phnom Penh %	Other urban%	Rural %
Piped in dwelling	5.1	45.4	7.2	0.7
Public Tap	1.3	2.9	1.6	1.1
Tube/piped well of borehole	19.0	8.0	24.8	19.4
Protected dug well	22.1	6.4	18.1	24.2
Rainwater	0.7	-	2.0	0.6
Tanker, truck or otherwise bought	6.1	31.5	12.8	2.6
Subtotal for protected sources	**54.3**	**94.2**	**66.5**	**48.6**
Unprotected dug well	15.5	0.4	9.7	17.8
Pond, river or stream	28.3	5.0	22.3	31.5
Other	1.9	0.4	1.5	2.0
Subtotal for unprotected sources	**45.7**	**5.8**	**33.5**	**51.4**
Total	**100**	**100**	**100**	**100**
Number of households in (000)	2,093	174	214	1,705

Of the total urban population of 1.79 million (1998 census), nearly a million live in the capital city of Phnom Penh while 0.8 million are distributed over the remaining 23 urban centers (20 provincial towns and 3 municipalities). The availability of water supplied by piped line in the provincial/municipal towns is as low as 15%, with service restricted to the central core areas of the town.

Water Supply Agencies and Their Role

The provision of drinking water falls within the responsibility of key ministries and public entities. The Ministry of Industry, Mines and Energy (MIME), The Ministry of Rural Development (MRD) and the Phnom Penh Water Supply Authority (PPWSA) are the three main agencies but others are also involved. A complete listing is provided in the table overleaf.

International Organizations and NGOs collaborate with and support these national agencies. Cambodia is a member of international and UN agencies including the WHO. The responsibilities of the government institutions are mostly separate from one another, but there are also some areas in which they collaborate and cooperate.

Agency	Role and Responsibility
PPWSA	The PPWSA serving the capital city of Phnom Penh is the largest provider in Cambodia. It operates as an autonomous public enterprise. PPWSA has three water treatment plants and in the near future a new treatment plant and an expanded treatment plant will be added to treat about 235,000m³ per day. PPWSA has implemented several water quality monitoring activities including the routine quality control in the treatment processes, general water quality analysis and distribution network quality control.
MIME	The Department of Potable Water Supply (DPWS) under the MIME is responsible for the development of urban water supply systems outside Phnom Penh. The DPWS is in charge of the promotion of piped water supply systems, with monitoring of water quality and water tariffs, and with technical assistance to the public and private drinking water suppliers. To effectively monitor water quality, the DPWS needs national standards for safe drinking water as well as a central laboratory and some regional lab capacity. The Technology and Standards Office of the Department of Industrial Technology (DIT) under the MIME analyzes bottled water quality for manufacture certification. A National Water supply Policy has been enacted in year 2000.
MRD	The Department of Rural Water Supply (DRWS) under the MRD is responsible for community water supply in rural areas. The DRWS collaborates with International Organizations/NGOs and with private sector initiatives to guide development of the rural water supply sub-sector. The MRD has issued the National Policy Framework for Rural Water Supply and Sanitation in 2002, which outlines the needs and approaches for community responsibility and self-help and private sector participation and the role of IO/NGOs. Beneficiary communities have been educated on the safe use and maintenance of their new facilities. Water Use and Hygiene Education is usually provided. In the rural water supply sector, water quality testing and laboratory capacity is generally very inadequate. Only a few parameters such as pH, Iron and Salinity are normally measured on-site using portable equipment.
MOWRAM Ministry of Water Resources and Meteorology	The MOWRAM is responsible for the overall management of the nation's water resources. Groundwater and Surface water policies focusing on irrigation in particular are included. The main activities are in the lower Mekong basin under the supervision of the Department of Hydrology and River Works in the lower Mekong basin. MOWRAM has completed a draft National Water Policy with support from the ADB and involving other water sector ministries. A National Water Sector Profile was also completed and has been discussed among the water sector players, including development of national drinking water quality standards.
MOH Ministry of Health	The Department of Food and Drugs under the MOH bears the responsibility for researching water borne diseases. The National Center for Health Promotion (NCHP) is engaged primarily in health communication and education activities.
MOE Ministry of Environment	The MOE is responsible for the conservation of national bio-diversity and environmental aspects of water pollution where it relates to the protection of human health.

Interaction of the Water Supply Agencies

The key water-sector institutions have conducted seminars and meetings on the various aspects of the provision of the drinking water. MRD and MIME provincial staff were, jointly trained in basic drinking water quality testing and monitoring in May 2000, with technical and financial support of the WHO. The Water and Sanitation Coordinating Working Group monthly meeting serves as a forum for all water and sanitation related issues among the government agencies and IO/NGOs in the sector.
There is also inter-ministerial cooperation in National Policy development and long-term strategy formulation.

Major pollution sources and pollutants

In terms of water quality, water pollution is not yet a significant problem. Consumers complain about taste, smell and color. Hard water is frequently cited for its damage to hair and calcium is widely believed to cause the formation of kidney stones. People are concerned about the turbidity of the river water and chlorine smell. Toxic algae in Phnom Penh's raw water and sedimentation tanks were reported in 2000. Toxic algae growths were also detected, especially in the late dry season from April to May in the Tonle Sap. These algae can produce toxins and release them into drinking water supply.

Pathogens are commonly found in surface water, however, and arsenic has recently been detected in 5 provinces in concentrations that exceed WHO standards. In August 2000, MRD and MIME completed a nationwide survey on the chemical quality of urban and rural drinking water sources with technical and financial support from the WHO. Drinking water sources representative for thirteen provinces were sampled and analyzed for more than 80 chemicals and pesticide compounds by a certified laboratory in Australia.

The survey reported that the chemical quality of most urban and rural drinking water sources was generally good. No pesticides were detected in any of the samples. Although not the subject of the survey, bacteriological quality was emphasized as the priority for the safe drinking water. Nitrites and nitrates were detected at elevated levels in several locations. Contaminants such as barium, chromium, fluoride, lead, manganese, molybdenum, and selenium were also found but appeared to be exceptions to the general trend. On the other hand, iron and other aesthetic concerns like hardness proved a significant issue for many rural consumers of groundwater.

The most significant finding of the survey was the naturally occurring arsenic in groundwater from certain areas in Cambodia. The element was detected at levels above the WHO guideline value of $10 \mu g\ l^{-1}$ in five of thirteen surveyed provinces. Some 9% of the randomly selected groundwater sources were affected with arsenic. The MRD hosted an inter-ministerial meeting to share the survey results, and the arsenic finding in particular. The meeting called for inter-ministerial efforts towards developing national drinking water standards and a national monitoring capacity. The findings were submitted to the Council of Ministers recommending a national arsenic response to be led by the MRD. Meanwhile the MRD has begun further field surveys with NGO partners to delineate the extent of the arsenic occurrence in three provinces, with WHO and UNICEF support.

Water Quality Standards and Water Quality Test/ Analysis Formats

Due to the lack of a National Standard for drinking water quality, different standards for some chemicals in drinking water, are used by individual laboratories in Cambodia as shown below:

Parameters	PPWSA	MIME
1. Color	x	x
2. Conductivity	x	x
3. Odor	x	
4. pH values	x	x
5. Suspended solids	x	
6. Turbidity	x	x
7. Total dissolved solids	x	x
8. Carbon dioxide	x	
9. Calcium hardness	x	x
10. Magnesium hardness	x	x
11. Total hardness	x	x
12. Aluminum	x	
13. Chloride		x
14. Chlorine	x	x
15. Copper	x	
16. Fluoride	x	
17. Iron	x	x
18. Manganese	x	
19. Nitrate	x	
20. Nitrite	x	
21. N-Ammonia	x	
22. Phosphorous	x	
23. Potassium	x	
24. Sulfide	x	
25. Sulfate	x	
26. Zinc	x	
27. Cyanide	x	
28. Chromium	x	
29. Coliform	x	x
30. E.Coli	x	x
31. Bacteria aerobes		

The water quality standard of the Pollution Control Department (PCD) of the Ministry of Environment shows higher values for the parameters. This is because its purpose is to control the pollution of the natural water sources.

The internal drinking water quality standards in Cambodia are mainly adopted from international standards or guideline values. This is partly donor driven with no reference to the actual situation in the country. Since Cambodia was under French colonial rule for nearly 100 years, French standards are still in popular use. During the UNTAC, when multinational experts started their missions in Cambodia, water quality was defined according to their recommendations.

The WB/UNDP technical team adopted WHO guideline values and referenced EU guideline values for drinking water for the Phnom Penh water supply. Health sector education in Cambodia is based mostly on the French system, and thus the National Laboratory (MOH) favors French standards for drinking water quality. However, during 1998 and 1999, the laboratory made changes in the numbers of parameters and the values of these standards by adopting values from WHO, Germany, Malaysia and Thailand.

The water quality standards differ according to their applications. PPWSA standard values are presented under two headings: the highest desirable level and the maximum permissible level. This was done because the values reflected existing international standards, but allowances were still needed to guide authorities faced with an inefficient treatment plant. Most of the PPWSA values are similar to the WHO Guideline values. The National Laboratory relies more upon microbiological parameters because bacteriological quality is much more the domain of the health sector than chemical constituents. The higher values of some chemical parameters found in the water quality standards of the Ministry of Environment are typical for use in monitoring untreated surface water and groundwater. These are not yet strictly aimed at drinking water quality monitoring.

National capacities in monitoring water quality and safety

The procedures for water quality monitoring also differ from one department to another. Among the laboratories engaged in water quality monitoring in Cambodia, the PPWSA and MOWRAM laboratories are the most efficient and experienced.

PPWSA monitors water quality in three levels (Routine tests at treatment plants every day; weekly tests of selected samples from the distribution system; and a general test of 32 parameters monthly). MOWRAM conducts monthly sampling of water from eleven stations along the Mekong and Tonle Sap rivers. DPWS of MIME intend monthly tests for provincial water supply works, but practically only quarterly tests have been done due to logistical constraints. The National Laboratory of MRD carries out occasional quality control of locally marketed bottled drinking water and ice. The MRD usually apply initial analysis for all newly constructed rural water supply facilities, mostly drilled wells with hand pumps.

Legislation, standards, regulations, and implementation guidelines

It is the mandate of the MRD to improve access to safe water supply and sanitation services in rural areas. In collaboration with other key line ministries, the MRD issued the "Water and Sanitation guidelines" in 1995 and the "Policy Framework for Rural Water Supply and Sanitation Sector" in 2001.

Contributions from other ministries include a "draft on water resources management" that is now in the final stages of preparation under the overall guidance of MOWRAM, while legislation for an appropriate water sector regulatory framework and water tariff reform" is being drafted by MIME.

A sub-decree on water pollution control was issued in April 1999 to support the authority of the Ministry of Environment on water pollution control. The MOE is committed to developing a national action plan for prevention of pollution of water sources. It consists of the establishment of national standards for pollution sources, including wastewater discharges to public areas or sewers. Collection and evaluation of data and the analysis of the results are part of the development of the national action plan, which is expected to be completed within three years.

MAJOR LIMITATIONS AND CONSTRAINTS

Water Quality and Health

The use of unsafe water and improper disposal of human wastes, in combination with low hygiene awareness, can result in sickness that prevents people from working and being productive, thus contributing to increased levels of poverty. The impact that lack of access to safe water supply services can have on health is indicated by high infant mortality rate of 89.4 per 1,000 live births. In Cambodia most infectious water related diseases are transmitted primarily through human and animal excreta. The majority of the rural population uses such water for drinking or for preparing food. The human pathogens transmitted orally by drinking water that present a serious risk of disease among the Cambodian population have been identified by Pasteur Institute Phnom Penh and other national hospital and private laboratories as *Salmonella enterica, Salmonella typhi, Salmonella paratyphi A,* other Salmonella, *Shigella flexneri, other shigella, Escherichia coli, vibrio cholerae, Campylobacter jejuni and coli*. Results from epidemiological studies on human feces show nearly 30.7% among 2170 samples containing one or more parasites. *Schistosomiasis Mekong* is found in the Mekong River where people that are living along this river are infected, primarily through contact with water during bathing or washing.

In Cambodia the failure to provide adequate protection and effective treatment of water exposes the community to the risk of intestinal and other infectious diseases such as diarrhea, dysentery, typhoid fever, cholera, parasites and gastro-enteritis.

The problems associated which chemical constituents of drinking water arise primarily from their ability to cause adverse health effects after prolonged periods of exposure. However, the Ministry of Health is unable to collect the information on health risks due to toxic chemicals in drinking water.

Issues

People see an important link between water and health, although there is generally very little information available at the community level regarding these issues. Infectious water related diseases are still endemic throughout Cambodia and the bacteriological contamination of drinking water is one of the most important health-related concerns. No pesticides were detected in any of the samples tested in a WHO assisted survey in 2000. It is concluded that pesticides do not currently present a significant health threat in Cambodia's drinking water.

However, it is important to note that the improper use or disposal of pesticides can result in occupational health problems and/or environment threats.

The major rivers in Cambodia appear to have very good chemical water quality. With proper treatment to remove suspended matter and neutralize harmful bacteria, this surface water can provide high quality drinking water. The chemical quality of Cambodia's groundwater presents greater challenges than that of its surface waters. Groundwater from certain areas may contain chemicals that could pose concerns for human health. Most of these chemicals are naturally occurring, although a few may result from human activity such as high nitrate levels. The most important finding of the WHO assisted Water Quality Assessment Survey in 2000 from a human health perspective is that in certain areas groundwater contains elevated levels of arsenic. Further testing will be needed to more accurately determine the extent of the arsenic problem in Cambodia. A few other chemicals including barium, chromium, fluoride, lead, manganese, molybdenum, nitrate, nitrite, and selenium were detected in the study areas. Nitrate and nitrite have been detected at levels exceeding their respective WHO Guideline Value in several locations. Consumers are more concerned with taste, odor and appearance of water than with other qualities. Therefore acceptability of groundwater is critical to the long-term success of water supply wells in rural areas. Several widespread misconceptions regarding the connection between water quality and health exist. The most frequently encountered misconception about water and health is the belief that calcium or hardness in drinking water causes kidney stones. Improved education of authorities in the water sector and of community members on this issue is warranted.

Recommendations

- A central national laboratory could be established, which should be independent from the key ministries, although these ministries should rely on this laboratory for 'Quality Assured' analyses.
- A national standard for all drinking water including tap water, bottled water, well water, etc. should be established as soon as possible so that monitoring of drinking water quality could be developed and improved. Such efforts require high-level commitments from several key agencies and input from technical experts and the support of external agencies.
- National and regional laboratory-supported monitoring networks should be set up to support the application of the national standards. Monitoring should be independent from the service providers and proactive with communities involved.
- Geological information, including available drilling logs from water supply programs, should be developed as an overall response to the arsenic issue.
- The concerned departments should take follow-up actions where water supplies exceed recommended health-based limits for chemicals.
- A greater emphasis on water quality should be placed in the RGC's policies and practices regarding water supply development.

Establishment of the National Standard for drinking Water Quality

The immediate task for water supply sector in Cambodia is to establish a National Standard for drinking water quality. Since each department uses various standards, depending on their own purposes, there is no standard and where there is, it is mostly introduced by the donor or funding agencies regardless of national requirements. The National Standard should be realistic and related to the actual requirements of the people's health.

Development of a National Water Quality Surveillance and Monitoring System

At present, various departments are monitoring water quality depending on their requirements not reflecting the consumers' health requirements. Even the water supply service providers are carrying out the monitoring for their operational purposes. Therefore, RGC should mandate one government agency to conduct monitoring and surveillance on behalf of the consumers as per the National Standard. This agency should not be a service provider but preferably a public health authority (or independent agency) with a mandate to protect the people's health and enforcing the National Standard.

Follow-up Nationwide Study on the Groundwater Quality for major health hazards

As found in the preliminary survey of the chemicals in groundwater, some hazardous chemicals have been detected in groundwater in Cambodia. Immediate action is required to conduct nationwide surveys for hazardous chemical constituents such as arsenic and fluoride. Such action requires cooperative efforts of all stakeholders, particularly of key players in the water supply sector with technical and financial support of IO/NGOs and external support agencies. In such action, the RGC requests the WHO to play a key role in facilitation and cooperation with regional and international partners.

Drinking Water Quality in the Lao People's Democratic Republic

Country Report prepared by
Dr Tayphasavanh Fengthong[1], Dr Somphone Dethoudom[2], Dr Onechanh Keosavanh[3]

Introduction

The Lao People's Democratic Republic or Lao PDR is a landlocked country covering an area of 236 800 km². The country shares its borders with the Socialist Republic of Vietnam, Kingdom of Thailand, Kingdom of Cambodia, People's Republic of China and Myanmar. Mountains cover about two thirds of the land area with altitudes ranging from 200 to 2820 m. There are 16 provinces, one municipality and one special region, 142 districts, and 10 912 villages. Lao PDR has a population of 5.3 million. The urban population constitutes 20% of the total population. The high mortality rate and low life expectancy reflect a low level of overall health conditions in the country. Malaria is the most serious public health problem. Acute respiratory illness and diarrhea also remain major causes of child mortality. About 55% of the total population has access to safe water, and 40% to proper sanitation facilities. Diarrhea, cholera, hepatitis and intestinal parasites are all listed as important communicable diseases. Most of these diseases are transmitted by the faeco-oral route and are, consequently linked to poor sanitation and water quality, poor hygienic practice and to inadequate available quantities of water.

Surface and ground water contamination

A quality survey of existing water facilities was completed in 1999. A test program over 50 samples from ten provinces was carried out by Ministry of Health with support from UNICEF. The main conclusions were the following:

Community health problems
In 60% of the communities that were using dug wells as their source of water, frequent outbreaks of diarrhea and related diseases occurred. This suggests that the source of the disease may be water borne and originate from the dug wells. Many of these wells were not protected. In comparison, the level of diarrhea and similar diseases in communities using hand-pumps or gravity fed systems (GFS), was much lower; 23% where hand-pumps were used and 16% for communities with GFS.

Water quality problems
It was noted that water from the dug wells had a higher turbidity than recommended in the WHO guidelines. This is probably due to external contamination. All the water pumped by the India Mark III hand pumps had a red iron coloration originating from the hand pump itself. The water from the GFS systems occasionally produced a scum when boiled.

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This is due to the calcium carbonate hardness of the water, likely to be related to the rock units underlying the mountainous areas in which GFS systems are installed.

Level of risks

Seventy percent of dug wells were found to pose intermediate risks to health while twenty percent were considered high risk. Causes of contamination to dug wells are several, with the main causes being the absence of fencing or covers thus allowing the water quality to be directly influenced by surrounding sources of pollution including nearby latrines. Poor drainage or faulty drainage, inadequate sealing and cracks around the wells similarly allow pollution to enter. The use of individually owned buckets and ropes is another obvious cause of contamination. Using hand pumps the risk of contamination was lower with 76% considered low risk, 19% intermediate risk and just 5% high risk. The main risks came from sources of contamination surrounding the pump and from poor drainage. The absence of fencing was of much less importance than in the case of dug wells. In the case of GFS systems 4 out of 6 of the systems were rated at low risk of contamination. The only recognized problem was 'ponding', this can be solved by improving the drainage around the facility.

Elemental concentrations and other measured parameters

Most of these are within the recommended WHO guidelines for drinking water with minor exceptions.

Acidity

Specifically in the south of the country the water is slightly acidic

Odor

The odor of the water was generally good. Where an odor problem did exist, it was usually due to contamination from an inorganic or organic source.

Iron

In 80% of cases where the concentration of iron was above the WHO standard, it was due to the India Mark III hand-pumps. The only health risk due to excessive iron concentrations is that the community may seek another water source as they think that water source is contaminated or dangerous to health because of its red coloration and strong taste.

Manganese

Two of the fifty water samples had concentrations above the WHO guidelines, it was noted that these were two India Mark III hand-pump facilities.

Chromium

All samples analyzed were above the WHO guidelines. There have been limited studies into the health effects of elevated chromium levels in drinking water.

Barium

All samples analyzed were above the level of 0.7 mg l^{-1}. Limited epidemiological studies have been conducted to investigate the health impact of elevated levels of barium.

Naturally occurring arsenic in groundwater
Recently the threat of naturally occurring arsenic in groundwater associated with certain geological formations has been investigated. UNICEF has organized testing of some 200 wells of perceived risk areas within the provinces of Attapeu, Savannakhet, Champassak and Saravan. Some wells have shown levels above the WHO guideline of 10 $\mu g\ l^{-1}$. Only one of the wells exceeded the 50 $\mu g\ l^{-1}$ limit proposed for Lao PDR.

Industrial and agricultural chemicals
These were not significantly present except for minor problems reported from close to some factories e.g. tanneries.

Soil erosion and run off
In the wet season these are mainly natural but there were possibly some human activities affecting this. This mainly affects surface water, with turbidity increasing markedly during this period. The main impact in urban schemes was the need for additional treatment.

Conclusions and recommendations

Currently the environmental risk to water quality caused by human activity is low. The government-led actions on water standards and other national actions such as integrated water resources management and river basin development planning, when fully developed and implemented, will have a marked impact on maintaining a healthy environment. The disease burden in Lao PDR is markedly affected by water quality and water management. Improvements in access to water in remote and near-urban areas plus improvements in drinking water quality will have a positive effect on reducing the burden. A community water quality surveillance system and public health risk assessment are needed in Lao PDR in order to systematically analyze the quality of the water and to know how to prevent public health hazards from different pollution sources. A system of health risk evaluation should be created to target the high-risk systems and as a result improve the health status of the population.

A set of recommendations to provide safer water options, not all just for Lao PDR, but some equally recommended for the countries of the region include:
- Information about the public health risks and hazards should be shared among the countries in South East Asia
- Knowledge and experience in public health risks assessment should be upgraded.
- Public health risk assessments should be conducted in some provinces and an action plan on public health risk control should be formulated.
- Community water quality surveillance programs should be initiated and a National Water Quality Standard should be established.
- The high concentrations of barium and chromium found in the earlier survey should be investigated and an arsenic mitigation program in some affected areas should be launched. The program of test boreholes should be continued.
- Communication for awareness creation should be encouraged and hygiene and health promotion should be brought to remote areas.

Effects of Heavy Metal Concentrations in Waste Water on Rice, Spinach and Earthworm

Prof. Dr. Le Huy Ba[1], *Eng. Nguyen Van De*[2], *Eng. Nguyen Thien Tu, Eng. Nguyen Tho*

Abstract

Heavy metals contaminating soils in areas near Ho Chi Minh City include Mn, Cu, Pb, Zn, Fe and Cd. These metals occur in different concentrations in river water, in the water of canals and in 'soil-contained' water. Heavy metals accumulate in earthworms at very high concentrations and are directly correlated with the concentration of these metals in the soil. Earthworms therefore can be used as an indicator for heavy metal contamination in soils. In vitro experiments show that the influence of Pb^{2+} (0. 63 – 0.75 mg l^{-1}) and Cd^{2+} (0.32-0. 43 mg l^{-1}) can be measured after the 7th day of growth and that after 21 days 100% of the test population is dead. It is further observed that the influence of Cd^{2+} on the growth of rice is stronger than the influence of Pb^{2+}. Morning Glory adapts itself to an environment polluted by Pb but at concentrations of 5.0 mg l^{-1} roots of the plant turn to black and the plant becomes necrotic after one week. At higher concentrations growth is stalled. Cd^{2+} kills Morning Glory at concentrations of 2.5 mg l^{-1}.

Introduction

Little research has been carried out on contamination by heavy metals near HCM City. This paper reports on the results obtained from some experiments aimed at identifying heavy metals in rivers and canals near the city and on the effects of heavy metals contamination on the growth of rice, morning glory and earthworms.

Methodology

In vitro, greenhouse and field experiments were carried out following the standard methods for the examination of water and wastewater of the American Public Health Organization (1992.). Correlation graphs and correlation coefficients were established using the method of Rumxki (Moscow, 1972.). The following main experiments were carried out:

Effects of Pb^{2+} and $Pb(NO_3)_2$ on the yield of rice downstream from Nha Be

Rice variety: VN95.2R.
Control Treatment 1: Waste water from Ho Chi Minh City to Nha Be and IRRI nutrient solution.
Control 2: Pb^{2+} = 0 mg kg^{-1}.
7 Treatments: 1/ Pb_0= 0.2 mg kg^{-1}, 2/ Pb_1= 0.5 mg kg^{-1}, 3/ Pb_2= 0.7 mg kg^{-1}, 4/ Pb_3= 1.0 mg kg^{-1}, 5/ Pb_4= 1.2 mg kg^{-1}, 6/ Pb_5= 1.8 mg kg^{-1}, 7/ Pb_6= 2.3 mg kg^{-1}.

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Effects of Cd^{2+} and $CdSO_4$ on the yield of rice downstream from Nha Be
Rice variety VN95.2R
Control Treatment 1: Waste water from Ho Chi Minh City to Nha Be and IRRI nutrient solution. Control 2: Cd^{2+} = 0 mg kg^{-1}.
7 variants: 1/ Cd_0= 0 mg kg^{-1}, 2/ Cd_1= 0.025 mg kg^{-1}, 3/ Cd_2= 0.315 mg kg^{-1}, 4/ Cd_3= 0.345 mg kg^{-1}, 5/ Cd_4= 0.535 mg kg^{-1}, 6/ Cd_5= 1.5 mg kg^{-1}, 7/ Cd_6= 1 mg kg^{-1}.

Effects of Pb^{2+} and Pb $(NO_3)_2$ on the growth of Morning Glory
Morning Glory from Rach Dia and Nha Be.
Control Treatment 1: Wastewater from HCM City to Nha Be and IRRI nutrient solution. Control 2: Pb^{2+} = 0 mg kg^{-1}
6 Treatments: 1/ Pb_0= 0 mg kg^{-1}, 2/ Pb_1= 1.00 mg kg^{-1}, 3/ Pb_2= 2.5 mg kg^{-1}, 4/ Pb_3= 5.0 mg kg^{-1}, 5/ Pb_4= 7.5 mg kg^{-1}, 6/ Pb_5= 10.00 mg kg^{-1}

Effect of Cd^{2+} and $CdSO_4$ on the growth of water morning glory
Control Treatment 1: Wastewater from HCM city to Nha Be and IRRI nutrient solution.
Control 2: Cd^{2+} = 0 mg kg^{-1}

Table 1. Chemical characteristics of waste water from Ho Chi Minh City (mg l^{-1})

Elements	Fe^{2+}	NH^+_4	NO_3^-	Cl^-	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^+	As^{2+}	pH	EC (mS/cm)
Concentration	20.5	3.6	5.8	568	0.03	0.06	0.01	0.08			6.93	3.48

Results

Heavy metal pollution in the Saigon River and canal systems down stream

Table 2. Heavy metal pollution in the Saigon River.

Fe (µg l^{-1})	Mn (µg l^{-1})	Zn (µg l^{-1})	Cu (µg l^{-1})	Cd (µg l^{-1})
2	0.9	1.7	0.9	10

In river water

Zn (mg l^{-1})	Cu (mg l^{-1})	Cd (mg l^{-1})	Ni (mg l^{-1})	Cr (mg l^{-1})
172	35	1.76	61	114

In suspended organic matter

Table 3. Tidal fluctuations of heavy metal pollution in the Saigon River and canal systems

Place	time	pH	EC-25^{0}C (μS/cm)	Mn (mg l^{-1})	Cu (mg l^{-1})	Zn (mg l^{-1})	COD (mg l^{-1})
Phuoc Loc							
River	17h15	6.5	1602.54	0.30	0.030	0.246	6.4
Field	17h15	6.6	1689.54	0.38	0.024	0.126	5.6
River	1h15	6.7	1688.67	0.80	0.048	0.314	7.2
Field	4h40	6.7	1725.21	0.24	0.008	0.126	6.4
River	5h15	6.9	1733.04	0.28	0.030	0.218	6.8
Field	11h40	6.6	1660.83	0.78	0.022	0.114	6.0
Muong Chuoi							
River	16h	6.3	990.88	0.58	0.046	0.230	15.6
Field	16h	6.3	968.88	0.32	0.042	0.388	6.4
River	23h	6.1	1075.36	0.66	0.034	0.116	6.6
Field	5h30	6.7	948.64	0.24	0.040	0.274	6.8
River	5h30	6.6	955.68	0.20	0.032	0.144	5.6
Field	10h20	6.2	1021.68	0.42	0.036	0.102	6.0

Note: High tide: 6h and 17 h. Low tide: 23h 30 and 11h20.

The fluctuations of heavy metal pollution in the Saigon River and in the downstream canal system are significant. These dynamics depend on the flow of the river, as influenced by tidal fluctuations, the concentration of metals in wastewaters and sampling location. On the fields the concentration is always higher than in the river and in the canal system.

Heavy metal contamination in sediment and soil

Table 4 shows, that while the concentration of heavy metals in itself is not very high the effective exchange between environments is high. It could mean that pollution in this environment is caused by cation exchange between organic matter and hydroxyl in water.

Table 4. Concentration of heavy metals in sediment and soil

		Humic acid					Fulvic Acid				
Material	Site	Acid	Cu	Zn	Fe	Al	Acid	Cu	Zn	Fe	Al
		(%)	(mg kg^{-1})				(%)	(mg kg^{-1})			
Sediment	RO	0.026	10.6	23.5	23.5	34.9	0.186	52.9	19.1	31.4	229.3
	MC	0.015	0.6	9.7	9.7	Trace	0.059	34.8	5.3	5.6	Trace
Soil	RO	0.067	3.2	13.0	13.0	17.9	0.016	2.0	1.4	17.2	12.1
	MC	0.184	5.6	9.2	9.2	23.9	0.023	25.2	6.8	6.0	111.0

Note: RO: Rach Ong canal; MC: Muong Chuoi canal

Table 5. Concentration of heavy metals in 2 soil horizons and in earthworms.

location	Sample	OM (%)	Pb ($mg\ kg^{-1}$)			Mn ($mg\ kg^{-1}$)			Cd ($mg\ kg^{-1}$)		
			2 acid Extraction	activity	Total	2 acid Extraction	activity	Total	2 acid Extraction	activity	Total
Long Thoi	Earthworm			9.0		14.3			0.7		
	A horizon	4.03	0.7	45.0	53.5	24.0	182.2	175.3	0.3	0.5	1.5
	B horizon	3.86	0.7	51.0		48.2			0.2		
Rach Ñia	Earthworm			4.2		10.8			0.0		
	A horizon	4.00	1.3	48.0	59.0	24.2	88.6	65.7	0.1	0.5	1.0
	B horizon	3.62	1.0	32.5		23.4			0.0		

Location	Sample	OM (%)	Cr ($mg\ kg^{-1}$)			Cu ($mg\ kg^{-1}$)		
			2 acid Extraction	activity	Total	2 acid Extraction	activity	Total
Long Thoi	Earthworm		6.3			43.1		
	A horizon	4.03	0.4	12.5	107.0	3.0	33.0	58.5
	B horizon	3.86	0.6			2.5		
Rach Ñia	Earthworm		3.2			36.1		
	A horizon	4.00	0.5	15.5	99.5	5.5	28.0	60.5
	B horizon	3.62	0.3			1.0		

Location	Sample	OM (%)	Zn ($mg\ kg^{-1}$)			Ni ($mg\ kg^{-1}$)		
			2 acid Extraction	activity	Total	2 acid Extraction	activity	Total
Long Thoi	Earthworm		62.5			6.9		
	A horizon		17.1	144.5	69.5	3.1	9.5	42.0
	B horizon		16.6	138.0		3.9		
Rach Ñia	Earthworm		60.2			3.2		
	A horizon	4.00	23.4	161.5	383.0	4.5	12.5	34.0
	B horizon	3.62	10.5	74.0		1.9		

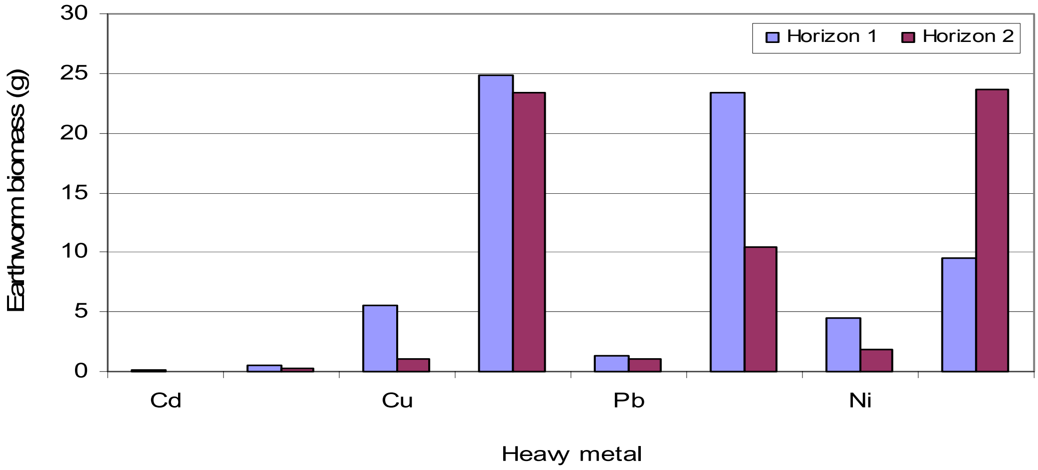
Note: Long Thoi is 25km and Rach Ñia is 34km from HCM City center

Table 5 shows that heavy metal concentration in the A horizon of the soil (0-5 cm) is always higher than in the B horizon (5-25 cm), indicating the surface accumulation of heavy metals.

Accumulation of heavy metals in earthworms

The total cumulative accumulation of heavy metals in the earthworm is about 600 - 650 mg kg^{-1} comprised of Zn 62.5 mg kg^{-1}, Cu 43.1 mg kg^{-1}, Mn 14.3 mg kg^{-1}, Pb 9.0 mg kg^{-1}, Ni 6.9 mg kg^{-1}, Cr 6.3 mg kg^{-1} and Cd 0.7 mg kg^{-1}.

Figure 1. Relationship between heavy metal and biomass of the earthworm



Effect of Heavy metal toxicity on the growing of rice

The results of these experiments are shown in the following tables.

Table 6. Effect of soil heavy metal contamination on rice root growth

Treatments	Root length (cm)
7Th day	
Control	6.60
Contaminated soil	2.40***
Fresh sand	5.20
Original soil	3.70
21st day	
Control	7.20
Contaminated soil	Die***
Fresh sand	7.60
Original soil	5.16
27th day	
Control	13.29
Contaminated soil	17.10
Fresh sand	13.10

Table 7. Effect of soil Cd^{2+} on the growth of rice leaves and stems (cm)

Days after growing	Control		Heavy metal contamination		Sand		Beginning	
	leaves	height	leaves	height	leaves	height	leaves	height
1	-	1.0	-	-	-	1.00	-	1.0
3	-	6.0	-	2.0	-	4.75	-	4.5
5	5.0	10.0	-	5.5	4.5	9.50	3.5-4.5	8.5-9
7	6.0	17.0	3.0-3.5	6.0	4.0-4.5	15.0	4.0-5.0	15.5

Effect of heavy metals (Pb^{2+} and Cd^{2+}) in the nutrient solution of young rice

When the concentration of Pb^{2+} > 0.5 mg l^{-1} the impact on rice growth increases by more than 50% (Table 8). With Cd^{2+} this effect is stronger, with Cd^{2+} > 0.25 mg l^{-1} affecting over 60% of young rice plants (Table 9). There is apparently a limited toxic influence of these two metals, with the LC_{50} of Pb^{2+} being 0.31 mg l^{-1}, and the LC_{50} for Cd^{2+} being 0.121 mg l^{-1}.

Table 8. Effect of Pb^{2+} in the nutrient solution on rice growth (%)

Treatments	Number of plants			Pb^{2+} (mg kg^{-1})		
	1 week	2 week	3 week	1 week	2 week	3 week
Pb_0	80	80	80	0.0	0.0	0.0
Pb_1	80	80	50	0.0	0.0	0.5
Pb_2	80	60	55	0.0	0.3	0.4
Pb_3	60	55	50	0.3	0.4	0.5
Pb_4	50	40	30	0.5	0.6	0.7
Pb_5	45	36	25	0.8	0.9	1.0
Pb_6	30	27	22	1.0	1.1	1.2

Table 9. Effect of Cd^{2+} in the nutrient solution on rice growth (%)

Treatments	Number of plants			Cd^{2+} (mg kg^{-1})		
	1 week	2 week	3 week	1 week	2 week	3 week
Cd_0	80	80	80	0.000	0.000	0.000
Cd_1	80	80	50	0.000	0.000	0.500
Cd_2	40	38	35	0.005	0.105	0.205
Cd_3	35	30	28	0.015	0115	0.215
Cd_4	28	20	18	0.025	0.125	0.225
Cd_5	20	17	15	0.400	0.500	0.600
Cd_6	30	27	22	0.500	0.600	0.700

Note: The number plants at the beginning of the test was 200

Table 10. Effect of Pb^{2+} in the nutrient solution of rice 21 Days After Planting (DAP).

Treatments	$Pb(NO_3)_2$ (mg l^{-1})	Pb^{2+} (mg l^{-1})	Rice growth (%)
Pb_0	0.00	0.00	good
Pb_1	0.50	0.31	good
Pb_2	0.40	0.25	good
Pb_3	0.50	0.31	Good 50%
Pb_4	0.70	0.44	100% death
Pb_5	1.00	0.63	100% death
Pb_6	1.20	0.75	100% death

Table 11. Effect of Cd^{2+} in the nutrient solution of rice 21 DAP.

Variants	$CdSO_4$ (mg l^{-1})	Cd^{2+} (mg l^{-1})	Rice growth (%)
Cd_0	0.000	0.000	good
Cd_1	0.025	0.014	good
Cd_2	0.205	0.110	good
Cd_3	0.215	0.120	good
Cd_4	0.225	0.121	Dead 50%
Cd_5	0.600	0.320	Dead 100%
Cd_6	0. 700	0.380	Dead 100%

There is an increase of biomass at 7 DAP with Pb^{2+} < 0.500 mg l^{-1} and Cd^{2+}< 0.025 mg l^{-1}. Similarly, at 21 DAP an increase in biomass is observed with Pb^{2+} < 0.600 mg l^{-1} and Cd^{2+}< 0.225 mg l^{-1} (Table 12).

Table 12. Effect of Pb^{2+} in the nutrient solution on rice biomass (Dry Weight)

Treatments	7 DAP		21 DAP	
	control	Pb^{2+}(mg l^{-1})	control	Pb^{2+} (mg l^{-1})
Pb_0	171.8	0.0	145.0	0.0
Pb_1	176.8	0.0	122.0	0.5
Pb_2	194.7	0.0	235.7	0.6
Pb_3	280.6	0.3	193.0	0.7
Pb_4	292.0	0.5	154.6	0.8
Pb_5	194.4	0.8	158.6	1.0
Pb_6	121.4	1.0	153.0	1.2
Cd_0	171.8	0.0	145.0	0.000
Cd_1	175.7	0.0	150.0	0.025
Cd_2	176.7	0.005	176.9	0.205
Cd_3	244.2	0.015	196.3	0.215
Cd_4	246.3	0.025	232.6	0.225
Cd_5	179.3	0.400	144.1	0.600
Cd_6	*209.8*	*0.500*		*0.800*

From other experiments it can be concluded that at equivalent concentrations of 0.6 mg l^{-1} Cd^{2+} is always more phyto-toxic that Pb^{2+}. This effect is stronger on rice stems as compared with the leaves and roots of the rice plant (Table 13).

Table 13. The biomass increase of straw, leaves and roots of rice plants as affect by concentrations of $Pb^{2+}$and Cd^{2+}.

Pb^{2+}					Cd^{2+}				
Treatment	mg l^{-1}	straw	Leaves	Roots	Treatment	mg l^{-1}	straw	Leaves	roots
Pb_4	0.6	30.2	27.1	4.10	Cd_6	0.600	28.1	31.0	8.60
Pb_5	0.9	38.2	32.3	14.8	Cd_2	0.110	31.3	27.1	14.3
Pb_6	1.1	34.1	39.0	22.0	Cd_1	0.008	34.4	28.0	22.6

Effect of Pb^{2+}, Cd^{2+} on growth of water spinach (water morning glory)

Wastewater has no effect on roots and the length of water spinach or on the biomass.

Table 14. Effect of city wastewater on the biomass of water spinach (mg)

Days after growing	Control	Waste water
7	980	990
14	2550	2545

Effect of Pb^{2+} and Cd^{2+} on the dry biomass of water spinach

Table 15. Effect of Pb^{2+} on the biomass of water spinach (Dry Weight)

Pb^{2+} Treatments (mg l^{-1})	Days after growing	
	7	14
Control	750	2600
1.0	740	2500
2.5	750	2550
5.0	750	1950
7.5	745	1800
10.0	750	1550

Table 16. Effect of Cd^{2+} on the biomass of water spinach (Dry Weight)

Cd^{2+} Treatments (mg l^{-1})	DAP	
	7	14
Control	750	2550
1.0	745	2600
2.5	750	2650
5.0	750	2400
7.5	745	600
10.0	600	500

Table 17. Survival rate of water spinach in nutrient solution with Pb^{2+} (%)

Pb^{2+} Treatments ($mg\ l^{-1}$)	DAP	
	7	14
1.0	100	100
2.5	100	100
5.0	100	80
7.5	85	50
10.0	90	30

Table 18. Survival rate of water spinach in nutrient solution with Cd^{2+} (%)

Cd^{2+} Treatments ($mg\ l^{-1}$)	DAP	
	7	14
1.0	100	100
2.5	100	100
5.0	100	95
7.5	100	45
10.0	70	20

Table 19. Length (cm) of water spinach in control and wastewater solutions

Treatment	Time of growing (days)															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Control	4.9	6.2	7.4	8.8	9.6	10.2	10.7	11	11.4	11.8	12.3	13.6	14.2	15.7	16.6	17.2
Waste water	5	6.8	8	9.3	9.9	11	12	13	13	15	16	17	17	18	18	19

Table 20. Length (cm) of water spinach in control and Cd^{2+} solutions

Cd^{2+} Treatment ($mg\ l^{-1}$)	Time of growing (days)															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Control	4.9	6.2	7.4	8.8	9.6	10.2	10.7	11	11.4	11.8	12.3	13.6	14.2	15.7	16.6	17.2
0.1	5	5.8	7.3	9	9.6	10.3	11.4	12	13.7	14.5	15.2	16.6	17.8	18.0	19.2	19.7
0.5	4.9	6.3	7.6	8.4	9.8	10.6	11.7	12.4	14.3	14.6	15.7	16	17.3	18.2	19	19.8
1	4.9	6	6.7	8.6	9.3	9.7	10.2	11.3	11.7	12.6	13.8	15	16.7	17	17.2	17.5
2.5	5	5.7	6.8	8.3	9.4	10.7	11.3	11.5	11.7	12.3	15					
5	4.8	6.2	7.4	8	8.6	10.2	10.6									

Table 21. Length (cm) of water spinach in control and Pb^{2+} solutions

Pb^{2+} Treatment (mg l^{-1})	Time of growing (days)															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Control	4.9	6.2	7.4	8.8	9.6	10.2	10.7	11	11.4	11.8	12.3	13.6	14.2	15.7	16.6	17.2
0.1	4.8	6	7.4	8.5	9	10.7	11.3	11.5	12	12.4	12.5	13.2	14.2	15.2	16.7	16.2
0.5	5	6.4	7.5	8.3	9.2	10.3	10.8	11.4	12.6	12.8	13	13.7	14.8	15.1	16.9	17
1	4.9	6	7.6	8.7	9.3	9.7	11.3	12.4	12.6	13	13.5	13.6	13.7	13.8		
2.5	4.9	6.3	7.2	8	9.1	10.3	11.4	12.6	13.1	13.4	13.4	13.5	13.5	13.5		
5	4.8	5.7	6.8	7.6	8.2	9.3	11.5	12.2	12.4	12.6	12.7					

Table 22. Length (cm) of root of water spinach in control and waste solution

Days after growing	Control	Waste water
7	4.7	4.8
14	6.7	7.1

Table 23. Length (cm) of root of water spinach in control and Pb^{2+} solutions (mg l^{-1})

Time of growing	Control	1	2.5	5	7.5	10
7	4.5	4.3	5.6	5.2	5.2	5.6
14	6.2	6	6.7	4	4.3	5.7

Table 24. Length (cm) of root of water spinach in control and Cd^{2+} solutions (mg l^{-1})

Time of growing	Control	1	2.5	5	7.5	10
7	4.7	5	4.2	4.9	4.1	4.8
14	6.3	6.1	5.6	4.1	3.9	2.3

Heavy metal accumulation in water spinach (water Morning Glory)

Table 25. The accumulation of Pb and Cd in water spinach plants after 15 days

Concentration (mg l^{-1})	Pb			Cd		
Experimental solution	1.0	5.0	10.0	0.5	2.5	5.0
Accumulation	1.63	1.90	2.67	0.20	0.37	0.41

Pb^{2+} and Cd^{2+} do not have a major effect during the first week of the experiment except when Cd^{2+} equals or is greater than 5.0 mg l^{-1}. However, during the second week the effect is very obvious. In general, water spinach (Morning Glory) is more robust at withstanding the effects of Pb^{2+} as compared to Cd^{2+}.

Conclusions

Wastewater from Ho Chi Minh City causes heavy metals pollution downstream from the city near Nha Be at a distance of 25-30km. The polluting heavy metals include in order of descending concentrations, Zn (3575 mg kg^{-1}) > Mn (120 mg kg^{-1}) > Cr (100 mg kg^{-1}) > Cu (60 mg kg^{-1}) >Pb (555 mg kg^{-1}) > Ni (37 mg kg^{-1}) > Cd (1.3 mg kg^{-1}). Significant heavy metal uptake is found in earthworm, so much so, that it is believed that this can be used as an indicator species.

The effects of Pb^{2+} (0.63 mg kg^{-1} to 0.75 mg kg^{-1}) and Cd^{2+} (0.32 to 0.43 mg kg^{-1}) concentrations in rice growth experiments become significant after 7 DAP, with an LC_{50} of Pb^{2+} of 0.31 mg kg^{-1}, and for Cd^{2+} of 0.121 mg kg^{-1}. The influence of Cd^{2+} on the growth of rice is stronger than the influence of Pb^{2+}.

Water Spinach also known as Morning Glory is able to adapt itself to an environment where water is polluted by Pb. However when the concentration of Pb exceeds 5.00 mg l^{-1} the roots of water spinach turn black and the plant becomes necrotic. At lower concentrations spinach can grow but when concentrations are increased to < 5.00 mg l^{-1} growth is stalled. In contrast, Cd^{2+} causes the death of water spinach plants at a concentration of 2.50 mg l^{-1}. The uptake of heavy metals in Morning Glory can reach 1.63 to 2.70 mg kg^{-1} for Pb and 0.25 to 0.5 mg kg^{-1} for Cd.

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Effects of Some Heavy Metals on the Growth of Grass Shrimp

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Introduction

Grass shrimps are distributed widely. They are an important source of food. Rearing grass shrimps has increased over the last few years, especially in the coastal provinces of the Cuu Long Delta in Vietnam resulting in significantly improved household incomes. However, contamination of water resources is a common occurrence and large numbers of grass shrimps are killed as a result of pollution. This has happened all over the country since 1993. Studies found the cause of these deaths and solutions were proposed. Grass shrimps however continued to die in large numbers. The research, presented in this paper indicates that the cause of these deaths may be due to heavy metal contamination. Phyto-toxicological studies using shrimps were undertaken to measure the effects of chemical and chemical and environmental variables in estuarine and marine environments on shrimp mortality.

Test materials and variables

Grass shrimps, marine and brackish water species, 22 days old from a shrimp farm in Baclieu Province, Vietnam were used during the experiments. The test shrimps have an average length of 2cm and weight of 0.1 g. The shrimps are grown under experimental conditions for several days before the beginning of tests.

The water supply used during the period of experimentation is near-shore seawater from Baclieu Province with low turbidity, high DO and low BOD. Salinity 19 (± 0.038), pH ranges from 8.0 – 8.5 and temperature is maintained at 28 – 30^{o}C. In addition, the water is filtered and chlorinated. The test shrimps are held in a glass tank of at least 8 litres capacity with flow through air and 2 to 3cm of sand over the bottom and a screen at the surface to prevent loss of test subjects. Ten shrimps are retained in each tank. Synthetic tablet food is provided to the shrimps four times per day.

Heavy metal compounds used throughout the experiments were $NaAsO_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$; $Cr(NO_3)_3$, $Fe(NO_3)_3$, $Hg_2(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$ as manufactured by BUDAFEST (Hungary). All heavy metal compounds are dissolved to pre-selected concentrations using distilled water and further diluted with near-shore seawater from Baclieu Province.

During the range finding toxicity tests over a 48 hours test period grass shrimps are exposed to a heavy metal concentrations ranging from 0.01, 0.10, 1.00, 10.00 and 100.00 mg l^{-1}. For the short term definitive tests, for 96 hours a series of different heavy metal concentrations is applied with different dilution factors. All tests are undertaken in triplicate.

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Evaluation

The symptoms of shrimps after contact with the different heavy metal solutions are observed and noted, as well as the number of dead and/or affected shrimps in each container at 3, 6, 9, 12, 24, 48, 72 and 96 hours after the beginning the test. Dead shrimps are removed immediately. Temperature, pH, DO, BOD, salinity, $N\text{-}NH_3$ and $N\text{-}NO_2^-$ are measured daily and at the beginning and end of each test.

Nonparametric statistical test for variance in concentrations of heavy metals between the average lethal threshold for shrimps and the analytical statement are used to evaluate the impact of treatments on shrimp mortality. A graph showing the toxicity of each heavy metal as expressed by a linear equation $y = ax + b$ is constructed with mortality rates on the y-axis ($y=M$) and heavy metal concentration on the x-axis ($x= \lg C$).

LC_{50} is determined from the linear equation of toxicity of each heavy metal on shrimps in the aquatic environment at different points in time. LC_{50} is defined as the lethal concentration at which 50% of the shrimp population dies after an exposure time of 96 hours.

Results

Arsenic toxicity and its effect (As^{3+})

Arsenic although widespread in plant and animal tissue, has become synonymous with "poison" in the public mind. In spite of its toxicity, it has been employed for its medical virtues in the form of organic arsenicals, and in partial prevention of selenosis. It appears that the stable, soluble inorganic arsenites and arsenates are readily absorbed by the digestive tract, abdominal cavity and muscle tissue. Arsenate has a low order of toxicity and does not inhibit any enzymatic activities due to its lack of affinity to hydroxo and thiol groups. However, ATP synthesis is inhibited by AsO_4^{3-} through uncoupling oxidative phosphorylation and the replacement of the stable phosphoryl group. In contrast, arsenite inhibits thiol–dependent enzymes, binds to tissue protein as keratin disulfides in skin and nails and is retained in the body for a prolonged period. The experiment shows that the mortality rates depend on the time of immersion and on the concentration of arsenic. At 0.01 mg As l^{-1}, 10% shrimp mortality occurs after 72 hours and 20% after 96 hours. Increasing the solution As concentration results in increased mortality rates. At 1 mg As l^{-1} 10% shrimp mortality occurs after 6 hours and 100% mortality occurs after 72 hours.

Table 1. Experimental data from hypothetical toxicity test of As^{3+} subjected to probit analysis

Solution As concentration (mg l^{-1})	No. of test shrimps	Shrimp mortality rate (%) over time (hrs)							
		3	6	9	12	24	48	72	96
0.0	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.01	10	0.0	0.0	0.0	0.0	0.0	0.0	10.0	20.0
0.03	10	0.0	0.0	0.0	0.0	6.7	10.0	23.3	40.0
0.1	10	0.0	0.0	0.0	0.0	10.0	33.3	40.0	50.0
0.3	10	0.0	0.0	6.7	20.0	43.3	53.3	66.7	70.0
1.0	10	0.0	10.0	30.0	53.3	80.0	86.7	100	100

Cadmium toxicity and its effect (Cd^{2+})

Cadmium (Cd) being the middle member of the periodic sub-group consisting of Zn, Cd, and Hg reveals intermediate properties. All three elements display a profound capacity of combining with SH. The stability of such complexes increases in the order Zn < Cd < Hg. In this experiment, shrimps become disorientated 8hrs after coming into contact with $Cd^{2+}$and die after 48hrs. At a solution concentration of 0.005 mg Cd l^{-1} 10% shrimp mortality occurs after 72hrs and 20% mortality after 96hrs.

Table 2. Experimental data from hypothetical toxicity test of Cd^{2+} subjected to probit analysis

Solution Cd concentration (mg l^{-1})	No. of test shrimps	Shrimp mortality rate (%) over time (hrs)							
		3	6	9	12	24	48	72	96
0.0	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.005	10	0.0	0.0	0.0	0.0	0.0	0.0	10.0	20.0
0.015	10	0.0	0.0	0.0	0.0	0.0	13.3	26.7	30.0
0.05	10	0.0	0.0	0.0	0.0	20.0	36.6	50.0	66.7
0.15	10	0.0	0.0	0.0	16.7	23.3	53.3	66.7	83.3
0.5	10	0.0	0.0	10.0	33.3	80.0	96.7	100	100

Copper toxicity and its effect (Cu^{2+})

Copper is found in enzymes capable of carrying oxygen as hemoglobin. Copper is also essential in a number of enzymes. Excessive intake of copper however results in its accumulation in the liver. Generally, copper toxicity increases when Mo, Zn, and SO_4^{2-} intake is low.

In this experiment, a solution concentration of 0.1 mg Cu l^{-1} which is known to be toxic to shrimps was used. At this concentration 3.3% shrimp mortality was observed after 48 hrs and 36.7% mortality observed after 96 hrs. At a solution concentration of with 10 mg Cu l^{-1} 16.7% shrimp mortality occurred after 6 hrs and 100% mortality occurred after 72 hrs.

Table 3. Experimental data from hypothetical toxicity test of Cu^{2+} subjected to probit analysis

Solution Cu concentration (mg l^{-1})	No. of test shrimps	Shrimp mortality rate (%) over time (hrs)							
		3	6	9	12	24	48	72	96
0.0	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	10	0.0	0.0	0.0	0.0	0.0	3.3	10.0	36.7
0.3	10	0.0	0.0	0.0	0.0	26.7	30.0	46.7	56.7
1.0	10	0.0	0.0	0.0	20.0	46.7	60.0	70.0	83.3
3.0	10	0.0	10.0	20.0	26.7	40.0	90.0	90.0	93.3
10.0	10	0.0	16.7	30.0	46.7	90.0	96.7	100	100

Chromium toxicity and its effects (Cr^{3+})

Chromium (Cr) is one of the least toxic of the trace elements. Generally the mammalian body can tolerate 100-200 times its total body content of Cr^{3+} without harmful effects. However, chromium (VI) compounds are approximately 100 times more toxic than Cr (III). The stomach acidity leads to reduction of Cr (VI) to Cr (III) of which gastrointestinal absorption is less than 1%. In this experiment, at a Cr solution concentration of 0.1 mg Cr l^{-1} 3.3% of the test shrimp population died after 48 hrs with 30% mortality at 96 hrs. At 10 mg Cr l^{-1}, 20% mortality was observed after 3 hrs with 100% mortality at 72 hrs.

Table 4. Experimental data from hypothetical toxicity test of Cr^{3+} subjected to probit analysis

Solution Cr concentration (µg l^{-1})	No. of test shrimps	Shrimp mortality rate (%) over time (hrs)							
		3	6	9	12	24	48	72	96
0.0	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	10	0.0	0.0	0.0	0.0	0.0	3.3	13.3	30.0
0.3	10	0.0	0.0	0.0	10.0	10.0	30.0	40.0	50.0
1.0	10	0.0	0.0	10.0	10.0	20.0	40.0	70.0	80.0
3.0	10	0.0	10.0	10.0	20.0	20.0	56.7	80.0	93.7
10.0	10	20.0	20.0	30.0	60.0	73.3	96.7	100	100

Iron toxicity and its effects (Fe^{3+})

Iron (Fe), the most abundant transition element and is essential in biologic systems (haemoglobin in blood, the oxygen-carrying protein molecule regarded as the most important iron (II) complex). In this experiment, high solution Fe concentrations of 3.0 mg Fe l^{-1} resulted in 93.3% shrimp mortality after 96 hrs. However, low solution concentrations of 0.1 mg Fe l^{-1} resulted in 16.7% mortality at 72 hrs and 23.3% mortality after 96 hrs.

Mercury toxicity and its effect (Hg^{+})

Mercury (Hg) is considered a nonessential but highly toxic element for living organisms. Even at low concentrations, Hg and its compounds present potential hazards due to accumulation in the food chain. Poisoning by methyl mercury compounds presents a bizarre neurological picture as observed in large-scale outbreaks in Japan and Iraq. The higher toxicity of Hg as compared to Cd cannot be attributed to the smaller ionic radius and greater penetration of Hg^{2+} ion. The profound capacity of the soft acid (acceptor) CH_3Hg^{+} to bind soft ligands such as –SH groups of proteins is a more plausible explanation for the high toxicity of methyl mercury compounds. Mercury in the test solution rapidly affected the test shrimps. Immediate reactions to mercury in solution were observed. At 0.5 mg Hg l^{-1}, 30% mortality rate was observed after 3 hrs and 100% mortality after 72 hrs. At solution Hg concentrations of 0.005 mg Hg l^{-1} 10% mortality was observed at 72 hrs and 16.7% at 96 hrs.

Figure 1. Fe^{3+} median lethal concentration (LC_{50}) determinations at three representative times by probit analysis and line of best fit.

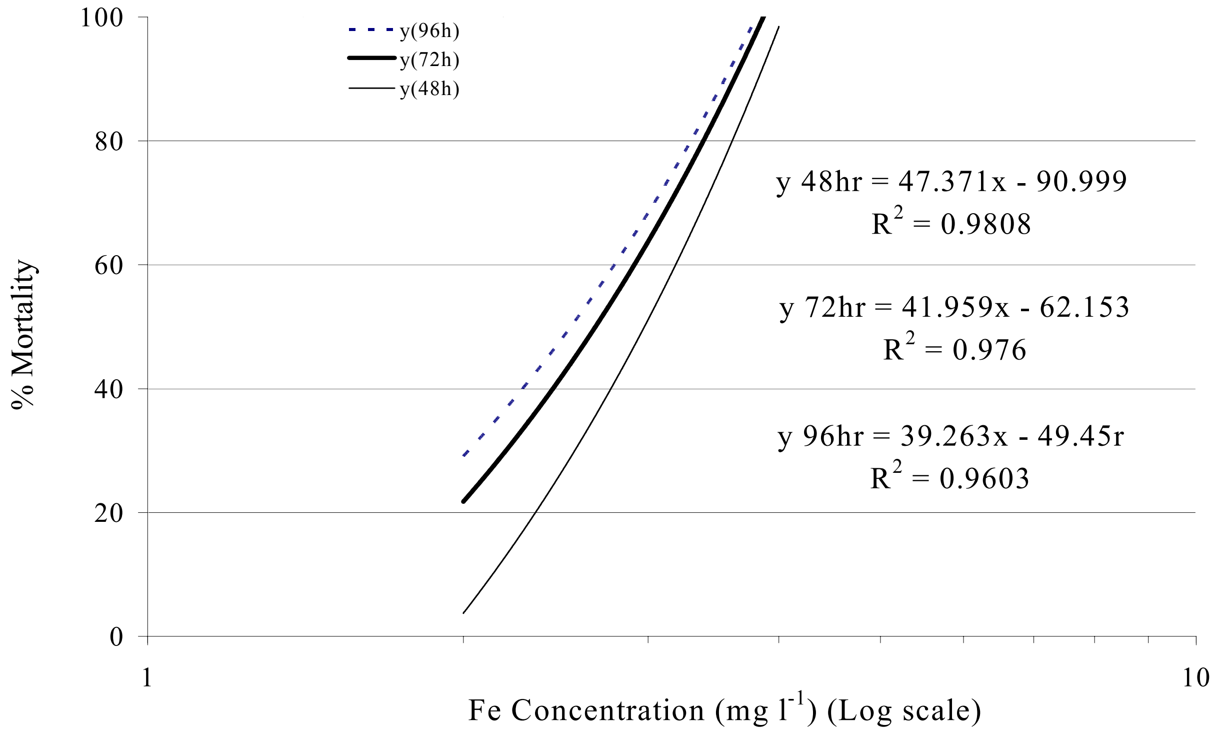
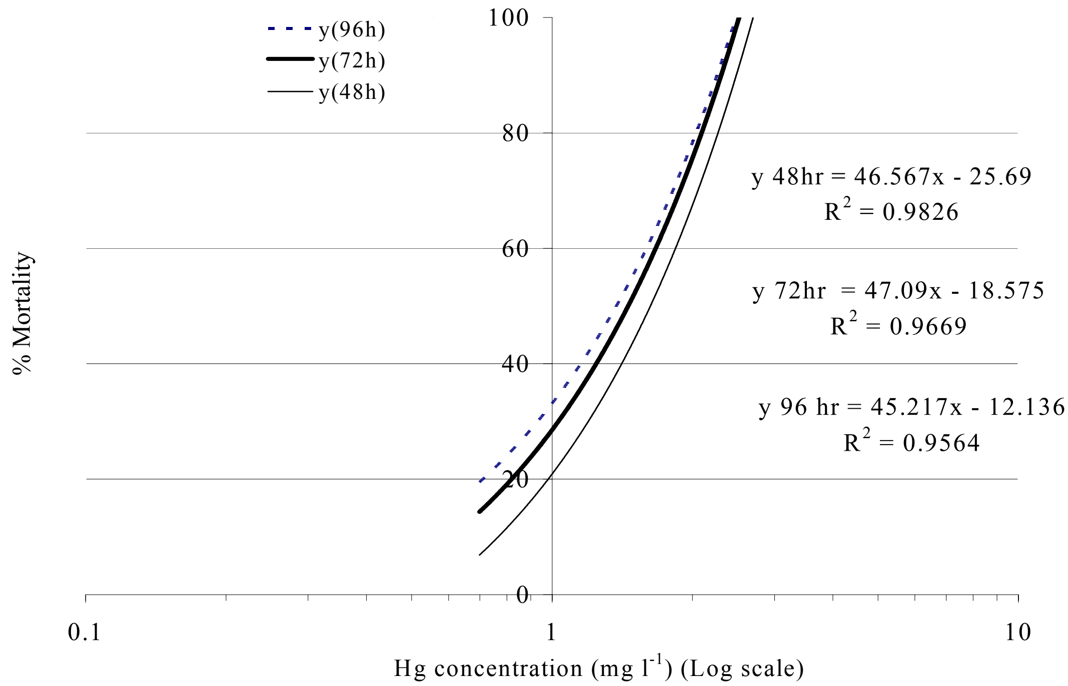


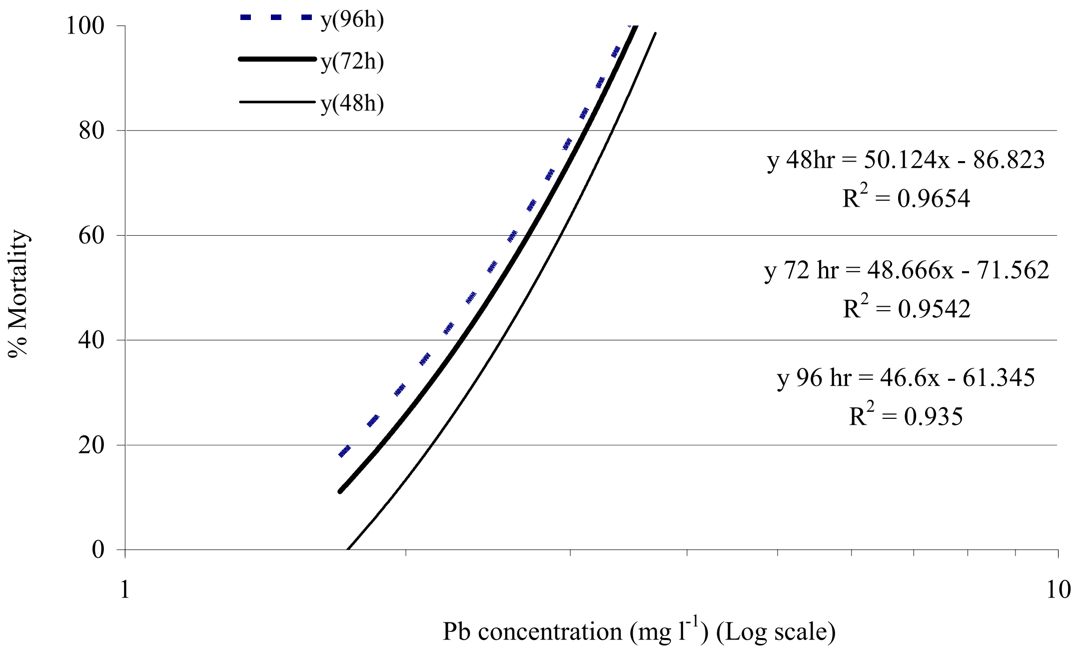
Figure 2. Hg median lethal concentration (LC_{50}) determinations at three representative times by probit analysis and line of best fit.



Lead toxicity and its effects (Pb^{2+})

Lead (Pb) resembles the divalent alkaline earth group metals in chemical behavior more than its own Group IVA metals. It differs from the Group IIA metals in the poor solubility of Pb salts such as hydroxides, sulfates, halides, and phosphates. Metabolism of Pb and calcium are similar both in their deposition in and mobilization from bone. Since Pb can remain immobilized for years, metabolic disturbances can remain undetected. Under normal conditions more than 90% of the Pb retained in the body is stored in the skeleton. The affinity of Pb^{2+} for thiol and phosphate-containing ligands inhibits the biosynthesis of haem and thereby affects membrane permeability of kidney, liver and brain cells. This results in either reduced functioning or complete breakdown of these tissues, since Pb is a cumulative poison. In this experiment a Pb solution concentration of 0.005 mg Pb l^{-1} resulted in shrimp mortality of 10% after 72 hrs. However, a solution concentration of 5.0 mg Pb l^{-1} resulted in 10% mortality after 3 hrs and 100% mortality after 72 hrs.

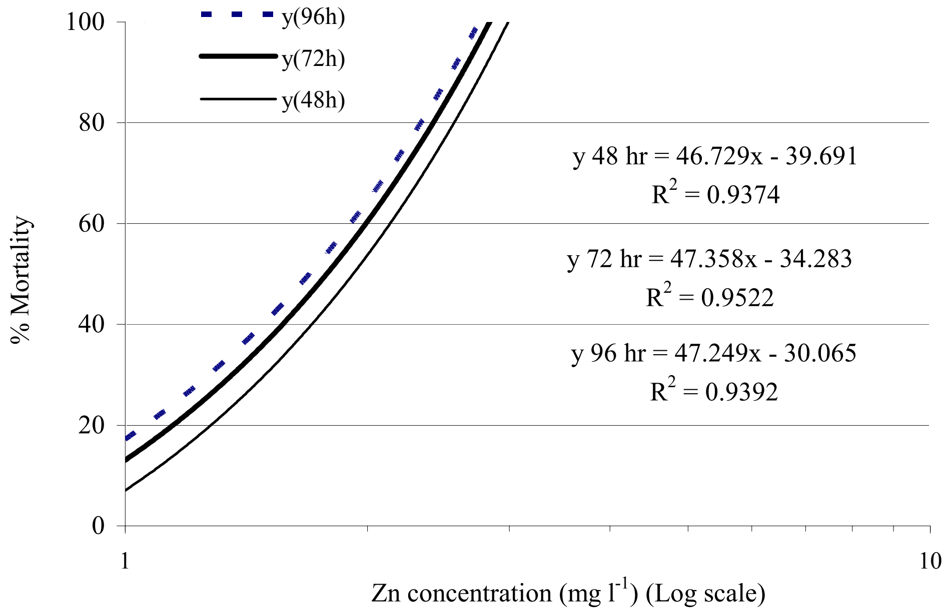
Figure 3. Pb median lethal concentration (LC_{50}) determinations at three representative times by probit analysis and line of best fit.



Zinc toxicity and its effects (Zn^{2+})

Zinc is one of the most abundant of the essential elements required by the human body. Zinc appears to be present in all mammals. As with cobalt (II), Zn (II) has the ability to occupy low symmetry sites in enzymes. In this experiment, a solution Zn concentration of 0.01 mg l^{-1} resulted in 10% mortality at 72 hrs. In contrast, at a solution concentration of 1.0 mg l^{-1} shrimp mortality was 10% at just 3 hrs and 100% at 72 hrs.

Figure 4. Zn median lethal concentration (LC_{50}) determinations at three representative times by probit analysis and line of best fit.



Conclusion

Heavy metals as contaminants in an aquatic environment cause very serious harm to the growth and development of grass shrimps. The results of the laboratory experiments presented in this paper allow the establishment of preliminary lethal concentrations associated with 50% shrimp mortality after 96 hours (LC_{50}-96hr) for different heavy metals as follows:

- As^{3+} = 67.61 µg l^{-1}
- Cd^{2+} = 28.84 µg l^{-1}
- Cu^{2+} = 177.83 µg l^{-1}
- Cr^{3+} = 269.15 µg l^{-1}
- Fe^{3+} = 338.84 µg l^{-1}
- Hg^{+} = 23.44 µg l^{-1}
- Pb^{2+} = 245.47 µg l^{-1}
- Zn^{2+} = 48.89 µg l^{-1}

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Environmental and Public Health Effects Due to Contamination from Mining Industries in Thailand

Country Report Prepared by
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Abstract

Detrimental impacts on human health as a result of mining and related activities have been observed at several places in Thailand. The most serious cases are mainly related to heavy metal and metalloid contamination in waters and soils. Arsenic poisoning as a result of long-term consumption of contaminated shallow well water was first recognized at Nakhon Si Thammarat Province, southern Thailand, in 1987 where chronic arsenic skin lesions were observed in 1,049 patients aged from 4 months to 85 years. Physical and chemical breakdown of arsenopyrite (FeAsS), an associated mineral of tin deposits, was suspected as the major cause. Arsenic concentration in water and soil was found to exceed the acceptable standard and guidelines by a factor of up to 100. A switch in mining methods from dredging to open pitting was interpreted as being the cause of the accelerated dispersion of FeAsS. Owing to several environmental and health mitigation measures, arsenic contamination and public health impacts at this vicinity have been gradually alleviated.

Lead (Pb) contamination in running water and stream sediments around mining and ore dressing sites in the Kanchanaburi Province, western region, was first observed in 1992. Primary and secondary Pb ore have been mined in the area both underground and in open pit for more than half a century. The environmental conditions deteriorated seriously when a tailings pond collapsed due to unusually heavy rain in 1998. A large volume of tailings containing Pb at concentrations ranging from 20,000 - 30,000 mg kg^{-1} was flushed into the natural drainage and as a result the concentration of Pb in water and bottom sediment increased significantly. This had a severe impact on the people living downstream. Average Pb content in blood of children < 6 years old was as high as 26.45 μg dl^{-1}. The situation improved after the flotation license was revoked and a clean up program was undertaken at the polluted stream and near the concentrator.

In another case of heavy metal contamination attributed to the mining industry, high concentrations of Pb in water, sediment and soil in the vicinity of abandoned tin mines was reported from Yala Province in the South of Thailand in 1993. In 1994 edible marine macrophytes in the bay downstream were found to have elevated Pb contents of 4.74 - 26.78 mg kg^{-1} (Dry Weight). A survey conducted during 1998–2002 however concluded that there are limits to the Pb contamination from the mined out area. Partly this was considered to be due to the alkalinity introduced by the surrounding limestone formations. Lead concentration in running water became lower downstream from the mines but increased again near the bay. The latter was probably influenced by boat repair activities in which Pb-based paints were used. Blood test surveys in 1995 discovered 96% and 98% of examined children from two primary schools in the proximity of the mines and the bay had levels of ≥10 μg Pb dl^{-1} in their blood. Recent follow up data, however, revealed lowering trends in these concentrations.

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In addition to the above there are several other cases waiting to be addressed. These and similar harmful experiences have given rise to public concern as to whether mining can be compatible with sustainable development. People and economies need minerals and metals for survival and therefore mineral development must continue but the crucial issue is how good environmental management can be assured. National regulations and regional and global agreements are formulated and enacted to achieve environmentally friendly economic development. Close cooperation and collaboration among countries, agencies and all stakeholders is also needed to accomplish the common ultimate goal of sustainable development.

Introduction

In accordance with national legislation and policies, the Royal Thai Government has an obligation to notify her citizens annually on the state of the environment including natural resources utilization and conservation as well as environmental quality. Although the overall national environmental aspects during these recent years revealed continued natural resources degradation, the quality of the environment as a whole had shown an improving trend. Ambient air quality monitoring data suggest cleaner outdoor conditions with reducing toxic gas emissions and total particulate matter. The quality of surface water obtained from 47 main rivers and 4 large reservoirs showed signs of recovery. As regards soil and groundwater quality there is a lack of data due to the absence of regular investigation and monitoring. Increasing land use for industrial and community settlements causes impacts to the environment. This is borne out by the rising number of patients suffering from pollution. Health effects in local communities adjacent to mining areas have been disclosed periodically. The environmental and public health impacts from mining activities are relatively severe in terms of coverage and numbers of affected people. These characteristics are clearly related to the enormous areas of disturbed land, bulk waste, long-term operation mis-management and subsequent natural degradation.

This paper emphasizes the environmental and public health impacts resulting from mining and mineral processing. Arsenic contamination in waters and soils as a result of tin mining and concentrating at Ron Phibun District, Nakhon Si Thammarat Province is highlighted as one of the most harmful instances of the last two decades. Lead dispersion from mines and tailing ponds at Kanchanaburi and in Yala Province are other severe incidents requiring continued remedial operations.

Arsenic Contamination in the Vicinity of Tin Mining and Processing

Contaminant Sources and Mechanism of Appraisal

Health problems attributed to arsenic contamination in water supplies in Thailand were first highlighted in 1987, following the diagnosis of a case of arsenical skin cancer at Ron Phibun District, Nakhon Si Thammarat Province. Mining has been an economic activity in the area for longer than a century and it was concluded that mining was the cause of the contamination. Arsenopyrite concentrations of around 1% are associated with economic mineral concentrations of the tin and tungsten minerals cassiterite and wolframite that occur in pegmatite and quartz veins throughout the granite mountain range. It was concluded that this was the sourec of As contamination. Placer deposits had been initially mined by dredging a century ago. During this period, minor arsenic release and contamination was believed to have taken place due to slight variations in groundwater levels.

Consequently, no intensive oxidation had occurred as a result of the dredging operations. However, when during the second half of the century the mining technique was changed to open pit mining of primary ore, exposure of the mineralized layers to the atmosphere stimulated the oxidization processes. Arsenic, contained in disseminated arsenopyrite in soil was liberated as arsenic and arsenous acid into the environment as follows:

$$4\ FeAsS + 13\ O_2 + 6\ H_2O \longrightarrow 4\ FeSO_4 + 4\ H_3AsO_4$$

When a number of the open pit mines were gradually abolished due to the collapse of the world tin market in 1985, the groundwater table recovered and the mobile arsenic compounds were dissolved. This same process on a smaller scale took place in association with smaller mining operations that exploited veins in mountainous terrain through adits or tunnels.

Environmental Investigation and Monitoring

Initial sample analysis indicated As concentrations in water and soil that exceeded the National Water Standard of 0.01 mg l^{-1} and soil guideline value of 50 mg kg^{-1} by up to a factor of 100. Surface water acidity ranged from pH 2.9 to 8.1 with pH increasing towards the lowlands. Arsenic concentrations in acidic waters close to the mining operations were lower than those in neutral waters adjacent to open pit operations.

This indicated that As dissolution and mobility is independent of antecedent pH. Monitoring data from 1992-1997 indicate that arsenic concentrations in running water around mountainous areas averaged 0.5 mg l^{-1} whereas those at the downhill alluvial plain exceeded 1.0 mg l^{-1}. However, longer-term systematic investigation of four major affected streams revealed continually decreasing concentrations of As in surface water.

Shallow groundwater from dug wells also showed decreasing trends in arsenic contamination. In 1990, maximum shallow well water As concentration was 9 mg l^{-1}. However, maximum shallow well water As concentration declined to 5.11 mg l^{-1} in 1994, 2.04 mg l^{-1} in 1999 and 0.60 mg l^{-1} and 0.10 mg l^{-1} in 2000 and 2001, respectively.

It is significant that the wells where the highest concentrations of arsenic were found during annual surveys were not always the same although those wells were normally situated in the same vicinity. This illustrates the complexity of the mechanism of dispersion and precipitation of arsenic and arsenic compounds. Arsenic species in surface and shallow groundwater was dominated by arsenate. Deep groundwater is normally clean since it is geologically confined to carbonate aquifers and separated from polluted shallow groundwater in unconsolidated sediments. However, a few deep wells were contaminated with arsenic probably through seepages in fractured limestone. In these deep groundwater wells arsenite is dominant. Deep well water sources are likely to pose a hidden risk and they need regular monitoring.

Distribution patterns of arsenic in soil and stream sediment corresponding closely with those in shallow groundwater. High arsenic contamination in surface and groundwater samples and soil and plant tissue samples was centered on two villages (Village No.12 and No.2) of Ron Phibun Sub-district covering a small area of 7-10 km^2. Arsenic contamination through inhalation is considered minimal. An investigation of ambient dust was conducted using high-volume samplers and falling-dust jars. The amount of total particulate matter as well as its arsenic content was found to be very low.

Public Health Effects

The Public Health Office at Ron Phibun District in April 1988 revealed that there were 1,049 patients suffering from skin disorders diagnosed as hyperpigmentation, *keratosis* and skin cancer. Their ages varied from 4 months to 85 years and their number was equivalent to 6.56% of the total population of Ron Phibun District. Most patients, over 75%, were diagnosed with pigment changes showing spotty dermal *melanosis* and pinheaded dermal papules on palm and sole. These manifestations and symptoms were related to chronic arsenic poisoning. The patients had been exposed to arsenic toxicity through drinking arsenic contaminated shallow groundwater from dug wells for a long period of time. The 1992 clinical survey reported that 89% of 2,400 pupils had high arsenic levels in their blood and 22% showed skin effects.

In 1995 a Japanese medical examination found no new patients but most registered patients still showed symptoms. Studies also addressed the correlation between patient's lodgings and areas of high arsenic contamination in shallow groundwater. According to a health study published by Oshikava, 1998 only 334 of 818 patients recorded during 1987 were traced and diagnosed for the developments and changes in the manifestation of the disease. Of these, 12 people died from cancer during 1987-1997. Only 16 people showed worse arsenical skin lesions whereas 98 people showed improvements in their condition and the remainder of 208 continued unchanged. A recent clinical survey conducted by the Ministry of Public Health disclosed a declining prevalence of arsenic manifestation from 26.3% in 1994 to 24.4% in 2000. The statistical significance of this 1.9% decline over the 6 year period is not stated. Health impacts from arsenic contamination in Ron Phibun District have recently shown decreases. This indicates the effectiveness of protection and mitigation measures implemented in the area.

Environmental Alleviation Measures

Mitigation measures to alleviate arsenic contamination and eliminate public health risk at Ron Phibun District have been implemented by several relevant organizations including the Ministry of Interior, the Ministry of Public Health, the Ministry of Natural Resources and Environment, the Ministry of Industry and several universities. Significant mitigation measures are listed as follows:

- Provision of large jars and containers for rain water collection
- Provision of clean water from uncontaminated deep wells
- Educating indigenous people to be conscious of arsenic exposure, toxicity and prevention
- Ordering miners and concentrators to implement environmental protection and reclamation to mitigate and remedy arsenic contamination
- Issuing a Ministerial Notification to prohibit mining and concentrating activities in the polluted area
- Collecting arsenic-rich residues from hilly areas and ore dressing plants for disposal in secure landfills
- Carrying out regular systematic environmental and public health monitoring
- Conducting and collaborating in research

Large jars and containers for rainwater collection were given to every house located in the polluted area. More than 80 deep wells were also drilled in Ron Phibun Sub-district. Hand pumps as well as electric pumps have been installed. Some wells were developed for piped water supply systems. Departmental orders were issued for environmental protection and improvements such as confining arsenic-rich waste in concrete lined waste dumps, recycling wastewater, treating effluents before discharge. A Ministerial Notification to prohibit mining activities in areas of Ron Phibun Sub-district was issued in 1994. Licenses for new concessions as well as for extension of mining, panning and ore dressing permits cannot be granted. Arsenic-rich residues collected from abandoned mining and concentrating sites were buried in secure landfill lined with 2 layers of HDPE, 1.5 mm thick. A drain pipeline system for leakage monitoring and observation was constructed to ensure the efficiency and safety of the landfill.

Lead (Pb) Contamination in the Vicinity of Pb Mining and in Areas with Potential for Pb Mineralization

Contaminant Sources and Mechanism Appraisal

Lead contamination in streams and bottom sediments around mining and concentrating areas at Kanchanaburi Province, western region, was initially addressed in 1992. The had area experienced historical mining and mineral processing for several hundreds of years as evidenced by antique mining equipment found in the area and large concentrations of high-grade Pb slag.

For the last 50 years the area has been mined for Pb and associated metals. The primary sulfide minerals found in the area include galena, sphalerite, pyrite and barite, all part of a strata-bound sequence of mineralization. Secondary minerals include cerussite and smithsonite, carbonates of Pb and zinc respectively. Open pit mining was generally utilized to extract these secondary ores. At present ore reserves of 6.72 and 1.90 million metric tons have been identified for primary and secondary deposits respectively.

Mining and mineral processing activities allowed sulfide minerals to be exposed and react with air and water. Oxidation and hydrolysis of sulfide minerals resulted in dissolution and increased mobility of heavy metals and the formation of acid mine drainage. Fortunately the area is geologically surrounded by limestone formations which neutralize acid mine water resulting in the precipitation of dissolved metals. As a result, the effluent from mines and associated flotation plants is normally compliant with the regulatory standards. The Pb contamination and dispersion is therefore suspected to originate from suspended sediments. This conclusion is supported by the results of extraction tests on concentrates and tailings. The leachate from sulfide and carbonate concentrates contained only <0.02-3.04 mg l^{-1} and <0.02-0.04 mg l^{-1} of Pb, respectively, whereas those of tailings contained <0.02-0.74 mg l^{-1} of Pb.

Environmental Investigation and Monitoring

In 1998, due to unusually heavy rain, a pond containing tailings from the flotation plant collapsed. As a result a large volume of mud with a Pb content of 20,000 – 30,000 mg kg^{-1} was flushed into a nearby stream, the Huai Klitty. The dam failure had a severe impact on indigenous people living downstream in Klitty Lang Village where fish from the creek was a major source of protein. In order to review the level and impact of the release of the Pb-rich mud detailed surveying and sampling of the stream and the stream waters in the proximity of the mines and flotation plant have been carried out since 1999. The water quality of Huai Klitty was examined regularly up and down stream from the concentrator over a distance of some 20 km. In 1999, total surface water Pb concentration upstream was 0.02 mg l^{-1}, this increased to 0.53 mg l^{-1} immediately downstream of the plant. At locations further downstream, Pb concentrations showed a decreasing trend before rebounding and fluctuating due to turbulence and the re-suspension of sediments.

Mining and mineral processing in the area takes place in four different locations, the Bo Ngam Mine, the Klitty Ore Concentrator, the Song Tho Mine and the Bo Yai - Bo Hoi Mines. The average concentrations of total Pb in stream water and bottom sediment upstream from the mining and mineral processing areas were 0.016-0.104 mg l^{-1} and 656-24,052 mg kg^{-1} respectively. Within the mining and ore dressing sites, the average concentrations of total Pb in water and sediment increased to 0.074-0.272 mg l^{-1} and 6,811-13,109 mg kg^{-1}. Downstream from the mines and flotation plant Pb concentrations in water and sediment averaged 0.065-0.092 mg l^{-1} and 1,914-40,053 mg kg^{-1}, respectively. It was conspicuous that high concentrations of Pb in bottom sediment throughout the streams pointed not only to contamination but also indicated anomalous values upstream, indicating that undiscovered mineralization may exist there.

Vegetation and aquatic animals from the proximity were collected and analyzed to assess the risk of eating plants and fish. Only a few edible fish species were found to contain Pb at levels exceeding the Maximum Permissible level of 1 mg kg^{-1}. Drinking water from the tap and from streams in 7 villages located around mining and mineral processing areas contained <0.45-16 µg l^{-1}, which is considered safe level for Pb.

Public Health Effects

As the area in general has good potential for Pb mineralization, the clinical surveys carried out by the Ministry of Public Health had been designed to cover not only the Klitty Lang Village affected by the tailings pond failure, but also another 6 villages. Most of these villages have no direct relation with mining or ore dressing activities since they are situated far upstream or out of watersheds influenced by mining. Blood examination at Klitty Lang Village in 1999, 2000 and 2002 showed average Pb contents in adults over 15 years old of 25.05, 29.56 and 21.33 µg dl^{-1}, respectively. Further, in 1999, 2000 and 2002 blood Pb concentrations in children <15 years old, were 24.08, 26.68 and 21.33 µg dl^{-1}, respectively.

The latest blood tests, carried out in 2002 indicated that the population of Klitty Bon Village, situated upstream and adjacent to the flotation plant, approximately 10 km north of Klitty Lang Village, had the highest average Pb content of 36.29 µg dl^{-1} in children <15 years old and 24.92 µg dl^{-1} in adults over 15 years old. It is critical to note that all children examined at the villages of Klitty Lang and Klitty Bon had blood Pb concentrations exceeding the internationally established maximum blood Pb concentration of 10 µg dl^{-1} with maxima of 41 µg dl^{-1} and 69 µg dl^{-1}, respectively. In addition, 86.7% of children at Klitty Lang Village demonstrated blood Pb concentrations ranging from 11-24 µg dl^{-1} whereas 81.8% of those at Klitty Bon Village exhibited blood Pb concentrations > 25 µg dl^{-1}. In the control villages the range of blood Pb contents was 7.47-17.93 µg dl^{-1} in children <15 years old and 5.61-15.09 µg dl in adult in adults over 15 years old with a maximum of 36 µg dl^{-1} and 25 µg dl^{-1} in each demographic group, respectively. In spite of prevalence of excessive Pb content in blood among the whole population, no clinical manifestation related to Pb poisoning has been confirmed. However, children are highly sensitive to Pb and being exposed to excessive Pb levels could cause neurological and hematological defects. The need of intervention to reduce the exposure levels is therefore urgent.

Environmental Alleviation Measures

To alleviate the adverse effects of Pb contamination caused by mining, mineral processing and the failure of the tailings dam, several remedial measures have been implemented on the basis of the "polluter pays" principle. The first immediate responsive measure was the order to stop the flotation process and to renovate the tailings pond. Clean up and reclamation programs to restore the environmental condition in the polluted stream and at the concentrator were established and implemented. Within 2.5 km of the flotation plant 3,753 metric tons of contaminated sediment were excavated from the Huai Klitty and dumped back into a tailing pond or buried in secure landfills. Two rock check dams were constructed across Huai Klitty to entrap remaining contaminated sediment for later excavation and landfill. The site of the Klitty Ore Concentrator has been reclaimed in accordance with the approved closure plan, before the rights were returned to the government. To compensate for the disturbance, the concentrator established a 1 million baht fund for the people of Klitty Lang Village. Agricultural protein, chicken and fish farming were also introduced to the villagers to provide alternative sources of protein to replacing fish from the Huai Klitty. Clinical examination and treatment have been carried on intensively. A number of committees at local, provincial, departmental and ministerial levels have been designated to negotiate, approve, enforce and implement relevant actions for a better quality of life and environment in the affected area. The issue has now also been brought to court.

Heavy Metal Contamination in the Proximity of Abandoned Tin Mines

Contaminant Sources and Mechanism of Appraisal

In 1993, high Pb concentrations in water, sediment and soils collected around abandoned tin mines of Bannang Sta District, Yala Province were reported. In 1994, marine *macrophytes* including sea grass and seaweed, in the bay downstream were found to have elevated Pb contents ranging from 4.74 - 26.78 mg kg^{-1}. These facts gave rise to public concern. In the mineral deposits of the area Zn, Pb and Cur are associated with tin in skarns. Weathering and erosion of various sulfide minerals have become the main driving mechanisms of heavy metal contamination. Samples of water and sediment were periodically collected along the streams from the mining areas to the bay downstream and analyzed for various heavy metals such as Cd, Pb, Zn, Cu, As, Mn and Fe. Lead, As and Mn demonstrated elevated concentrations around the mined out areas. As for Cd, Zn, Cu, and Fe, concentrations remained close to background values. Recent data from systematic surveying during 1998–2002 shows that the contamination of Pb, As and Mn from abandoned mines was confined to within a specific area due to the buffering effect of the alkaline environment generated by the limestone formations in the area. Acid mine drainage with a pH of 2.0 to 3.0 was brought up to pH 7.0 within a distance of 500 meters. The concentration of Pb, As and Mn in running water decreased with increasing distance from the mines. Elevated Pb concentrations were identified again in the bay. This was caused by contamination from other sources probably by boat-repair activities using Pb-based paints.

Environmental Investigation and Monitoring

According to regular investigation on environmental quality in the watershed of abandoned tin mines during 1998-2002, contamination of Pb, As and Mn in surface water showed levels significantly elevated above background. Water samples collected upstream of the mined out area contained potential toxic elements below the standard limits. When the stream passed through the mined out area, most collected water samples showed high contents of Pb, As and Mn. In 1998, prior to the initiation of the mitigation project, Pb, As and Mn concentrations were 0.19, 0.36 and 4.7 mg l^{-1}, respectively.

During the period of project implementation, 1999-2001, the maximum concentrations of Pb, As and Mn decreased to 0.13, 0.21 and 2.10 mg l^{-1}, respectively. In 2002 when the mitigation project had been finished, the maximum concentrations of Pb, As and Mn were lower than 0.08, 0.20 and 1.60 mg l^{-1}, respectively. During 2000-2002, the average concentrations of Pb and Mn were found to be below National Standard limits. As regards arsenic concentration, the average remained high and fluctuated above the National Standard. Nevertheless, where the stream flowed away from the abandoned mine, all metal contents decreased to levels below the National Standard. Lead in sediments upstream of the abandoned tin mines averaged 1,610 mg kg^{-1}, while stream sediments collected on site of the mined out area averaged 5,903 mg kg^{-1}. In contrast, approximately 3 km downstream of the mined out area Pb concentrations decreased significantly to an average of 379 mg kg^{-1}. Lead in soil at residential areas in the vicinity of abandoned tin mines ranged from 197-1,087 mg kg^{-1}. Cultivated fish contained 0.12-0.64 mg Pb kg^{-1}. The highest concentration of Pb in plant tissue was 1.852 mg kg^{-1}.

Public Health Effects

There is no record of any manifestation indicating negative public health effects due to Pb contamination in the area. However, it is undeniable that elevated Pb levels in this particular location contribute to some adverse effects on the local communities. The evidence to support the existence of this problem is found in the results of a study the Prince of Songkhla University in 1995 on Pb contamination among schoolchildren living near the abandoned tin mines of Yala Province.

Two primary schools in the mining area of Bannung Sta District with respectively 46 and 127 pupils aged between 6 to15 years were investigated. Approximately 96% and 74% of children in each school had a Pb-in-blood level of $\geq$10 μg dl^{-1}. Moreover, 24% and 7% of those showed contents $\geq$20 μg dl^{-1}. Most of these children's residences were built in areas of extensive mine waste dumps. In addition, children from two other primary schools located near the bay were examined for Pb-in-blood content. In total 98% of 61 pupils and 65% of 37 pupils demonstrated Pb-in-blood levels of $\geq$10 μg dl^{-1} but only 10% of 61 pupils had blood Pb levels $\geq$20 μg dl^{-1}. This study was limited to children between 6 to15 years as this particular group was thought likely to intake Pb dust by ingestion through putting hands into the mouths. Recent follow up data, however, revealed declining trends in the number of affected pupils and in blood Pb contents. According to 2001 data from the Provincial Public Health Office the average Pb-in-blood content for 250 children from the same schools in mined out areas had decreased to 6.02 μg dl^{-1} with only 11.2% of the pupils having a concentration $\geq$10 μg dl^{-1}. These improvements indicate the effectiveness of the countermeasures implemented in the area since 1999. However, intensive monitoring must be continued to safeguard the health of the affected communities.

Environmental Alleviation Measures

To provide a safe environment to local residents in the vicinity of abandoned tin mines, improvement programs including secure landfill and capture of mine wastes were launched in 1999. A Total of 130,000 m^3 of mine wastes were captured. In total, 30,000 m^3 were buried in a secure landfill lined with HDPE. Another 50,000 m^3 were covered with compacted clay. The remaining 50,000 m^3 were gathered and surrounded with a clay barrier before being covered with compacted clay and topsoil. Earth-cover vegetation and fast growing trees were later planted over 22 acres. The environment and public health have shown signs of improvement. There is a decreasing content of Pb in stream water and in the blood of schoolchildren. Over the next years, more mine waste in the adjacent area will be securely stored to ensure better environmental quality and quality of life for the local residents.

Other Relevant Environmental Problems and Risks

Almost 20 years ago, there was a leak in the pipeline delivering leached sludge containing Cd, Pb and Zn from the Zn refinery in Tak Province. This event caused heavy metal contamination in soil and stream sediment around the plant. Remedial measures included lime stabilization and excavation of contaminated soil and sediment and dumping these back into the secure residue pond of the refinery. An illegal secondary Pb smelter in Ratchaburi Province, central Thailand, was found to contaminate soil and crop nearby for several years through stockpiles of used batteries on bare soil and emissions of Pb fumes and dust. As a result, cows fed with contaminated maize produced contaminated milk. The owner was arrested and the smelter was demolished. The area is now designated as a polluted site and entrance is prohibited.

Soil as well as surface and shallow groundwater in the Northeast in the provinces Sakon Nakhon, Udonthani, Nakhon Ratchasima, Mahasarakam and Nongkay, have been contaminated with salt from natural sources and human activities. Several regulations and measures have been enforced, including area designation for salt production from brine pumping and waste rejection into underground. Close inspection and monitoring to prevent and alleviate salinity impacts on rice paddy fields and surface water quality as well as land subsidence are consistently undertaken. In addition, in 1975 villagers at Rong Kwang District, Phrae Province suffered from Mn poisoning through drinking of contaminated stream water passing through Mn mines. Clinical surveys in 1978 reported that almost 80 villagers manifested the symptoms of *manganism*, including shaking, clumsiness, shuffling walk, abnormal balance, speech difficulties and lack of facial expression. Among the examined people, 76 from 80 had Mn contents in blood over 8 $\mu g\ dl^{-1}$ with a maximum value of 60.93 $\mu g\ dl^{-1}$ and minimum of 5.01 $\mu g\ dl^{-1}$. The recommended maximum allowable limit for Mn in blood is 4 $\mu g\ dl^{-1}$. New sources of clean water were provided and the mines were abolished.

Fluorine (F) contamination in groundwater has been reported in several places especially close to the fluorite mines of northern Thailand. Fluorite concentrations in contaminated areas were found to be over the National Standard of 1 mg F l^{-1} by a factor of 3-4 and sometimes by a factor of 10. The most critical case so far, in Lumphun Province, a few years ago, there were a number of students diagnosed with mottled teeth derived from over-intake of F. This incident has become an incentive for the dental society to initiate an effort for problem prevention and alleviation.

Conclusions and Recommendations

The mining industry has played an important role as a fundamental segment of the economy in supporting and promoting other upstream industries in driving Thailand's economic and social development. It can bring prosperity as well as disaster to society and to the environment. Exploring for and exploiting minerals normally disturbs and deteriorates to some extent the surroundings. Public health risks may result. Harmonious national policies and strategies on the development and conservation of mineral and other natural resources are therefore crucial to secure the quality of people lives.

Environmentally sound management in mining development needs to be planned and implemented from project commencement throughout the operation and to the designed rehabilitation. Environmental protection and mitigation tools should be promulgated and continually enforced to achieve the national and global aims of environmental sound promotion in this sector. Participation of the local community, considered as one of the important stakeholders is through commenting on submitted mining applications.

The enforcement of environmental impact assessment (EIA), land use designation, liability insurance, rehabilitation bond and decentralization of inspection and monitoring of the mining industry are examples of the efforts required to pursue environmental friendly mineral development. International cooperation and collaboration are also necessary for the achievement of the ultimate international goal of sustainable development.

Filter Technology: Integrated Wastewater Irrigation and Treatment, a Way of Water Scarcity Alleviation, Pollution Elimination and Health Risk Prevention

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Abstract

The use of urban wastewater in agriculture is a widely established practice for alleviating water scarcity situations and reducing or even eliminating the purchase of chemical fertilizers. However, unregulated irrigation with untreated wastewater poses serious public health risks, as sewage is a major source of excreted pathogens that cause gastro-intestinal infections in human beings. Wastewater may also contain highly poisonous chemical toxins from industrial sources that may cause much more serious long-term health risks. Reuse after proper treatment is normally recommended as the main solution of preventing health risks. Unfortunately, because of the high cost of engineering plants, most cities in developing countries do not have sufficient wastewater treatment capacity, and the perspectives of the capacity increasing in these cities are bleak. Planned and regulated wastewater irrigation with crop limitations and proper irrigation methods (for example local irrigation) may to some extent, prevent health risks. But for a given territory, it is often impossible to limit the type of crops to be grown.

This paper introduces the FILTER (Filtration and Irrigated cropping for Land Treatment and Effluent Re-use) technique, an improved land treatment technique developed at CSIRO, Australia and tested both in Australia and China. FILTER combines the use of nutrient-rich wastewater for intensive cropping with filtration through the soil to a subsurface drainage system. Therefore, FILTER has the capacity to handle high volumes of wastewater in a relatively small land area and during periods of low cropping activity or periods of high rainfall. In order to produce minimum-pollutant drainage water which meets general environmental criteria for re-use and discharge to surface water bodies, the wastewater application and subsurface drainage in the FILTER system needs to be managed to ensure adequate removal of pollutants, while maintaining required drainage flow rates. Trial results indicate that a well-managed FILTER technique can reduce pollutant levels in drainage waters below EPA limits, while maintaining crop yields and nutrient removal to potentially make it a sustainable system.

Keywords: wastewater treatment, wastewater irrigation, pollutant removal, controlled subsurface drainage.

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Background

The use of urban wastewater in agriculture is a widely established practice, particularly so in urban and peri-urban areas of arid and seasonally arid zones. Lunven (1992) estimated that one tenth or more of the world's population currently eats food produced on wastewater (but not always in a safe way).

In China, the amount of wastewater discharged every year is about 60 billion tons, approximately the same as the annual runoff of the Yellow river. Except for a few big cities, wastewater is not properly treated before being discharged into surface water bodies in most places of the country and causes water pollution thus further compounding the water scarcity problem. At the same time, agriculture and cities are consuming more and more fresh water owing to population increases and economic development. Especially in the arid and semi arid part of North China, the water scarcity situation is much more serious than in other places of the country. In these places, wastewater has been one of the important sources of irrigation water. It is estimated that the total area frequently irrigated with wastewater in China is about 4 million ha. Wastewater is an important source of irrigation water as well as a source of plant macro-nutrients (N, P and K) and trace elements (Zn, Cu, Mo, B etc). Wastewater irrigation can alleviate water scarcity situations and allows farmers to reduce or even eliminate the purchase of chemical fertilizer and organic matter that serves as soil conditioner and humus replenishment.

However, unregulated irrigation with untreated wastewater poses serious public health risks, as sewage is a major source of excreted pathogens - the bacteria, viruses, protozoa and the helminthes (worms) that cause gastro-intestinal infections in human beings. Wastewater may also contain highly poisonous chemical toxins from industrial sources. Relevant groups of chemical contaminants are heavy metals, hormone active substances (HAS) and antibiotics. The risks associated with these substances may, in the long-term turn out to constitute a greater threat to public health and be more difficult to deal with than the risks from excreted pathogens.

In order to prevent health risks, reuse after proper treatment is normally recommended as the main solution. There exists a large array of technological and process options for wastewater treatment. The most common systems of wastewater treatment in use in cities around the world are engineering plants which remove the main pollutants in the wastewater and release the treated effluent with lower concentrations of pollutants into natural water bodies for downstream reuse or as a disposal approach. A disadvantage of this engineering approach is that the engineering plants at large sewage works cost millions of dollars to build and have high operating costs, especially where a high level of nutrient and chemical removal is required to protect sensitive freshwater and marine environments. Due to low financial capacity, most cities in undeveloped countries have insufficient engineering plants and are not able to treat more than a modest percentage of urban wastewater. The perspectives regarding the increase in wastewater treatment capacity in these cities are bleak. Besides, such plants also generate waste which requires disposal.

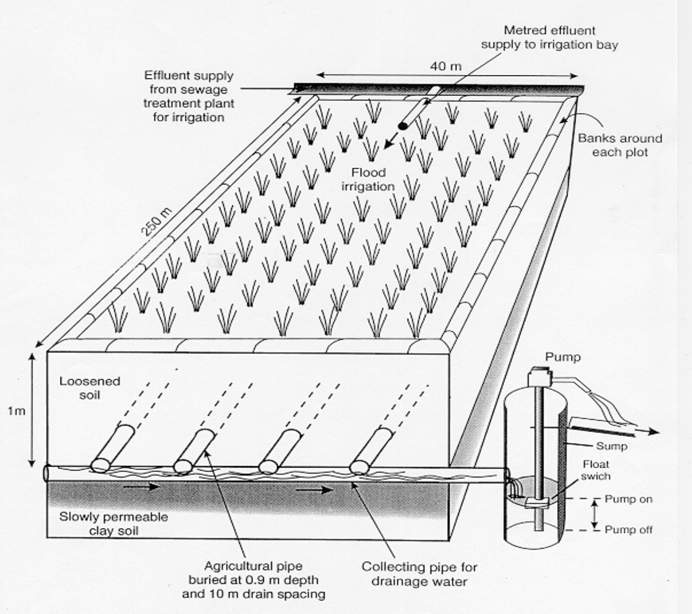
Another option to prevent the health risks is planned and regulated wastewater irrigation with crop limitations and proper irrigation methods (for example local irrigation). But for a given territory, it is not easy, often impossible, to limit the type of crops to be grown. For this reason, planned and regulated wastewater irrigation is often only a theory.

Introduction to FILTER (Filtration and Irrigated cropping for Land Treatment and Effluent Reuse)

Against this background, the FILTER (Filtration and Irrigated cropping for Land Treatment and Effluent Reuse) technique was developed in Australia (Jayawardane, 1995). By using this system, wastewater can be treated in a relatively small area of land with selected crops so that pollution of agricultural produce and health risks due to large-scale wastewater irrigation can be prevented. The FILTER technique combines using the nutrient rich effluent or wastewater for intensive annual cropping, with filtration through the soil to a sub-surface drainage system during periods of low cropping activity and high rainfall. It provides wastewater treatment throughout the year, thereby eliminating the need for expensive wastewater storage. The treated wastewater can be reused for irrigation or discharged to water bodies meeting the EPA requirements.

The FILTER technique can be categorized as a rapid, controlled flow system, which is a hybrid system that combines some of the hydraulic flow characteristics and wastewater renovation process of the slow infiltration, rapid infiltration and overland flow systems. The structure of the system is shown in Figure 1. The flow of wastewater or effluent, to the sub-surface drainage system, is controlled by regulated pumping. Wastewater or effluent application and sub-surface drainage can be regulated to ensure adequate soil conditions for crop growth and pollutant removal rates, thereby producing low-pollutant drainage waters which meet EPA criteria for reuse or discharge to surface water bodies.

Fig 1. Schematic diagram of FILTER plots



Each fortnightly wastewater application cycle or filter event consists of four consecutive stages. These four stages are wastewater application (irrigation), followed by a post-irrigation equilibration period and by a pumping period (until drainage outflow approximately matches the net inflow) and finally a no-pumping equilibration period (leading to flattening of the water table). The manipulation of these four-stage wastewater application and drainage operations could be used to maximize the removal of nutrients, and increase the uniformity in nutrient distribution and retention in the soil across the FILTER plots. The FILTER technique was field tested in both Australia and China. This paper presents the field results on the pollutant removal and crop growth measurements, carried out to assess the pollutant removal effect of the FILTER system at the FILTER trial sites in Griffith, NSW of Australia and Wuqing county, Tianjin municipality of China.

Tests and results

In Griffith, four irrigation bays (430 m long by 82, 80, 86 and 102 m wide) with 0.4 m banks were constructed to provide good control of irrigation. A subsurface drainage system was installed within the pilot trial area, which was connected through the collector drains and the main drain to the main sump, fitted with an electric pump and flow meter. The subsurface drains were spaced 8 m apart at a depth of 1.2 m. The irrigation channels and associated structures for controlling and monitoring irrigation were installed. A dethridge wheel, MACE flow and current meters were used to measure irrigation and drainage volume.

In autumn 1998, two of the bays were sown with Coolibah Oats at a rate of 90 kg ha^{-1} and 150kg of di-ammonium phosphate (18:20) fertilizer was drilled in with the seed. The other two bays were planted with ryegrass pasture mix; 17 kg multimix ha^{-1}, 6 kg demeter fescue ha^{-1}, 8 kg Victorian rye ha^{-1} and 5 kg guard rye ha^{-1}. Eight irrigation/FILTER events, of 2 weeks duration each, were carried out during that winter cropping season.

In Wuqing, ten wastewater irrigation and filtration plots, measuring 60m x 40m each, were constructed. The site consists of two FILTER plots with drains spaced at 5m, two FILTER plots with drains spaced at 10m, two FILTER reuse plots on which the drainage water from the above four FILTER plots were reused, three irrigated plots with no drains and one plot used for soil sampling to measure the soil hydraulic properties. A sub-surface drainage system was installed in each of the FILTER plots at a depth of 1.2 m, which was connected through the collector drains to the sump of each FILTER plot. The sump was fitted with an electric pump to discharge the filtered water from the subsurface drains. A pipe for conveying irrigation water and associated structures for controlling and monitoring irrigation were installed.

In winter 1999, the trial plots were sown with a winter wheat crop. Five irrigation/filter events were used for the first cropping season during the spring 2000. Continuous irrigation and drainage water samples were collected during the trials. Samples were stored at 4 ^{o}C before pH, Electrical Conductivity (EC), Biochemical Oxygen Demand (BOD_5), Total Suspended Solids (TSS), ammonium, oxides of nitrogen (NOx), total kjeldahl nitrogen (TKN), total phosphorus (TP), total fecal coliforms, and oil & grease were determined.

The soil profile was sampled up to a depth of 1.4 m and the core divided into intervals of 20 cm. The samples were analyzed following the methods of Rayment and Higginson, (1992).

When the crops were harvested, dry matter and grain yields were recorded. The crops were analyzed for total N following the method of Etheridge et. al., (1998) whereas TP and micronutrients were determined following the method of Zarcinas et. al., (1987) in order to estimate nutrient removal. Results of pollutant concentration and pollutant load reduction during the filtration events in Griffith site are shown in Table 1. For the Wuqing experimental plots changes of the concentrations of TP, BOD5 and COD in the effluent and drainage water are shown in Figures 2, 3 and 4. Load reduction of pollutants and their comparison with results from Griffith site are shown in Table 2.

Table 1. Pollutant concentration and pollutant load reduction during the Filtration events in Griffith site

Pollutant	Pollutant concentration ($mg\ l^{-1}$)*		Pollutant loads ($kg\ ha^{-1}$)		%Removal
	Incoming effluent	FILTER drainage	Effluent	Drainage	
Total phosphorus	6.1	0.39	46.7	1.7	96
Total nitrogen	19	15	131.4	55.9	57
Organic nitrogen	6.3	1.5	46.3	6	87
Ammonium-N	12.5	0.2	19.2	6.1	99
Nitrate-N	0.4	13.3	1.7	49.2	Increase
BOD_5	10.3	0.6	80.1	3.9	95
Oil & grease	1.8	0	15.9	0	100
Total suspended solids	71	16.9	70.8	16.9	76
*E.coli (CFU/100 mL)	170	4		0	98

**E.coli* is expressed as colony forming unit (CFU) per 100 ml of effluent

Figure 2. The Total-P concentration (mg l^{-1}) in the effluent applied and drainage waters from Wuqing FILTER 5m and FILTER 10m plots.

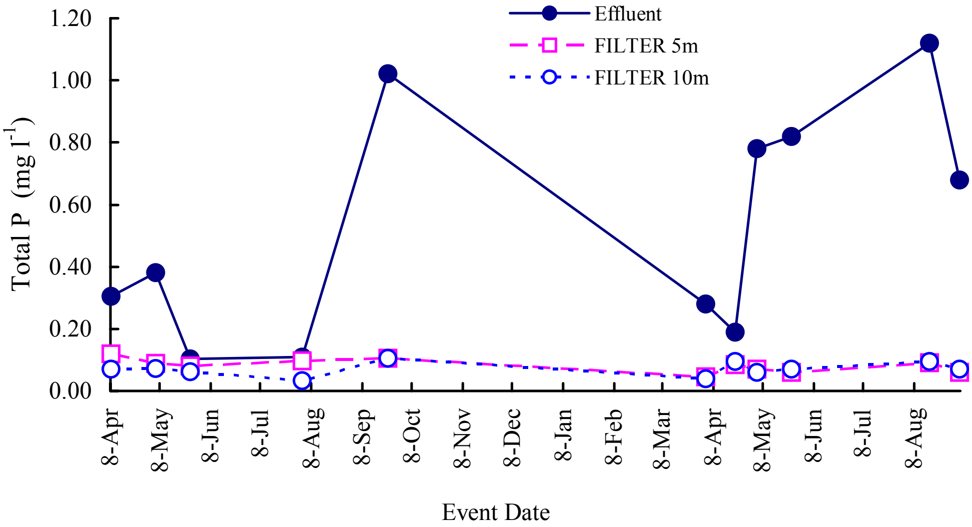


Figure 3. The BOD_5 concentration in the effluent applied and drainage waters from Wuqing FILTER 5m and FILTER 10m plots.

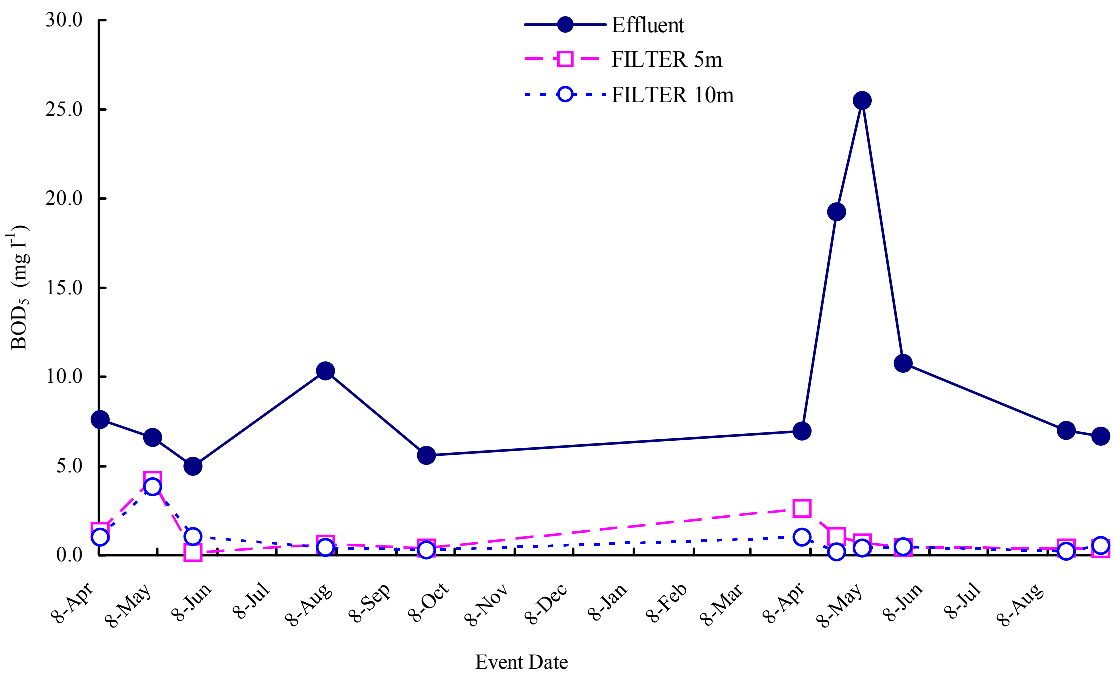


Figure 4. The COD concentration in the effluent applied and drainage waters from Wuqing FILTER 5m and FILTER 10m plots

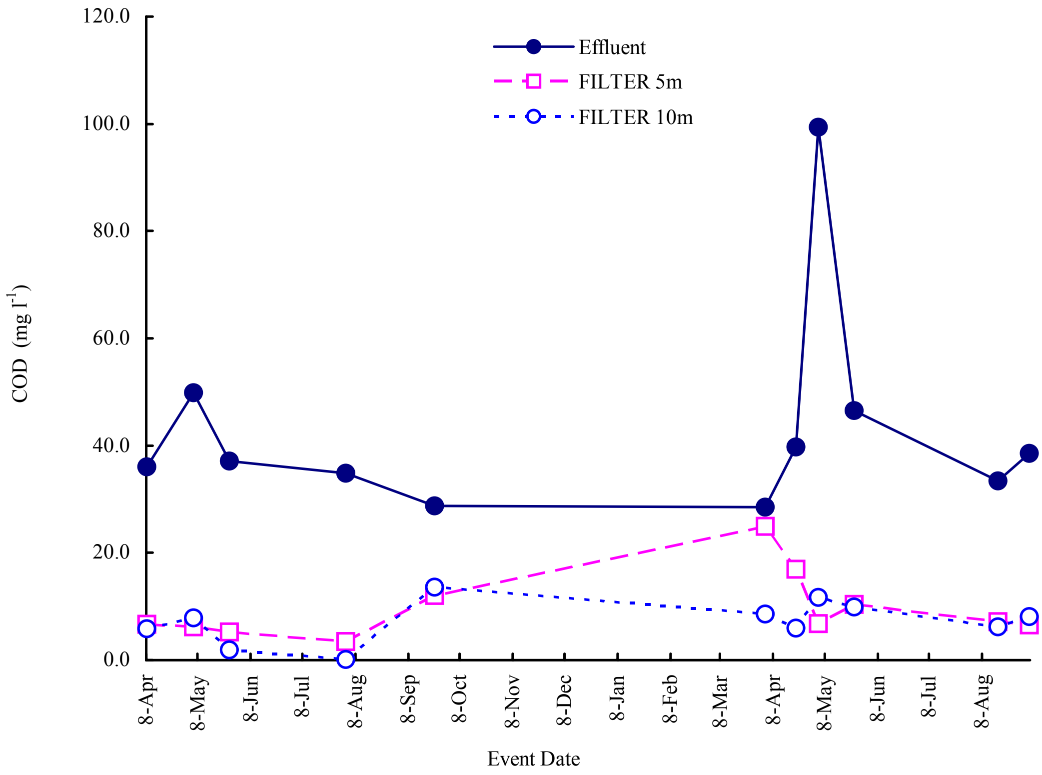


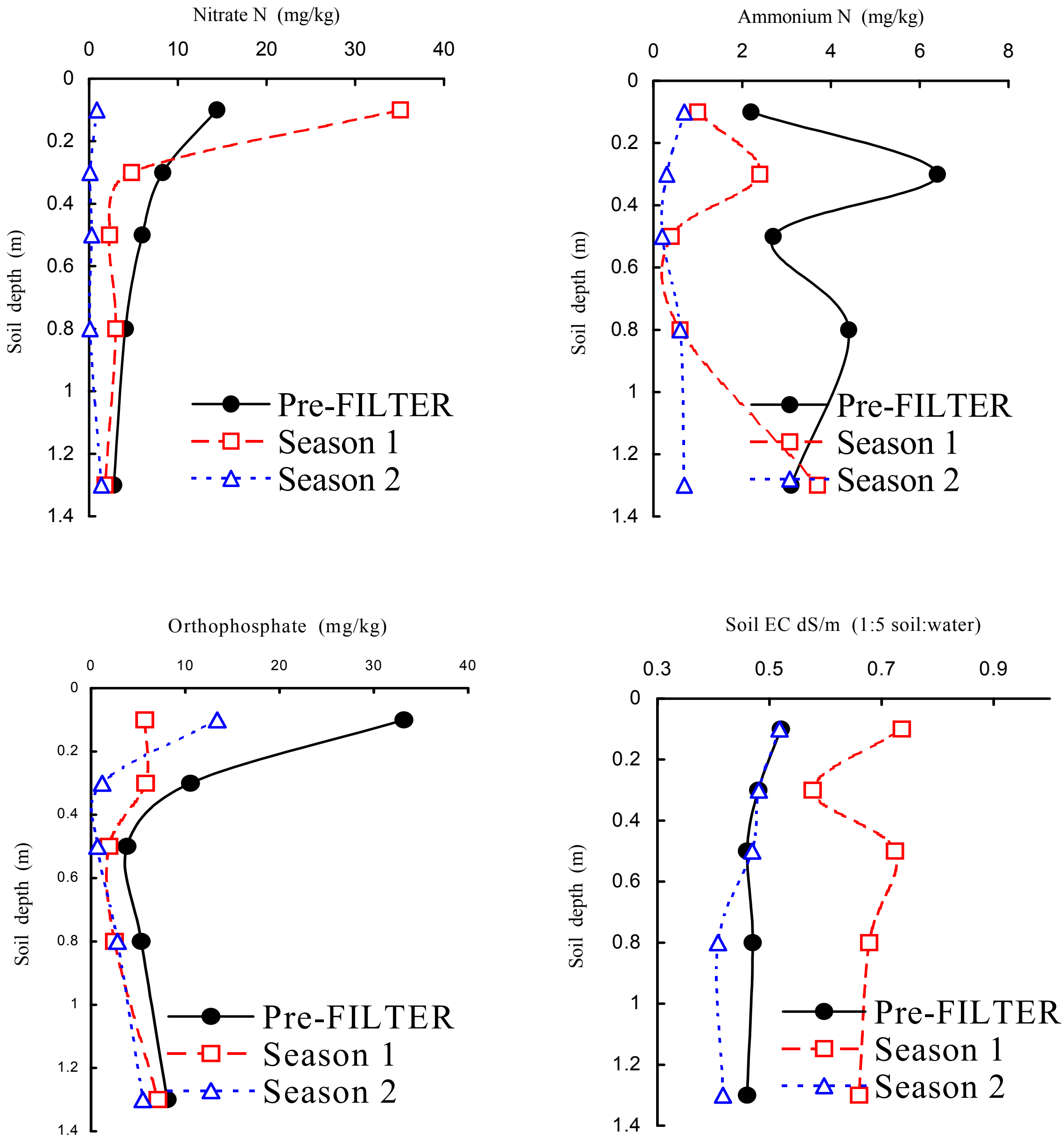
Table 2. Pollutant load reductions (%) of Wuqing and Griffith Pilot FILTER Trial sites, and reductions in mean E. coli counts

Pollutant	Total-P	Total-N	SS	BOD5	COD	E. coli
Griffith	96	58	85	95		98
Wuqing 5m	99	82	68	61	75	
Wuqing 10m	99	86	81	79	86	

From the results it can be observed that the pollutants can be substantially removed by using the FILTER technique. For the pathogens, utilizing E.coli count as the indicator parameter, can also be significantly reduced. Sampling of drainage waters from Griffith FILTER plots for E.coli during a filter events showed that the average number of E.coli in effluent water was 170 cfu /100 ml of effluent, whereas in drainage water this was reduced to 4 cfu /100 ml. The maximum total aerobic bacteria count in the effluent applied was 24,000 cfu /100ml, while the count in drainage water was 1300.

Previous studies have shown that heavy textured soils can provide an effective filter to remove microorganisms from sewage effluent, where bacteria are physically strained and the much smaller viruses are usually adsorbed. Due to soil chemical and biological activities, the FILTER system on heavy soils could effectively reduce E.coli, thereby producing drainage waters with lower risk of pathogen infestation

Figure 5. Changes in the content of extractable soil NOx-N, extractable soil NH4-N, extractable soil phosphorus and soil salinity in FILTER 5m plots



In a separate trial involving the spiking of the applied effluent with the full range of pesticides used in agriculture enterprises in the area, the pesticide loads in drainage waters were reduced by more than 98% (Data not shown). This means modified FILTER systems may thus be used to treat other industrial and commercial effluent containing chemicals which adsorb onto soil particles. The changes in extractable soil NOx-N content, extractable soil NH_4-N content, extractable soil phosphorus content and soil salinity in Wuqing FILTER 5m plots during 1999-2000 wheat cropping season and the cropping season followed are shown in Figure 5

For the 2M KCl extractable soil NOx-N (oxidized nitrogen) and extractable soil NH_4-N, there has been a considerable reduction in most of the soil layers during the first cropping season and a further reduction during the second cropping season. The extractable soil phosphorus content in the FILTER 5m plots still shows a slight decrease at the end of the winter cropping season, in spite of high phosphorus fertilizer application. The soil phosphorus content shows little change from the start to the end of the summer cropping season. This means a balance of soil phosphorus content between the addition from effluent irrigation, fertilizer applying and leaching from drainage. The changes of pollutant content in Wuqing FILTER 10m plots are very similar to the changes observed in the FILTER 5m plots.

Reasonable yields were obtained with substantial removal of N, P, K and Ca (Table 3). This data can be used to calculate the land area required to maintain nutrient balance, and to develop short-term and long-term options for nutrient management. These results emphasize not only the use of nutrients from wastewater for cropping, but also the economic benefits through crop production. Further, through the combination of FILTER design and cropping management it will be possible to avoid build up of nutrients at the reuse site.

Table 3. Removal of nutrient by crops in FILTER trial

Crops	Average Yield (t ha^{-1})		Nutrient removal (kg/ha)			
	Dry Matter	Grain	N	P	K	Ca
Pasture (Griffith)	12.5		182	21.4	142	19.8
Oats (Griffith)	13.4		76	19.9	131	12.1
Wheat (Wuqing)	12.5	3.94	139	20		

Summary and conclusions

From the results of the FILTER trials carried out in Griffith and Wuqing, it is suggested that the FILTER system can reduce pollutants, including pathogens and toxins, in drainage water to a reasonable level. This makes the technique a good option to be used separately or combined with other treatment methods for the treatment and reuse of wastewater, preventing health risks due to large-scale wastewater irrigation. In addition, during the operation of the FILTER system no accumulation of pollutants in the soil profile occurred, indicating the sustainability of the FILTER system in the treatment of wastewater and/or disposal of effluent. Further, good crop yields can offset the construction cost of the FILTER system this makes the FILTER technique more economically reasonable to be utilized for treating effluent.

In short, through the combination of an appropriate FILTER design and irrigation/drainage/cropping management, it is possible to develop a sustainable and economically reasonable system, which can reduce pollutant levels of effluent to a reasonable level, avoids build up of nutrient at the reuse site and prevents health risks due to large scale wastewater irrigation.

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Ground Water Contamination in Cambodia

Country paper prepared by
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Introduction

Cambodia borders on Thailand in the northwest and the west, Lao PRD in the northeast, Vietnam in the southeast and the east and the Gulf of Thailand in the southwest. Its total area is 181,035 km^2 with a population of about 11,437,000, according to the 1998 census. Agricultural land accounts for about 20% of the total area. Approximately 67% of the total land area remains forested. About 2 million hectares are used for rice cultivation. Cambodia is an agricultural country. Approximately 84% of the total population lives in rural areas of which 80% are farmers.

The country has abundant water resources and possesses a huge potential for the development of multipurpose water resources projects, covering irrigation, water supply, hydropower production, navigation, and tourism. The exploitation of these water resources however requires an improved institutional capacity as well as adequate financial support. About 82% of the total cultivated area in Cambodia is rainfed. Deforestation, erosion and sedimentation in the Tonle Sap Lake, in the rivers and in other lakes are at the origin of changes in the hydrological regime that cause floods, droughts, the shifting of the stream courses of rivers and changes in rain patterns.

In Cambodia large quantities of water are contained in the Mekong and other rivers and streams, in lakes and in groundwater resources. The latter are estimated at close to 17.6 billion m^3. The exploitation of these resources is very limited at present and large financial allocations are needed in order to properly develop the national water infrastructure in line with the national policies.

Surface Water

The Mekong River originates in the Tay Tang Mountains in Tibet, it has a length of 4800 km and a catchment area of 795,000 km^2. The Mekong River passes through China, Myanmar, Lao PDR, Thailand, Cambodia and Vietnam before entering the South China Sea.

At its confluence with the Tonle Sap River near Phnom Penh, the Mekong River receives a considerable discharge from the Tonle Sap Lake during the dry season (November to March.). Here, the river is divided into four branches: the upstream and downstream Mekong River branches, the Tonle Sap River and the Bassac River.

The Mekong River flows through Cambodia, over a distance of about 480 km. Its total drainage covers about 86% of the land area of the country and brings annual floodwaters of about 475,000 million m^3. These floodwaters enter partially into the Great Lake and inundate both sides of the Mekong and Bassac Rivers. This plays an important role in the maintenance of soil fertility. The Mekong River has a suspended silt load of between 300 to 600 g m^3, resulting in the sedimentation of several mm of silt per year.

The Mekong water is rich in lime and potash; its neutrality (pH 6.3-7.4) helps in reducing to some extent the acidity of the Cambodian soils. The mean annual discharge entering Cambodia exceeds 300 billion m^3 and it is estimated that with the contribution of downstream tributaries, some 500 billion m^3 are discharged into the sea annually. At Kratie Province, the peak discharge occurs during the August/October monsoon when it may reach 70,000 m^3 s^{-1}.

A particular aspect of the Mekong system in Cambodia is Tonle Sap Lake. The lake functions as a natural flood stabilizer in which some 20% of whole Mekong River floods are regulated by reverse flows into the lake mainly between June and September. The remaining 80% floods the lowlands of the country as well as the delta in Viet Nam.

During the monsoon flood season the overflow from the Mekong is diverted, expanding the size of Tonle Sap Lake area many times, flooding and fertilizing the surrounding rice plains and providing abundant supplies of fish. By September/October, the volume of water in Tonle Sap Lake may increase to 72 billion m^3 and the lake area may expand to 16,000 km^2.

The flow of Mekong River is closely linked to the rainfall pattern. Large areas of Cambodia around the Tonle Sap, Tonle Bassac and Mekong Rivers are flooded during the rainy season. Pollution generated along the rivers may be transported during the rainy season to the Tonle Sap Lake. The rich natural resources of the Mekong River and its tributaries contribute not only to Cambodia, but also to the neighboring riparian countries, playing an important role in socio-economic development.

Groundwater

Groundwater is used in Cambodia for both community and town water supply and for irrigation. To date, there has been no comprehensive investigation of the national groundwater resources. However, there have been two studies, both under the auspices of the US Geological Survey. The first (Cushman, 1958) was a reconnaissance of the lowland area to determine the availability of groundwater for dry season irrigation. The second was a general description of groundwater availability based on test drilling data and well records obtained in the course of a USAID rural development program between 1960 and 1963. The program drilled 1100 wells, of which some 800 were productive. Depths ranged from 2m to 209 m, with an average of 23 m. Information is also available from well drilling programs undertaken since the 1980s by NGOs and international organizations, particularly by OXFAM and UNICEF who have drilled more than 5000 wells throughout the country. These wells were generally to depths of 20 m to 50 m. The most recent information on these wells however, mainly relates to their location and characteristics.

The Mekong lowlands consist broadly of alluvial material overlying shale, slate and sandstone bedrock. The low hills and plateau areas are mostly underlain by igneous rocks and limestone. The depth of alluvium is 70 m or more. The alluvium consists of sandy silt in the upper part and of clayey silt in the lower. There are occasional sand beds of up 1 m thickness. Two types of alluvium are recognized, an older one and a younger one. The younger alluvium is situated under the Mekong and Tonle Sap Lake flood plain. Except for the occasional thin sandy beds and lenses, the alluvium has a low hydraulic conductivity and the yield is very low, typically 0.2 l s^{-1}. Yields from the sandy layer are higher, typically of the order of 1 l s^{-1}. For those UNICEF wells for which records are available, many have a yield of more than 3 l s^{-1}, while less than 3% are reported as having yields in excess of 10 m^3 hr^{-1} (2.7 l s^{-1}).

In January 1996, the Government of Japan signed an agreement to fund a project for the supply of clean water to the Phnom Penh municipality and rural areas by using groundwater. About 30% of this groundwater was to be obtained around Phnom Penh. No artesian aquifers were found, the area being underlain at depths ranging from 18 m to 80 m by hard crystalline rock. The best well yielded 3.3 $l\ s^{-1}$, and the average of seven production wells was 1.33 $l\ s^{-1}$.

Ground water levels

In Cambodia the productivity of aquifers in the eastern part of the country is high, whereas the aquifer productivity in the western part is low. Groundwater levels of existing wells have been surveyed since February 1997. These monthly base measurements continued until November 1997. Twenty-six wells were selected for monthly monitoring. Most of these are dug wells or combined wells. The results of these groundwater level measurements show values of 1.7 to 2.25 meters for dug wells and 4.75 to 5.5 meters for drilled wells. The lowest groundwater levels were observed in January to July 1997 while maximum levels occurred between October-November 1997. The groundwater levels along the Mekong and Bassac River show a steep rise from June-July, 1997. It is presumed that those groundwater levels are influenced by the water level changes of the rivers.

Groundwater Contamination

Groundwater in Cambodia is generally good quality, but high iron contents and increasing salinity levels have been noted in Svay Rieng and Prey Veng Provinces. Also, water sampling in four provinces in northwestern and southern Cambodia indicate high levels of iron, TDS and fluoride in groundwater. Many shallow wells are contaminated by fecal coliforms. All water samples in Battambang failed to meet WHO water quality guidelines. Contamination of water resources has led to frequent outbreaks of cholera.

Groundwater samples for chemical analysis were collected from 54 existing wells and 24 newly drilled wells (test wells) in May-June 1997. The following are some of the results within different provinces:

- In Svay Rieng Province the trace element chemistry, is dominated by Na, HCO_3 and Cl.
- In Phnom Penh $NaHCO_3$ is dominant along with Ca and Mg.
- In Prey Veng, Na, Ca and Mg dominate along with HCO_3 and Cl.
- In Kompong Speu, most samples contain Ca and HCO_3.

When the results are compared with the guideline values for drinking water issued by the WHO, many of wells have higher values than the WHO standards.

Geology and the occurrence of groundwater

On the basis of landforms, geology and occurrence of groundwater, Cambodia can be divided into three main regions namely, the Mekong Lowlands, the Southwestern Highlands and the Coastal Plain of Southwestern Cambodia.

The bedrock underlying the Mekong Lowlands consists predominately of a series of consolidated sediments of shale, slate, sandstone and limestone of Triassic and older age. The Southwestern Highlands consist of several massive mountain ranges. These ranges commonly have relatively steep sides and flat tops. The main mass of the Highlands is formed by the Cardamoms and Elephant mountains. The Highlands are made up of a series of metamorphosed sandstone, slate, schist and quartzite units. In the vicinity of the city of Pailin these are associated with a large mass of gabbro and rhyolite.

Alluvium

In Cambodia, the alluvial units constitute some of the most important sources of groundwater. The alluvium, whether it is older alluvium or young alluvium, may be composed of sand, silt and clay and mixtures of these constituents. The clay portions have a low permeability and may yield water at very slow rates. The sandy beds and lenses of the alluvium are some of the best water-producing horizons. Their average yield is about 16 m^3 h^{-1} in drilled wells. Groundwater from alluvium is generally believed to be of good chemical quality and suitable for most purposes in Cambodia. In many areas, dug wells are important as sources of domestic water supply.

Basalt and other igneous rocks

Data available on the water-yielding capacity of basalt quote yields of 30-50 m^3 h^{-1}. A large area of the country in Kompong Charm Province in the northeast is underlain by basalt. The quality of water from basalt is good and suitable for most purposes. Other igneous rocks occurring in the country are gabbro, rhyolite, diorite, and granite. The water-yielding capacity of these rocks, either fresh or weathered, is believed to be similar to basalt.

Post-Triassic Sandstone and Conglomerate

A large part of the highland area and a large area between Kompong Cham and Pursat Province are underlain by these rock types. The original porosity and openings along joints and bedding planes make these rocks somewhat permeable. No deep wells are known to penetrate the sandstone and conglomerate beds. The groundwater from sandstone and conglomerate should contain little mineral matter as the rock consists mostly of silica.

Limestone

Limestone has limited distribution in surface exposures. Almost no data are available on the water-bearing capacity of limestone, but it is believed that limestone could yield substantial water.

Triassic Metamorphic rocks

Triassic rock units consisting of sandstone, shale, slate, quartzite, and schist appear to underlie a large portion of the Mekong Lowlands. The yields are considered to be low.

Conclusions and Recommendations

- In conclusion, surface water will probably always be the predominant source of water supply for all purposes, particularly for irrigated agriculture. Groundwater could provide an important source of supplemental water during the dry season. It could also be a principal source of water for small industries, minor irrigation and domestic use.
- No hydro-chemical or hydrological evaluation has been done for many groundwater sources. At the same time, in many instances data available have not been fully utilized and interpreted. In addition, Water quality standards have not been established.
- Elevated arsenic values have been found in some areas but systematic testing has not been done. No facilities are available in the country for arsenic analysis and samples have to be sent abroad.
- A national focal point is needed for hydrogeological assessment and groundwater monitoring and evaluation.
- An (inter-ministerial) arsenic/groundwater task force is needed to bring together available groundwater management and expertise, to evaluate existing groundwater/geology data for a better understanding of the groundwater system and its main hydro geological process, to use existing/new groundwater data for evaluation of water contamination and other groundwater management issues and to coordinate the collection, storage and exchange of data among others to advise the government on laboratory facilities, quality standards and future groundwater management issues.

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Groundwater Pollution in the Hanoi Area, Vietnam

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Abstract

Water supply in Hanoi is mainly from groundwater. Exploitation of groundwater for domestic and industry use in Hanoi started in 1909. From an initial use of some 20,000 m^3 d^{-1} the volume of water extracted has steadily increased to over 500,000 m^3 d^{-1} at present. It is estimated that in 2010 the volume will be close to 1,000,000 m^3 d^{-1}. The pumping of large volumes of groundwater has negative impacts such as the lowering of the groundwater level, the enlargement of the cone of depression, land subsidence and groundwater pollution. Groundwater pollution in the general Hanoi area occurs in the two main aquifers, the Holocene aquifer and the Pleistocene aquifer, the latter being the main production aquifer. The pollutants are nitrogen compounds, biological and organic matter and toxic elements such as arsenic and mercury. Pollution by nitrogen compounds has been studied since the 1990's. The results show that the main contaminant is ammonia. The polluted area and the concentration of pollutants increase with time.

Introduction

Hanoi is located in the Red River delta it has an area of 900 km^2, 7 urban districts and 5 sub-urban districts and a population of 2.7 million inhabitants. Most of the Hanoi area is flat with elevations below 20m, but in the north the Tam Dao hills are up to 462 m high. Annual rainfall in the Hanoi area is 1600mm. The rainy season from May to October accounts for 85% of annual rainfall. The Red River is the largest river in the northern part of Vietnam. It passes through Hanoi and in the center of the city is joined by the Duong River. The average volume of water transported by these two rivers through Hanoi is 3500 m^3 s^{-1}.

Groundwater resources in the Hanoi area

Most of the groundwater under the Hanoi plain is contained in quaternary sediments, in two main aquifers. The Holocene aquifer or upper aquifer is distributed widely over an area of 530km^2. The upper part consists of clayey and sandy layers and has a thickness of up to 10 m. The lower part is made up of various sands, at times mixed with gravel. The average thickness of the aquifer is between 9.2m in the north and 13.3m in the south of the Red River delta area.

The transmissivity for the Holocene aquifer is from 20 to 800 m^3 d^{-1}. The water level is in general 3-4m below the surface however in the south of the Red River the water level is lower due to groundwater pumping. The specific capacity in test wells is from small to 4.5 l s^{-1}. The recharge sources are rainfall, irrigation and river water. Groundwater losses occur through discharge into the river in the dry season and through evaporation and percolation into lower aquifers. The groundwater is fresh the TDS, mainly calcium carbonate is below

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0.5 g l^{-1}. The iron concentration in most areas is between 0.4 to 10 mg l^{-1}, manganese is from 0.2 to 2.0 mg l^{-1}, ammonia is from very low to very high in the south of the city. In the Thanh Tri district this concentration can go up to100 mg l^{-1}. The Holocene aquifer is sufficient for small-scale water supply. Producing groundwater from this aquifer is done by dug wells and small diameter shallow wells.

The Pleistocene aquifer is situated lower in the stratigraphic sequence. The depth to the top of this aquifer is 2-10m in the north, 5-22m in Gia Lam and 10-35m in the south. There is a weakly permeable layer between the upper aquifer and the lower aquifer. Between the Red and Duong rivers this layer thins out so that the two aquifers are overlying each other directly creating a "hydrogeological window". The Pleistocene aquifer is made up of sand mixed with cobbles and pebbles and has a thickness of 10-35m. The transmissivity is from 200 to 1600 m^3 d^{-1}. The specific capacity in the tested wells in most cases is over 1 l s^{-1}. The aquifer has a significant potential for the supply of groundwater. The groundwater is fresh, the TDS, mainly calcium carbonate, is up to 0.78 g l^{-1}. The iron concentration is high from 0.4 to 50 mg l^{-1}, the manganese concentration ranges from 1.0 mg l^{-1} to 4-5 mg l^{-1}. Ammonia concentration in the Thanh Tri district, in the South of city is very high with an area of 80 km^2 having over 10 mg l^{-1}. The lower aquifer has been used for the main water supply of Hanoi since the beginning of the last century. Groundwater pumping from the wells at Yen Phu began in 1909. Since then the amount of groundwater pumped has been increasing with time, from 20,000 m^3 d^{-1} in 1954 to the present rate of well over 500,000 m^3 d^{-1}.

Water supply for domestic purposes and drinking and for industry and manufacturing is mainly derived from groundwater. Public groundwater supply is managed by Clean Water Business Companies. Water is drawn from 10 well fields and other small stations from a total of 150 wells approximately. The average daily withdrawal from these wells is 420,000 m^3. The whole volume is drawn from the lower aquifer. Companies, economic units and organizations (Schools, hospitals, institutes.), also withdraw groundwater. This is done from about 500 wells drilled into the lower aquifer with an approximate production of 150,000 m^3 d^{-1}. Rural groundwater is produced from shallow small diameter wells pumping water from the upper aquifer. The treatment and extraction equipment in use is very basic. The number of these wells is increasing with time. In 1999, 150,000 m^3 d^{-1} was produced from 150,000 rural wells. The demand for drinking water and for water for domestic uses is increasing. According to the Water Master Plan for Hanoi this demand may reach 700,000 m^3 d^{-1} in 2010 and 1,400,000 m^3 d^{-1} in 2020.

Negative impacts caused by groundwater pumping

Most production wells' capacities are designed on the basis of exploration results. But some private wells are drilled randomly, therefore groundwater pumping will have some negative impacts such as land-subsidence, the lowering of the water table and pollution.

Land subsidence

The study of land subsidence in the Hanoi area is still preliminary, but land subsidence has been discovered. In 1988, the Hydrogeological and Engineering Geological Division No 2 constructed 32 benchmarks South of the Red River for the measurement of land subsidence. From 1991 to 1995 the Transportation Public Work Service managed these benchmarks with sponsorship from the Finnish Government, and added 13 benchmarks. The results of the studies in the period 1988-1995 show that most of the urban area and its vicinity suffer from land subsidence. The highest land subsidence of over 10 mm yr^{-1} is in the center and to the South of Hanoi city. The rate of land subsidence is highest in Giang Vo – Thanh Cong and Phap Van with a value of 20-44 mm yr^{-1}. Since 1997 the Institute for Technical Science and Construction has been studying land subsidence at 6 stations in and around Hanoi with similar results. From the results some conclusions can be drawn as follows;

- Areas from where large volumes of groundwater are withdrawn, and which are underlain by weak, soft strata (mud, peat, organic matter) have the highest rate of land subsidence.
- Land subsidence velocity is reduced with time.
- The reasons for land subsidence can be many, but groundwater pumping is the main reason.

Lowering of the groundwater level

Intensive pumping of groundwater has affected the groundwater equilibrium, especially south of the Red River. The cones of depression beneath the city and in surrounding areas have become very large, with the largest cone having an elliptic cross section of which the long axis extends from Co Nghue to Ngoc Hoi and the shorter axis, perpendicular to the Red River, from Ha Dong to Yen Phu. In this large cone there are many smaller cones, reflecting the location of the well fields. The cones of depression exhibit several different levels of intensity between areas where the water table is almost at 0 meters and areas where the drawdown is at –14 meters. Not only the size of the cone of depression grows over time, the drawdown itself becomes larger over time. This is not so much in evidence near the Red River itself, as the aquifers get replenished there, but away from the direct influence of the river, water table levels of –32 meters have been measured.

Groundwater pollution

The groundwater pollution in Hanoi has been studied over a long time, but those studies have not been systematic and the results are not yet complete. However some conclusions can be drawn from the results available. Nitrogen compounds, organic and bacterial matter and pollution by heavy metals have been studied at different levels.

Groundwater pollution caused by Nitrogen compounds

Pollution of groundwater by nitrogen compounds in the southern part of Hanoi, has been studied by the Northern Hydrogeological Engineering Geological Division since the early 1990s. Water samples were taken twice per year once each in the dry and rainy seasons. The studied nitrogen components are NH_4^+, NO_2^- and NO_3^-. Table 1 below shows the standard limits (STLs) that were applied for the degree of pollution of groundwater by nitrogen compounds.

Table 1. Standard limits for the degree of pollution of groundwater by nitrogen components.

Compound	STL for drinking water, mg l^{-1}	Degrees of pollution, mg l^{-1}			
		Clean	Light pollution	Moderate pollution	Serious pollution
NH_4^+	3	<0.5	0.5-3	3-10	>10
NO_2^-	0.1	<0.1	0.1-0.5	0.5-1	>1
NO_3^-	5	<5	5-10	10-50	>50

The results of the studies show that there is serious ammonia pollution of groundwater. The concentrations of this compound are high and are increasing over time; they are distributed over a large area. Nitrite and nitrate are rarely found in elevated concentrations. Table 2 below illustrates the results obtained for ammonia over the years.

These results show that the average ammonia concentration in groundwater is higher than the standard limit for drinking water. The ammonia concentration in the upper aquifer is higher than in the lower aquifer, indicating that the pollutants migrate downward. In addition, the ammonia concentration in both aquifers is increasing with time. Further, the ammonia concentration in the upper aquifer is changing strongly with time, influenced directly by the sources of pollution and by climate factors. The lower aquifer does not show such variation. The northern part of the city does not show similar ammonia pollution.

Table 2. Ammonia concentration in groundwater in the south of the Red River 1992-2002

Year	Season	Holocene aquifer (qh)			Pleistocene aquifer (qp)		
		No of samples	Concentration, mg l^{-1}		No of samples	Concentration, mg l^{-1}	
			Max	Average		Max	Average
1992	Dry	41	58.1	7.1	43	58.1	4.2
	Rainy	42	64.5	8.7	46	51.6	4.7
1993	Dry	42	34.6	5.2	43	24.2	4.4
	Rainy	45	48.4	5.1	48	19.3	4.1
1994	Dry	43	84.7	7.6	48	33.6	5.1
	Rainy	49	51.7	4.3	51	17.4	3.7
1995	Dry						
	Rainy	50	100.0	11.9	52	80.0	7.4
1996	Dry						
	Rainy	40	128.0	16.8	47	128.0	7.6
1998	Dry	30	144.0	11.1	42	100.0	8.9
	Rainy	27	151.5	11.2	42	42.0	8.5
1999	Dry	31	168.0	16.1	42	44.0	8.7
	Rainy	29	157.2	16.2	40	45.5	9.3
2000	Dry	31	178.0	18.7	41	50.4	7.5
	Rainy	27	118.0	14.7	39	30.5	6.9
2001	Dry	36	204.0	14.6	18	32.0	7.5
	Rainy	38	56.4	8.1	37	39.2	5.2
2002	Dry	34	92.4	16.9	46	72.4	11.1
	Rainy	32	135.2	17.5	47	64.0	9.54

Groundwater pollution caused by organic matter.

Total organic matter content is studied at the same time as the nitrogen compounds, by determining the level of oxidation. The results, in mg l^{-1} O_2, are presented in the Table 3.

Table 3. Oxidation of groundwater south of the Red River 1992-2002 (mg O_2 l^{-1})

Year	Season	Holocene aquifer (qh)			Pleistocene aquifer (qp)		
		No of samples	Concentration, mg l^{-1}		No of samples	Concentration, mg l^{-1}	
			Max	Average		Max	Average
1992	Dry	41	16	3.79	43	11.36	2.7
	Rainy	40	25.6	5.99	46	67.2	4.14
1993	Dry	42	13.44	3.98	43	10.88	2.56
	Rainy	45	21.12	4.46	48	12.8	3.71
1994	Dry	43	21.76	3.52	48	11.2	2.77
	Rainy	49	16.2	3.10	51	64	4.79
1995	Dry						
	Rainy	50	132	12.05	52	14.72	4.16
1996	Dry						
	Rainy	42	46.4	9.28	46	17.6	5.83
1998	Dry	30	26.6	9.10	41	20,8	7.22
	Rainy	26	31.6	8.91	41	24	7.89
1999	Dry	31	28.8	10.52	41	22.8	8.92
	Rainy	29	31.2	10.94	39	68	10.31
2000	Dry	31	33.2	9.16	41	31.2	8.32
	Rainy	27	31.6	10.05	39	34	9.07
2001	Dry	35	38.4	9.87	18	19.2	6.24
	Rainy	38	19	6.32	37	13.7	4.62
2002	Dry	34	21.84	7.24	46	14.32	5.49
	Rainy	32	23.2	7.26	47	13.2	4.76

These results are similar to the results for ammonia. The average value in groundwater is higher than standard limit for drinking water. The oxidation values in the upper aquifer are higher than in the lower aquifer indicating that the pollutants percolate from surface downward. The values are, in both aquifers, increasing with time. The polluted area is in the south of the city. Preliminary studies in 2000 by Pham Hung Viet of the Center for Chemistry and Environment of the University for Natural Sciences on concentrations of volatile organic substances - benzene, toluene, chloride derivatives - in groundwater are so far incomplete and inconclusive.

Groundwater pollution by microbes.
Microbe pollution by *coliform* (Standard limit 3 100ml^{-1}) and *fecal coliform* (Standard limit zero) was studied in 1993 by Do Trong Su of the Research Institute for Geology and Mineral Resources. The results are presented in Table 4.

Table 4. Microbe concentrations in groundwater in Hanoi area, 1993

Season	Holocene aquifer (qh)			Pleistocene aquifer (qp)		
	Number of study samples	Number of samples - higher value than standard	%	Number of study samples	Number of samples - higher value than standard	%
Dry	36	28	77	31	15	48
Rainy	14	7	50	20	9	45

These results indicate that microbe values in groundwater in both aquifers are higher than the standard limit. The groundwater in the upper aquifer is more seriously polluted than in the lower aquifer. Microbe pollution in the dry season is more intense than in the rainy season. The main microbe elements are *fecal coliforms*.

Groundwater pollution by heavy metals.

Heavy metal pollution has been studied, though not yet in a very coherent manner. To date the best results are available for arsenic contamination. In 1994 relatively high arsenic concentrations were reported from the Hanoi area and in 1999 from Hai Ba Trung district. Subsequently UNICEF sponsored a study on arsenic levels in production wells. The results showed that 25% of the collected samples had concentrations of arsenic that were higher than the standard limit. A later study of arsenic in groundwater, also sponsored by UNICEF, was executed by the Northern Hydrogeological Engineering Geological Division. A large number of samples was collected from locations all over Hanoi in the dry season of 2000 and in the wet season of 2001 (Table 5). The results indicate that in the north of the Red River and the Duong River in Soc Son and Dong Anh districts the samples are taken only in the lower aquifer. The number of samples having a concentration higher than the STL is small. In the south of the Red River and the Duong River, 1.8 to 59.7% of samples have As concentrations higher than STL. In the Gia Lam area, the number of samples having an As concentration greater than STL in the upper aquifer is larger than in the lower aquifer while in the Tu Liem district, this is the other way around and in Thanh Tri and in the urban area the degree of As pollution in both aquifers is the same. In all study areas groundwater is heavier polluted in the dry season than in the rainy season.

Table 5. Arsenic in groundwater, Hanoi area.

Area	Holocene aquifer		Pleistocene aquifer		Max. value mg l^{-1}
	Dry season 2000	Rainy season 2001	Dry season 2000	Rainy season 2001	
Dong Anh					
No. of samples			78		0.105
No. of samples with concentration > STL			6		
Percentage %			7.7		
Soc Son					
No. of samples			37		0.196
No. of samples with concentration > STL			1		
Percentage %			2.7		
Gia Lam					
No. of samples	20	19	72	72	0.274
No. of samples with concentration > STL	8	2	13	2	
Percentage %	40	10.5	18.1	2.8	
Thanh Tri					
No. of samples	72	72	24	23	0.292
No. of samples with concentration > STL	43	29	13	9	
Percentage %	59.5	40.3	54.2	39.1	
Tu Liem					
No. of samples	55	55	25	25	0.216
No. of samples with concentration > STL	8	1	9	3	
Percentage %	14.5	1.8	36	12	
Urban area					
No. of samples	47	46	42	43	0.331
No. of samples with concentration > STL	18	12	17	8	
Percentage %	38.3	26.1	39.5	19	

Summary

Intensive groundwater pumping can be a direct cause of pollution as it causes lowering of the groundwater table creating a cone of depression and a large hydraulic gradient. Environmental pollution in Hanoi is very serious. Domestic and industrial wastewaters are not treated and in most cases are allowed to flow untreated into the natural drainage. Landfill and large cemeteries in some areas can be sources for microbes, nitrogen and organic matter. This is considered the main reason for the serious ammonia and organic matter pollution in the South of Hanoi. The urban area has been over-drilled for groundwater and there has been exploitation of clay for the manufacture of bricks and tiles, big areas have been excavated for waste dumps, construction work is ongoing on a large scale. All these can be causes of pollution, especially pollution that will trickle downwards from the surface. Composition and origin of sediments can be causes of pollution. Organic matter in soils, mud, peat can be sources for nitrogen compounds. Fine sediments high in organic matter can be sources of arsenic pollution.

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Heavy Metals Pollution in Paddy-Soils near Ho Chi Minh City Caused by Wastewater Discharge and the Influence of Cadmium on Rice

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Abstract

Most of Ho Chi Minh City's industrial factories were founded 25 years ago. Their equipment and machinery is now outdated and there are no wastewater treatment systems. Wastewater flows directly into rice fields and pollutes water resources and the soil environment affecting agricultural production. This paper presents the results of a research project investigating 6 heavy metals (Cd, Cu, Zn, Pb, Hg, Cr) at 126 points in rice fields including 14 wards and villages of districts No.2, No.7, No.9, Binh Chanh, Thu Duc and Nha Be. The results indicate that the paddy soils are polluted by industrial and household wastewater and that there is a threat from Cd pollution. Concentrations of Cd in soil range from 4.7-10.3 mg kg^{-1}.

Addition of Cd to the soil at concentrations ranging from 5-40 mg kg^{-1} *in dry soil shows that, Cd concentration in soil at levels > 25 mg* kg^{-1} *affects agricultural characteristics and crop yields. However, these influences depend on the rice variety. The content ratios of Cd in soil: roots: straw: brown rice was roughly 10:200:10:1. Accumulation of Cd in brown rice in field experiments is lower (10-20%) as compared with green house experiments. Cadmium concentrations in brown rice grown in areas that are affected by high Cd wastewaters of HCMC exceeds the internationally recognized Maximum Level (ML) for Cd in rice grain of 0.2 mg Cd* kg^{-1} *as established by the Joint FAO/WHO Food Standards Programme, Codex Alimentarius Commission (CAC). This is of considerable concern as rice constitutes a major intake pathway of Cd with confirmed direct negative impacts on human health.*

Introduction

Ho Chi Minh City (HCMC) is the largest city in Vietnam. It is located in a special geographical position where many favorable conditions for economic development converge. The city covers an area of 2,056km^2 and supports a population of 5,225 million. It has the highest rate of development in industry and handicrafts in Vietnam. In 2000 HCMC had 1,000 industrial factories, 28,500 handicraft foundations and 12 industrial zones. Most industrial zones have been operating since before 1975. They now find themselves with outdated equipment and without wastewater treatment systems. This wastewater is discharged into canals and flows directly to cultivated areas. This has resulted in serious pollution of soil and agricultural water, especially for the rice-fields and aquaculture areas of the suburbs. Although the HCMC government carried out monitoring and assessment of heavy metals in river water, groundwater, sludge from rivers and canals, vegetation, aquatic life heavy metal pollution in rice-fields and its influence on rice

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have not been studied. The research presented in this paper focuses on 6 heavy metals (Cd, Cu, Zn, Pb, Hg, and Cr). Samples were collected from 126 points in rice-fields polluted by wastewater from industrial and domestic activities. Sampling activities covered 14 wards and villages of 5 districts and counties, namely Nha Be and Binh Chanh Counties, District 2, District 7, District 9 and Thu Duc District.

Equipment and methodology

The selection of study areas and the collection of samples were based on UNESCAP and CCME methods. Soil samples were collected from rice-fields at a depth of 3-15cm. Consequently, soil samples were analyzed under controlled laboratory conditions. Heavy metals in soil were analyzed using the polarographic method and heavy metals in rice were determined by neutron activation. After analyzing for 6 heavy metals in soils, it was concluded that Cd has a high pollution potential for rice-fields in the areas investigated.

Determination of the influence of Cd in soil on the growth of rice was initially investigated in an experiment in which 6 rice plants were grown in the same pot with 4.5 kg of dried soil collected from the investigated areas. Cadmium was added to these soils at 0, 5, 10,15, 20, 25, 30, 35 and 40 mg kg^{-1}. De-ionized water was used for irrigation. The experiment used rice variety VND95-20, a popular variety, and was conducted in a green house in which humidity; temperature and light were standardized and controlled. Larger scale field based trials were also conducted to investigate the growth, development and accumulation of Cd in rice. These trials were conducted in Cd-polluted areas with two rice varieties VN95-20 (high production rice) and VD20 (aromatic rice). Soil samples were collected at Nha Be County and 5 levels of Cd were applied namely 0, 15, 20, 25, and 30mg kg^{-1} dried-soil. Mixed soil was poured into square wooden trays (100x100x30cm) containing a nylon liner large. Thirty rice plants per cultivated per tray. Data were analyzed as ANOVA standardization using MSTATC and IRSTAT 4.01

Results of research and discussion

Analyses of 6 heavy metals (Cd, Cu, Pb, Hg, Zn, and Cr) from 126 sampling points in rice-fields directly polluted by wastewater from HCMC are presented in Table.1. The results for Cr and Pb indicate some level of pollution, but compared to standards in use in some European countries they are just slightly in excess of acceptable limits. Hg and Cu were within limits. The concentration of these elements in soil was lower than the permissible standard (TCCP). The concentration of Zn was high in some cultivated areas, especially near some factories and industrial zones. In comparison, significantly elevated levels of Cd were observed with maximum concentrations ranging from 9.9 to 10.3 mg kg^{-1}. These rice-fields receive water directly from 3 systems namely the Tan Hoa - Lo Gom canals, the Te - Doi canals and the Tau Hu - Ben Nghe canals. Those canals are known by the local people in HCMC as “dead canal” and the “center of heavy metals”. These canals receive wastewater from many sources of the city, domestic wastewater, industrial wastewater, wastewater from service activities and especially wastewater from textile factories and handicraft foundations. This wastewater has not been treated before being discharged into the drainage systems and rice-fields.

Table.1: Concentration of heavy metals in paddy soil, polluted by wastewater from HCMC (mg kg^{-1})

Location	Number of samples	Cd	Cu	Zn	Pb	Hg	Cr
Nha Be	88	9.9	28.6	110	61.7	0.09	125.3
District 7	4	4.7	22.7	233	39.0	0.05	115.4
Binh Chanh	10	10.3	31.0	197	58.0	0.21	119.0
District 2	10	5.5	33.1	435	43.6	0.34	44.8
District 9	6	4.9	29.5	568	40.5	0.03	54.3
Thu Duc	8	6.8	30.0	282	44.3	0.20	84.3
Maximum Permissible Levels							
Holland		1-5*	50-100	200-500*	50-150	0,5-2	100-250*
England		1-3	140	280	35	0 –1	0-100
Germany		3+	100+	300+	50+	2+	100+

In comparison, in 1996, the center for experimental analysis reported Cd levels in mud of the Nhieu Loc- Thi Nghe Canals ranging from 28-35 mg kg^{-1}. In addition, in 1998 the Institute for Environment and Resources reported that the average value of Cd concentration in the Sai Gon - Dong Nai River system was between 9.7-25 mg kg^{-1}. Also, Cd concentration in spinach fields at Vinh Loc, Binh Chanh County was 5.09 mg kg^{-1} (Bui Cach Tuyen, et al., 1994). Cadmium is one of the 8 elements that polluted the sludge of the Tan Hoa - Lo Gom Canals (Ngo Quang Huy, et al. 1999). A study of 8 soil types in Nha Be County (Table 2) shows that Zn and Cd occur in high concentrations in 3 soil types namely Pfm, Ppm and Sj2m. For the other 5 categories, the concentration of Cd and Zn decreases with the distance from the source of pollution (Kuo, et al., 1983).

Table 2. Distribution of heavy metals in some soil types in the research area (mg/kg)

	Soil type	Cd	Cu	Zn	Pb	Hg	Cr
1	Red-Yellow alluvial soil (Pfm)	16.7	27.5	130.0	78.1	0.19	133.1
2	Alluvial soil/ potential acid sulfate soil (Ppm)	14.0	29.4	102.4	63.8	0.07	136.5
3	Actual acid sulfate soil (Sj_2m)	14.5	28.7	102.1	66.8	0.15	133.8
4	Actual acid sulfate soil, read rusts (Sj_2Rm)	7.6	23.6	83.8	70.2	0.12	124.3
5	Actual acid sulfate soil, depth layer (Sp_2m)	12.4	27.7	92.7	59.4	0.12	129.7
6	Actual acid sulfate soil, organic (Sp_2hm)	7.8	18.6	97.2	67.1	0.11	121.3
7	Potential. AAS, Shallow acid layer (Sp_1m)	8.0	30.0	99.0	76.3	0.09	140.5
8	Potential. AAS, many organic (Sp_1hm)	8.0	23.2	87.7	71.2	0.08	120.5

Table 3 indicates that increasing soil Cd concentration delays rice plant growth. This may be due to the fact that Cd is toxic to rice roots. A total Cd concentration in soil above 20 mg kg^{-1} will restrict the growth process of rice, and decrease the length of the rice plant. This in turn leads to a decrease in biomass. However, this value is only provisional as in reality it is the bio-available Cd fraction that is critical.

Table 3. Effect of soil Cd concentration applied as Cd salts on the agro-characteristics and the dry yield of rice

Cd (mg kg^{-1})	Duration (days)	Length (cm)	Dried Biomass (g/pot)$^{(*)}$
0	108	82.8	17.7
5	107	84.0	17.4
10	107	80.2	17.2
15	106	79.7	16.5
20	108	76.2	15.6
25	110	70.8	14.4
30	113	61.2	13.6
35	115	60.7	13.3
40	116	60.0	11.7
CV (%)	-	2.48	10.02
$LSD_{0,01}$	-	4.85	419

(*) at 64 days after planting

Table 4 shows that high concentrations of Cd in soil decrease the number of rice ears per pot. Cd concentrations > than 30 mg kg^{-1} resulted in a > 40% decrease in the number of rice pannicles per pot. This infers a significant reduction in yield. Table 4 also indicates that concentrations of Cd in soil between 25-30 mg kg^{-1} will cause productivity decreases ranging from 31.6-32.0 % and soil Cd concentrations between 35-30 mg kg^{-1} will cause a 40.1-53.8 % decrease in productivity. This is confirmed by greenhouse experiments on VND95-20 rice.

To confirm these results, the project carried out field experiments with five concentrations of artificially applied Cd namely 0, 15, 20, 25, 30 mg kg^{-1} and two rice varieties namely VND950-20 and VD20.

Table 4. Effect of soil Cd concentration applied as Cd salts on the number of ears and the yield of rice

Cd (mg kg^{-1})	No. panicles pot	1000 grain weight (g)	Unfilled grain (%)	Yield (g pot^{-1})	% as compared with control
0	17.0	23.6	29.2	29.6	100
5	16.0	23.2	30.2	30.6	103.6
10	15.0	22.8	29.5	27.1	91.6
15	13.7	22.8	31.7	24.0	81.2
20	11.7	21.7	35.3	23.7	80.3
25	11.7	20.5	35.8	20.1	67.9
30	11.0	20.5	42.2	20.2	68.4
35	9.7	19.9	50.2	17.7	59.9
40	9.0	19.4	44.4	13.6	46.2
CV (%)	12.26	8.56	8.01	5.49	-
LSD <0.01	4.28	2.83	8.01	3.47	-

Table 5 demonstrates that for VD20 rice variety the number of ears/m^2 decreases at Cd concentrations >15 mg kg^{-1}. The influence on VND95-20 rice at this concentration is not clear. However, at soil Cd concentrations >25 mg kg^{-1} the number of empty rice-grains per ear of VND95-20 rice variety increased. Similar findings were observed for VD20 at soil Cd concentrations >30 mg kg^{-1}.

At soil Cd concentrations >20 mg kg^{-1} the productivity of VND 95-20 rice decreased to between 630-1730 kg ha^{-1}. In contrast, the productivity of VD20 decreased only at soil Cd concentrations >30 mg kg^{-1}. In addition, from a grain quality perspective increasing soil Cd content results in variety specific alterations in the protein and amylase content of rice-grains (Table 6).

Table 5: Effect of soil Cd concentration applied as Cd salts on the yield of aromatic rice variety VN20 and the high yield variety VND95-20

Cd (mg kg^{-1})	No. Panicles /m^2		Grains per ear		Estimated yield (t ha^{-1})	
	VND 95-20	VD 20	VND 95-20	VD 20	VND 95-20	VD 20
0	225	214	99	129	5.31	4.51
15	203	182	101	132	4.90	4.53
20	200	168	100	122	4.68	4.35
25	217	171	77	136	3.90	3.13
30	202	165	73		3.58	3.77
CV (%)	7.10		8.98		8.33	
LSD $_{<0.05}$	22.13		15.40		5.82	

Table 6. Effects of soil Cd concentration applied as Cd salts on the rice grain protein and amylase contents of aromatic rice variety VN20 and the high yield variety VND95-20

Cd (mg kg^{-1})	Protein (%)		Amylase (%)	
	VD20	VND95-20	VD20	VND95-20
0	6.95	8.58	12.92	17.90
15	6.56	8.43	11.80	15.70
20	6.94	8.28	11.63	17.77
25	7.13	8.08	12.75	14.66
30	737	7.94	12.92	16.82

Table 7 shows the concentration of Cd accumulated in the different parts of the rice plant as a result of cadmium uptake from soils. Accumulations are highest in roots, about 20-30 times higher than in stems and leaves and about 100-200 times higher than in grains. Roughly this translates to a ratio for Cd in soil: roots: stems and leaves: rice grains of 10:200:10:1. In addition, the results indicate that at similar total soil Cd concentrations the accumulative capacity of Cd in brown rice in the fields is much lower as compared to that in the greenhouse experiments (Table 7). The results also indicate that under both field and greenhouse conditions all brown rice Cd concentrations exceed the internationally recognized Maximum Level (ML) for Cd in rice grain of 0.2 mg Cd kg^{-1}.

This ML is established by the Joint FAO/WHO Food Standards Programme, Codex Alimentarius Commission (CAC). Specifically, MLs are established by the Codex Committee on Food Additives and Contaminants (CCFAC) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA). The ML is based on the 'safe' lifetime consumption of rice and the level recommended by the Codex Alimentarius Commission (CAC) to ensure the free movement of rice in international trade.

Table 7. Relationship between soil Cd concentration applied as Cd salts and accumulation of Cd in different parts of rice plants.

Cd in soil (mg kg^{-1})	Cd in rice plant (mg kg^{-1} dried biomass)			
	Roots	Straw, leaves	Brown rice	
			Green house	Field
0	39	3.57	0.35	0.32
5	205	10.89	1.08	-
10	323	27.40	2.66	-
15	376	38.21	4.21	0.54
20	652	44.80	5.77	1.17
25	756	45.20	8.23	2.02
30	814	46.80	9.65	2.21
35	1275	57.22	9.56	-
40	1402	56.54	9.30	-

Note: Internationally established ML for Cd in rice grain is 0.2 mg Cd kg^{-1} as established by the 34th Session of the CCFAC (Rotterdam, The Netherlands 11-15th March 2002).

Table 8. Concentration of Cd in rice grains growing on polluted soil at Bình Chaùnh District, HCMC, Vietnam

Sampling Location	Cd in soil (mg kg^{-1})	Cd in rice (mg kg^{-1})	
		Straw, leaves	Brown rice
BC3	7.6	1.26	0.38
BC5	9.8	2.03	0.52
BC9	14.5	2.37	0.55
BC12	10.3	2.09	0.56
BC13	9.6	1.96	0.55
BC14	9.9	1.28	0.41
BC32	10.3	2.33	0.48

Note: Internationally established ML for Cd in rice grain is 0.2 mg Cd kg^{-1} as established by the 34th Session of the CCFAC (Rotterdam, The Netherlands 11-15th March 2002).

It is important to note that Cd concentrations in all the rice grain samples collected from Bình Chaùnh District, HCMC exceed the internationally recognized Maximum Level (ML) for Cd in rice grain of 0.2 mg Cd kg^{-1}.

Conclusions and recommendations

Rice fields south of HCMC are polluted by wastewater high in contents of several heavy metals, especially Cd. Concentrations of Cd in soil range from 4.7-10.3 mg kg^{-1} exceeding European country MP levels by a factor of 2 - 3. Cadmium accumulates easily in red-yellow alluvial soil, in alluvial soil on acid sulfate soil and in alluvial soil on actual acid sulfate soil. Cadmium concentrations above 25 mg kg^{-1} applied as Cd-salts affect the agronomical characteristics of cultivated rice and cause decreases in productivity. Increases in the concentration of Cd in soils cause higher levels of Cd in rice. The ratio of Cd in soil: roots: stem/ leaves: and brown rice is approximately 10:200:10:1. The accumulation of Cd in rice under field experiments is much lower than the accumulation in greenhouse experiments. Cadmium concentrations in brown rice grown in areas that are affected by high Cd wastewaters of HCMC exceeds the internationally recognized Maximum Level (ML) for Cd in rice grain of 0.2 mg Cd kg^{-1} as established by the Joint FAO/WHO Food Standards Programme, Codex Alimentarius Commission (CAC). This is of considerable concern as rice constitutes a major intake pathway of Cd with confirmed direct negative impacts on human health.

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Release of Arsenic from Minerals to the Water Phase

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Abstract

Severe and widespread contamination by arsenic(As) in groundwater and drinking water has been recently revealed in rural and sub-urban areas of the Vietnamese capital of Hanoi with similar magnitude as observed in Bangladesh and West Bengal, India. This fact has prompted the need to investigate the possible mechanisms for such widespread contamination and develop suitable techniques for lowering As concentrations in water supply. In the present study, laboratory-scale experiments were performed to assess the possible release of As from solid phase into water phase under both anaerobic and aerobic conditions. Various chemical equilibria governing the speciation of different ions in the water phase and in alluvial sediments are discussed. Under anaerobic conditions, the release of As seems to be closely related to the content of MnO_2 in sediments, the reduction of Fe(III) to Fe(II) and the formed sulfur content. Elevated MnO_2 content may inhibit the release of As to groundwater. The reduction of As concentrations in water phases could be due to the formation of Fe_2AsS or AsH_3. In aerobic conditions, the hydrothermal oxidation process was proposed as a plausible mechanism of release of As from As-rich mineral surfaces to water phases. In acidic conditions, As concentrations increased due to the more effective release from mineral surfaces. In neutral medium ($pH \approx 7$), As release was less efficient, which could be due to the co-precipitation onto ferric hydroxide. The possible mechanisms suggested in this study may be useful to explain the elevated contamination of As in surface waters of upstream sections of rivers in mountain areas in northern Vietnam and in underground water of River deltas and are critical for moving to the next stage in developing suitable techniques for lowering As concentrations in groundwater and drinking water in Vietnam.

Keywords: Arsenic release, aerobic, anaerobic, arsenic-rich mineral surfaces, sorption, groundwater, surface water.

Introduction

In recent years, the naturally occurring contamination by As in groundwater in Asian countries has received particular attention. The concern over serious health effects caused by As poisoning has been observed in Bangladesh and West Bengal, India (Chowdhury et al., 2000). In Vietnam, due to the similar composition of groundwater as in Bangladesh, elevated contamination by As has been anticipated. Public media have also voiced concern that As contamination in groundwater may become a key environmental problem in Asian developing countries in the 21st century (Christen, 2001).

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To address this issue a comprehensive monitoring survey of the status of As contamination in groundwater and drinking water in Hanoi, the capital of Vietnam and surrounding areas was undertaken (Berg et al., 2001). Our results clearly demonstrate widespread and elevated contamination by arsenic in groundwater and the water supply in sub-urban and rural areas of Hanoi (Berg et al., 2001). The magnitude of pollution was similar to that observed in Bangladesh, with a large number of well waters containing As concentrations exceeding the Vietnam standard of 0.05 mg l^{-1}. This severe situation led to further research towards the understanding of possible mechanisms of widespread As contamination in groundwater and the development of suitable techniques for lowering As concentrations. In 1992, D. V. Can (Can, 2001) observed extraordinary high As concentrations in water of some streams during field investigations in a highland area upstream of the Ma River in northern Vietnam. Subsequent surveys showed that various As-rich minerals, such as arsenopyrite occur widely in this area.

The possible mechanism of As contamination in water of streams in a mountain area may be due to the weathering of As-rich minerals (McArthur et. al., 2001). In Vietnam, there is a relatively large pyrite mine located about 60 km from Hanoi city. In addition, a number of gold mining sites with arsenopyrite are located over a large area of northern Vietnam.

The gold mining activities in northern Vietnam have been extensive in recent years and As-rich minerals have been distributed to the land surfaces during gold mining. If the hypothesis is correct that weathering processes may be a cause of As in surface waters, the contamination by As in surface water would be a serious concern in the near future for a large area of northern Vietnam. In fact, surface water from the Red River has been evaluated and it has been found that As concentrations in some locations reached a level of 0.09 mg l^{-1}, exceeding the Vietnam Standard of 0.05 mg l^{-1}). This fact prompted the investigation of the mechanism of As release to surface water from mineral surfaces.

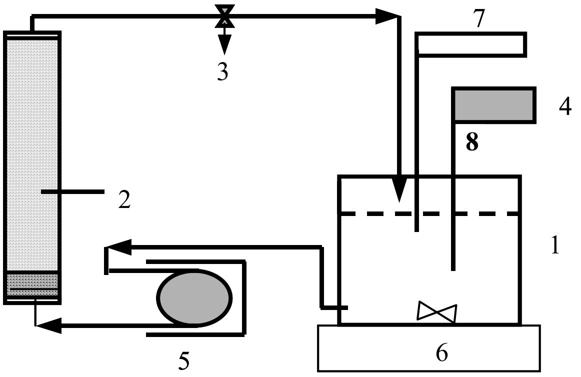
This study investigates the possible mechanisms of As contamination in groundwater, based on observations in well waters in the upper and lower aquifers of the Red River delta (Berg et al., 2001). The mechanisms of release of As from various solid phases were investigated under anaerobic and aerobic conditions. These experimental investigations may be useful for understanding the mechanism of As contamination in water sources and may be critical to developing suitable techniques for lowering As concentrations in water supply and drinking water in Vietnam.

Methodology

Experimental setup for investigation of mechanism of As release to groundwater under anaerobic conditions

A batch experiment was performed to investigate the release of As in groundwater. The experimental setup is described in Figure 1. The main components consist of an anaerobic column, supply pump and the de-oxygenation apparatus. The anaerobic column has a height of 700 mm, a diameter of 45 mm and was constructed in 3 layers. The first layer consists of humus collected from the earth surface. The second layer is a coarse gravel (2 - 5 mm diameter) and the third layer contains clean sand spiked with 0.001 % As (relative to mass of the dry sand layers) in the form of AsO_4^{3-} and 0.005 % MnO_2 co-precipitated with 0.1% Fe(III) in the form of $Fe(OH)_3$. The water phase is prepared as similar to natural water with the composition as shown in Table 1. To maintain anaerobic conditions throughout the system, water was pumped from tank (1) to the anaerobic column (2) from the lower end of the column through the layers and finally the water was pumped back to the tank (1).

Figure 1. Schematic diagram of the experimental setup for the investigation of As release from alluvial surfaces under anaerobic conditions.



1: Water tank
2: Anaerobic column
3: Sampling valve
4: De-oxygenating apparatus
5 Pump
6: Magnetic stirrer
7: Additional nutrient and trace elements pump

The experiment was run for 56 days continuously. Water samples were collected every 24 hours at the upper end of the anaerobic column by a three-way valve and were analyzed for various parameters such as total As, Fe, Mn, nitrate, phosphate, ammonium, sulfate, sulfur and dissolved oxygen. Chemical analysis of these ions in water samples followed the methods described in Standard Methods for Examination of Water and Waste Water (Franson, 1995), (Table 2).

Experimental setup for the investigation of mechanisms of arsenic release to groundwater under aerobic conditions

The experimental apparatus is illustrated in Figure 2. The main component is an aerobic column. The column has a diameter of 45 mm, a length of 700 mm and is packed with 2 layers.

Table 1. Composition of the water phase in the anaerobic experiment.

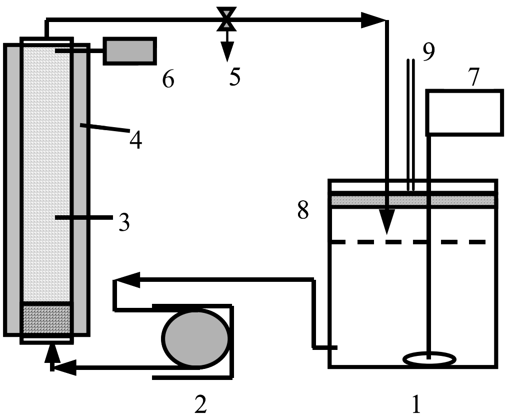
Composition	Conc. (M)
Ca^{2+}	1.0×10^{-3}
HCO_3^-	2.4×10^{-3}
NO_3^-	3.0×10^{-4}
SO_4^{2-}	5.2×10^{-3}
Na-glutamate	1.2×10^{-3}
PO_4^{3-}	6.0×10^{-7}
Mg^{2+}	6.0×10^{-5}

Table 2. Analytical methods for the determination of various parameters in anaerobic and aerobic experiments.

Composition	Analytical method
As	HVG - AAS
Fe, Mn	AAS
NO_3^-, PO_4^{3-}, NH_4^+	Colorimetry
SO_4^{2-}	Conductimetry
S^{2-}	Colorimetry (Methylene blue)
Oxygen	Iodometry

The lower layer consisted of minerals derived from weathering processes. This mineral was taken from Soc Son district, about 40 km north of Hanoi. The upper layer was sand spiked with 0.2 % arsenopyrite. Rainwater was used as the water phase. The water was continuously saturated in oxygen throughout the experiment. The temperature was kept constantly at 25 or 38°C. The water phase was pumped into the aerobic column from the lower end and then back to the reservoir tank (1). The composition of the rainwater is given in Table 3.

Figure 2. Schematic diagram of the experimental setup for the investigation of As release from mineral surfaces under aerobic conditions.



1: Water tank
2: Circulative pump
3: Sand and mineral packed column
4: Heating cover
5: Sampling valve
6: Thermometer
7: Air bubble generator/ oxygen absorber
8: Sol remover
9: Air outlet/ supplementary nutrient inlet

Table 3. Composition of the water phase (rain water) in aerobic experiment.

Parameters	As ($\mu g\ l^{-1}$)	SO_4 ($mg\ l^{-1}$)	NO_3 ($mg\ l^{-1}$)	Fe ($mg\ l^{-1}$)	NH_4 ($mg\ l^{-1}$)	HCO_3^- ($mg\ l^{-1}$)
Concentration	0.8	11.6	8.2	0.087	2.4	13.6

Results and Discussions

Release of As from mineral surfaces to groundwater under anaerobic conditions

The anaerobic experiment was run for 56 days. The various parameters of the water phase in the outlet of the system were measured and results are presented in Figures 3 and 4.

Figure 3. Chronological evolution of Fe, Mn and As concentrations in the water phase of the anaerobic experiment.

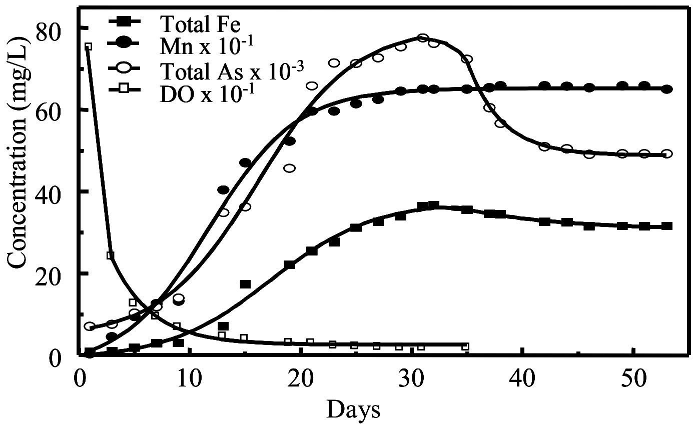
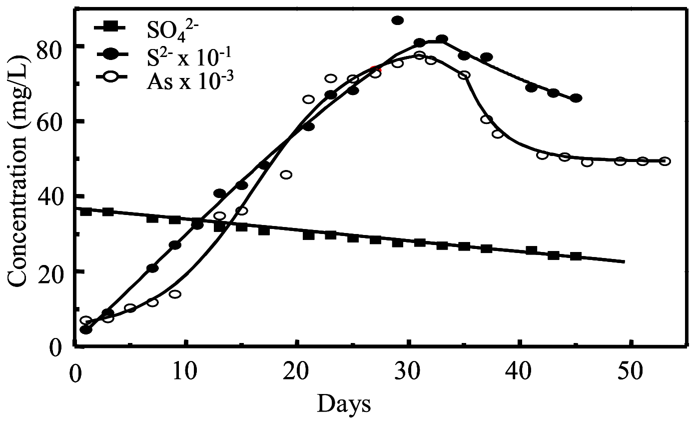


Figure 4. Chronological evolution of sulfate, sulfur and As concentrations in the water phase of the anaerobic experiment.



Chronological variations of various ions in the water phase indicate that the reduction of MnO_2 to Mn(II) started under oxygen - depleted conditions (dissolved oxygen < 2.4 mg l^{-1}). The Mn(II) concentrations increased and remained relatively constant after 30 days. Fe concentrations increased slowly during the first days and the reduction of Fe(III) significantly increased after 15 days. At that time, more than 80 % of MnO_2 was reduced to Mn^{2+}. This result indicates that under anoxic conditions, the reduction of MnO_2 to Mn(II) was faster than the reduction of Fe. This phenomenon can be explained by the higher redox potential of MnO_2/Mn^{2+} as compared to that of $Fe(OH)_3/Fe^{2+}$ in the relatively neutral medium (pH ≈ 7) (Nickson et. al., 1998). From day 15 to 30, concentrations of Fe(II) increased rapidly and then declined and remained relatively constant until the end of the experiment. The suspended precipitation of FeS was formed in the system when Fe(II) concentrations decreased. Overall, the mechanisms of various processes involved in the anoxic system can be expressed by the following reactions:

$$\textit{Organic matter and } SO_4^{2-} \xrightarrow{\textit{Bacteria}} CH_4 + CO_2 + NH_4^+ + S_2^- + \ldots$$

$$MnO_2 + 2e + 4H^+ = Mn^{2+} + 2H_2O$$
$$Fe(OH)_3 + e + H^+ = Fe(OH)_2 + H_2O$$
$$Fe(OH)_2 + 2CO_2 = Fe^{2+} + 2HCO_3^-$$
$$Fe^{2+} + S^{2-} = FeS$$
$$2Fe^{2+} + MnO_2 + 4H^+ = 2Fe^{3+} + Mn^{2+} + 2H_2O$$
$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$$
$$S^{2-} + H_2O \Leftrightarrow HS^- + H^+$$

The dynamics of As in the anoxic water phase indicate that the release of As and Fe(II) to the water takes place at the same time (Figure 3). It is therefore hypothesized here that As in alluvial sediments is mainly present in the form of arsenate [As(V)] and predominantly adsorbed onto Fe(III) hydroxide. In the anaerobic experiment, when Fe(III) is reduced to Fe(II) in the presence of dissolved bicarbonate, the reduction of As(V) to As(III) takes place simultaneously (Nickson et. al., 2000). In addition, when the MnO_2 content in the solid phase was still high, the re-oxidation of AsO_3^{3-} to AsO_4^{3-} and the re-precipitation of arsenate are plausible. The process can be presented as follows:

$$FeAsO_4 + 3e + 2H^+ \Leftrightarrow Fe^{2+} + AsO_3^{3-} + H_2O$$
$$M_3(AsO_4)_2 + 4e + 4H^+ \Leftrightarrow 3M^{2+} + 2AsO_3^{3-} + 2H_2O$$
$$AsO_3^{3-} + MnO_2 + 2H^+ = AsO_4^{3-} + Mn^{2+} + H_2O$$
$$3M^{2+} + 2\,AsO_4^{3-} = Me(AsO_4)_2$$

(M: Metal ion)

After 30 days, As and Fe(II) concentrations decreased, but not as a result of the lower reduction of Fe(III) to Fe(II). The decreased Fe(II) concentration is related to the formation of precipitated FeS. For the reduction of As concentration after 30 days, it is hypothesized that there might be a formation of FeAsS and/or AsH_3. The reasons for the concomitant decrease of both As and Fe concentrations need further investigations.

The chemical processes described above suggest that the release of As under anaerobic reduction of organic matter in aquifers is closely related to the MnO_2 contents in alluvial sediments, the reduction of Fe(III) to Fe(II) and the amount of FeS formed. When MnO_2 levels in sediments are high, the reduction of Fe(III) and the release of As is inhibited.

In addition, the groundwater quality at various locations in Hanoi was also tested and found to have elevated arsenic concentrations in iron-rich water. In contrast, in manganese-rich water, concentrations of Fe and As were low (Table 4). These field observations are consistent with the results observed during the anaerobic experiment as discussed earlier. However, a number of chemical equilibria as well as interactions among various phases may complicate the behavior of arsenic in aquifers. Further studies are required for this topic.

Table 4. Mean concentrations of Fe, Mn and total As in groundwaters collected from various locations in Hanoi city.

Metals level ($mg\ l^{-1}$)	Location							
	MD	NH	NSL	LY	YP	PV	HD	TM
Total Fe	0.31	0.62	1.20	2.15	4.78	4.50	8.33	5.64
Mn^{2+}	0.95	1.63	0.86	0.37	0.38	0.11	0.13	0.26
Total As	0.03	0.04	0.40	0.06	0.39	0.34	0.26	0.06

Note: MD, NH, NSL, LY, YP, PV, HD and TM refer to the following locations: Mai Dich, Ngoc Ha, Ngo Sy Lien, Luong Yen, Yen Phu, Phap Van, Ha Dinh and Tuong Mai, respectively.

Release of arsenic from mineral surfaces to groundwater under aerobic conditions

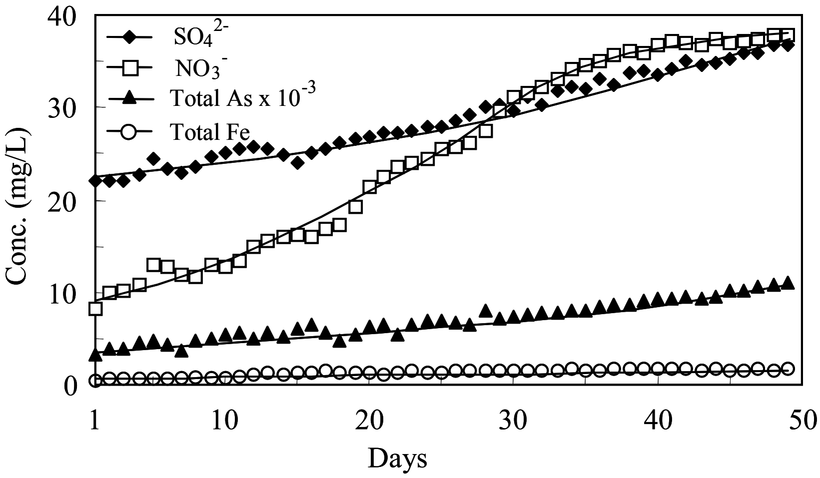
The aerobic experiment was run for 50 days at atmospheric conditions (25°C and 1 atmosphere) with oxygen - rich water (dissolved oxygen >7 mg l^{-1}). The results are shown in Figure 5. Sulfate concentrations in the water phase increased at a rate of about 0.25 mg l^{-1} per day. The oxidation of pyrite takes place according to the following reactions:

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$
$$2Fe^{2+} + 1/2O_2 + 2H^+ = 2Fe^{3+} + H_2O$$

Arsenic concentrations also increased with time at a rate of 0.2 µg l^{-1} per day, about 3 orders of magnitude lower as compared with sulfate concentrations. However, the oxidation processes that release sulfate to the water phase takes place in parallel with the release of arsenate from arsenopyrite:

$$4FeAsS + 11O_2 + 6H_2O = 4Fe^{2+} + 4AsO_3^{3-} + 4SO_4^{2-} + 12H^+$$
$$2AsO_3^{3-} + O_2 = 2AsO_4^{3-}$$
$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$$

Figure 5. Chronological variation of Fe, sulfate, nitrate and As concentrations in water phase in aerobic experiment.



In addition, a certain amount of Fe was also released to the water. Nevertheless, Fe concentrations were actually found to be low and their chronological increase was negligible. Under oxic experimental conditions and a pH range of 6.3 - 6.8, most Fe^{3+} ions released from the mineral surfaces were hydrolyzed and re-precipitated in the form of $Fe(OH)_3$ and remained in the solid phase. Only small amounts of Fe were dissolved in the water phase in the form of $Fe(OH)_2^+$ or bicarbonate (Barnes, 1997). This phenomenon led to the sorption of arsenate anions onto the solid phase and subsequently inhibited the release of As to the water phase. Sulfate ions were less strongly adsorbed and their concentrations were substantially greater than those of arsenate (Figure 5). During the experiment, the pH of the solutions slightly increased. When the pH was rapidly lowered through continuous CO_2 purging of the water solutions, the Fe and As concentrations apparently increased. For this, the re-dissolution of precipitate $Fe(OH)_3$ may be a plausible explanation.

The aerobic experiment was also performed at a higher temperature of 38°C. The oxidation process was faster as was evidenced by a more rapid elevation of sulfate concentrations. However, the chronological dissolution of Fe and As in the water phase remained relatively similar to that observed in the experiment at 25°C. Nitrate concentrations increased at both temperatures due to nitrification of ammonium that was present in the inlet solutions and the release of nitrate from the sediment material packed in the lower part of the aerobic column.

Considering these observations, it is suggested here that hydrothermal oxidation is a main factor controlling the release of As from As-rich mineral surfaces to surface water. The mechanism of this process was similar to the oxidation of sulfide to sulfate. At acidic pH values As concentrations increased substantially. Under neutral pH conditions, the release of As is less efficient due to the co-precipitation to iron hydroxide phases. This phenomenon may be a possible explanation for the elevated As contamination in some streams observed in the headwaters of Ma River, Northern Vietnam. This river flows through an area with some gold mining sites with occurrences of arsenic-rich minerals.

Conclusions

Weathering processes are a potential cause for the release of As from As-rich minerals to water phases. Subsequently, As is trapped in alluvial soil layers and again released to water phases during anaerobic bio-disintegration. These are naturally occurring processes following a series of complicated mechanisms.

The preliminary experiments presented in the paper under both oxic and anoxic conditions provide insight into the mechanisms of widespread As contamination in water resources of Vietnam. Such work is critical in order for researchers to move to the next stage in developing suitable techniques for removing and/or lowering the As concentration in groundwater and drinking water in Vietnam.

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Soil and groundwater contamination in the red river delta plain and numerical modeling of the contaminant transport

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Abstract

The Red River delta plain is an area where various types of industry are concentrated and where the densely populated and important economic triangle of Hanoi, Haiphong and Quangninh is located. Environmental degradation of the Red River delta plain is consequently, a reality. The total population in the delta plain is approximately 17 million, of which 19.84% represents the urban population. The natural land area of the Red River delta plain is approximately 1.5 million ha. Of this, 1.25 million ha is currently utilized of which agricultural land constitutes 0.8 million ha. There are numerous industrial plants and factories together with a great number of so-called "traditional craft" industries, the waste management and treatment of which have not been appropriate. Solid waste and wastewater that has not been properly treated are dangerous for the soil and groundwater environment. Meanwhile, there are abundant groundwater sources in the plain, both in term of quantity and quality. Groundwater has been abstracted for domestic use and other economic purposes for a long time over the whole of the plain. Therefore, environmental management and protection are essential for protecting the soil and the groundwater resources in the area. The authors have made an overview of the environmental loading caused by different economic activities, presented some data of soil and groundwater contamination, generalized the groundwater potential of the plain and present a scenario for possible groundwater contamination by migration of the contaminants from waste by numerical modeling.

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Soil and Groundwater Protection in the South-East Asia Region

John Chilton & David Kinniburgh[1]

1. Soil Quality and Soil Protection

1.1 BACKGROUND

Soils are an integral part of the natural environment and central to agriculture as well as to the sustainability of natural habitats. The natural fertility of soils varies widely and is often substantially enhanced by modern agricultural practices such as fertilization and irrigation. 'Soil quality' reflects the ability of soils to maintain such production on a sustainable basis and without permanent damage to the essential functioning of the soil. These functions include, for example, the breakdown of soil organic matter, microbiological processes such as nitrification and the maintenance of soil structure. The physical characteristics of the soil are important as the loss of soil structure and the cultivation of ever steeper slopes can result in significant soil erosion. This is already of concern in the region. Soil chemical contamination is also of concern and it is this aspect that is of concern in this programme.

'Heavy metals'[2], such as zinc, cadmium, copper, lead, nickel and chromium are present in all soils but are usually found at low concentrations. 'Baseline' concentrations vary depending on soil type, soil parent material and type of heavy metal but are usually in the range 0.1–200 mg/kg. Enhanced concentrations are found in soils from naturally mineralised areas but more commonly arise where heavy metals have become dispersed as a result of human activity since heavy metals are used in a wide variety of industrial processes. These include mining, manufacturing and waste disposal as well as some agricultural activities such as the use of phosphate fertilisers and metal-containing pesticides. As a result of their use in many industries, heavy metals are concentrated in many waste streams. Furthermore as a result of their dispersion into the environment, topsoils tend to be most heavily contaminated. Heavy metal contamination of soils and sediments is often used as an indicator of the beginnings of industrial activity.

The pathways by which heavy metals contaminate the soil vary from direct pathways via mining, waste disposal and agricultural activity as well as more indirect pathways such as atmospheric deposition. Their impacts depend on the use of the affected land. Heavy metal contamination of agricultural land can have serious impacts on crop growth and crop quality and in urban areas is often of concern in terms of pollution of underlying aquifers. If the contamination is confined to industrial areas, then the concern is less than if widely dispersed. Therefore the reduction of the dispersion of heavy metals in the environment is a major concern in most industrial societies. Once contaminated, it is extremely difficult and expensive to decontaminate soils.

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[2] The term 'heavy metal' is used loosely here to include both the strictly 'heavy' metals such as lead and cadmium as well as the transition metals such as copper and zinc.

The relationship between soil contamination and crop contamination is complicated and depends on many soil and plant factors. Critical factors are the ability of the soil to adsorb the heavy metals and thereby maintain a low concentration in the soil solution and the interactions between the various heavy metals, e.g. Cd uptake can be affected by competition from other metals such as Zn and Cu. Soil pH strongly affects the amount of adsorption – adsorption of most trace metals is much lower under acid conditions potentially resulting in greater plant uptake and greater toxicity. Therefore one of the key ways in which the effects of heavy metal contamination of soils can be mitigated is through control of soil pH, specifically the application of lime.

Most heavy metals are very strongly bound by natural organic matter and so tend to be found at high concentrations where organic matter contents are high. This includes the biosolids found in wastewater and sewage sludge. The nature and extent of contamination strongly depends on the upstream sources. Therefore the use of either untreated wastewater or biosolids in agriculture poses a potential long-term threat.

Heavy metal availability in soils will change with flooding as in rice production. There will be an increase in pH of up to 2 pH units which will tend to decrease availability but an increase in iron and manganese oxide dissolution which could increase availability. It is likely that the former effect will dominate. Aeration of sulphide-rich soils will lead to a decrease in pH and potential release of heavy metals.

Soils contaminated by heavy metals pose a threat in two ways: (i) directly through their toxic effect on the growth of crops thereby reducing crop yields, and (ii) indirectly by entering the animal and human food chain could adversely impact on human health. Even a reduction of crop yield by just a few percent could lead to a significant long-term loss in production. Heavy metals may also have deleterious effects on the microbial functioning of soils, again with important long-term consequences. Zinc, for example, can reduce grain yields as well as reducing microbial activity especially of nitrifying organisms (those organisms that convert ammonium to nitrate). Zinc is usually not present in toxic amounts in the food crop – indeed it is an essential element at low concentrations – but the crop may suffer at high zinc concentrations. Cadmium on the other hand can be taken up by crops in sufficient quantities to be of concern for human health before it impacts on crop growth. In humans, excessive cadmium can lead to renal failure.

Some food importers are now specifying maximum heavy metal contents for imported food and so any deterioration of food quality could have an impact on the export security of food crops.

Therefore the protection of soils from heavy metal pollution is an essential aspect of maintaining soil and food quality. Many countries now have legislation to control the contamination of heavy metals to soils and the wider environment.

1.2 SITUATION IN SOUTH-EAST ASIA

It is clear that the rapid industrialisation of much of South-East Asia has led to the potential for heavy metal contamination of soils in a variety of ways and on a variety of scales. The principal ways are:

- **Mining activity:** Spread of mine spoil and tailings and, in some cases, by the use of heavy metals in ore processing, e.g. the use of mercury in gold mining. Examples can be found throughout the SE Asia region with well-documented examples especially from Thailand. Much mining activity in the region is artisanal and unregulated resulting in pollution over quite a large area. For example, it is estimated that some 5,000–10,000 ha in Thailand are contaminated with cadmium. New mining legislation in Vietnam with an enhancement of its enforcement will hopefully reduce future contamination but there is still a legacy of largely unknown extent to contend with.

- **Industrial activity:** The processing and reclamation of metals by industry has led to the widespread contamination of soils in urban and peri-urban areas. It can even happen in more rural areas where cottage industries are processing metals. An example is the contamination of soils in Dai Dong village, Lam district as a result of the reprocessing of copper waste. Soil contamination extended to more than 300 m away from the recycling operation.

- **Wastewater reuse:** Wastewater is potentially a valuable source of both water and nutrients and there is a long history of the use of untreated wastewater for irrigation in much of SE Asia including Vietnam. In Vietnam, some 30 cities use wastewater and about 5000 ha of land are believed to be irrigated directly with wastewater. Some of the remaining wastewater is inadvertently used because it is mixed with surface water in canals carrying irrigation water. This can result in contamination travelling large distances largely through the transport of contaminated sediments.

  While the use of treated wastewater would be much better both for human health and for the environment, this seems unlikely to be adopted on a large scale in the near future. Because of the lack of treatment and the mixing of industrial and domestic wastewaters, often with storm water, the heavy metal content of wastewaters can be expected to be variable but high. The low and often declining pH of many SE Asian soils under cultivation could lead to an increasing plant availability of heavy metals. This declining pH will be exacerbated by the heavy fertiliser nitrogen applications now common in much of the region. Liming is sometimes practiced largely to increase the calcium concentration of crops rather than controlling the soil pH *per se* or the heavy metal content of crops. In some cases, the pH of soils in the Red River delta has declined from about pH 6.5 to pH 5.5, an order of magnitude increase in acidity, in a matter of years. This could have a significant impact on heavy metal uptake by crops including rice.

- **Fertilisers** – Aside from the indirect effect of nitrogen fertilisers on soil acidification, phosphate fertilisers can increase the soil load of various trace metals, most notably cadmium and uranium. The extent of this contamination very much depends on the geological source of the phosphate rocks used in making the fertilisers. The available evidence in Vietnam appears to indicate that the phosphate fertilisers are quite low in cadmium (about 2.5 mg kg^{-1}) and so should not pose a serious threat. The uranium content is unknown but is quite likely to be similarly low.

The overall situation therefore appears to be one of rapid change with the potential for the serious, long-term pollution of soils. However, the documented cases of pollution in Vietnam and elsewhere in the region refer to quite small areas of land, and in situations where pollution might reasonably be expected to have taken place. The lack of more widespread systematic data and an understanding of the scale of potentially-polluting processes such as wastewater use make it difficult to assess the situation in the larger, unsampled areas. Establishing this should therefore be an early focus of the project.

There appears to be most concern about the cadmium concentrations in rice in the region. In Japan, there are examples of areas such as the Jinzu River basin where cadmium contamination of the environment has led to excessive cadmium concentrations in the rice with probable adverse health outcomes.

A recent survey showed that the mean concentration of cadmium in polished raw (uncooked) rice is about 50 $\mu g\ kg^{-1}$. Cadmium in food is usually the major pathway (c.f. water and air) and a study in Japan showed that rice contributed about 30% of the daily dietary intake of cadmium.

2. Groundwater Quality and Aquifer Protection

2.1 CONTEXT

Hanoi, Ho Chi Minh City and other cities and towns in Vietnam do not have conventional piped sewerage collection and treatment systems, even in the oldest-established central parts. It appears that domestic wastewater and effluents from small-scale industrial premises have instead been discharged into open street drains, and thence to the existing rivers which have become canalised wastewater collectors where they pass through the city. Over the course of time, the open drains have gradually become enclosed channels to improve the sanitary condition of the streets, and the canals were observed to be have been at least partly lined. For Hanoi, therefore, several hundred thousand cubic metres per day of untreated wastewater are conveyed out of the city by this means.

The city has grown up close to the Red River over a complex sequence of alluvial material which is at least several hundred metres thick and contains two important and extensively exploited aquifers, the uppermost mainly by shallow private wells and the lower by the municipal supply wellfields. Recharge comes from the Red River, from storm drainage, leaking water mains, rainfall and leakage from the wastewater canals.

A groundwater quality study undertaken by BGS and GSV in 1994 and 1995, together with data presented at the seminar indicate that some impacts on groundwater are already significant. Thus, ammonia concentrations in groundwater beneath and to the south of Hanoi were in the range 5–20 $mg\ l^{-1}$ in 1994–95 in both the Upper and Lower Aquifers, and appear from data presented at the seminar to be somewhat higher now. This is a cause for concern in its own right as a serious groundwater pollutant, and also for the change that it brings to the hydrochemical environment, leading to greater mobility of contaminants such as arsenic. There also appears to be some evidence of mercury contamination in the groundwater from beneath Hanoi. Bicarbonate concentrations are also somewhat elevated beneath the city, reflecting the organic loading from wastewater.

The organic loading also increases the trihalomethane (THM) potential from chlorination of public water supplies. This risk needs to be assessed, although preliminary work by the Vietnam/Swiss collaborating team found that existing guidelines for THM formation were not currently being breached. This needs to be regularly monitored for the wellfields within and to the south of the city especially if the extent of pollution is increasing.

A further impact of the rapidly increasing urbanization and associated growing water demand is the accelerating drawdown of groundwater levels. Hanoi's abstraction of groundwater for municipal supply has reached 600,000 to 700,000 m^3 d^{-1}, and an elliptical cone of depression beneath the city and surrounding areas covers about 200 km^2 with water level declines of 0.3 to 0.4 m yr^{-1} beneath some wellfields. A relatively newly observed impact is that of land subsidence, which was reported as being 20–44 mm yr^{-1}, and 30 mm yr^{-1} in a 2 km^2 area around the Phap Van wellfield south of the city. This is a high rate of subsidence. The situation is considered to be so severe that plans are being made to supplement the supply by taking and treating surface water from the Red River. This is expected to start with a scheme for 150,000 m^3 d^{-1} in 2005, rising to 500,000 m^3 d^{-1} by 2020.

2.2 IMPACTS ON GROUNDWATER QUALITY

2.2.1 Artisan Handicrafts and Recyling

Reference was made at the seminar to the possible impact of small-scale artisanal handicraft industries and village level businesses recycling metals from waste.

The two relevant presentations were detailed case studies of two individual villages recycling lead and copper respectively, from which it was not possible to get an overall view of the distribution and scale of such activities, although it is assumed to be quite widespread. As mentioned above, significant contamination was demonstrated in soils and local paddy field irrigation waters and ponds in both cases. In the former, elevated lead and zinc concentrations in groundwater were not observed, in the latter no sampling of groundwater was undertaken.

Localised but high levels of pollution of groundwater from the leaching of surface deposited wastes has been observed for chromium from tanneries in Mexico, India and Pakistan. In this case, however, the threat to groundwater is unlikely to be great from disposal at the ground surface of solid and liquid wastes, unless very large amounts of waste are leached, or disposed into pits, ponds or soakaways, by-passing the soil.

2.2.2 Mining

The potential impact of small-scale mining in Vietnam was referred to but not covered in the seminar presentations. In general, mining is likely to occur in the hilly and mountainous regions and to be associated with hard rock areas of the country rather than the alluvial plains. Thus, although these areas will have some rice cultivation, they are not likely to be areas of significant groundwater usage. The distribution, scale and character of such mining, methods of extraction, waste generation and waste disposal should be briefly covered in the initial collection of relevant data in activity 2 of the project using DGMV as the primary source.

2.2.3 Irrigated agriculture

The widespread practice of irrigated agriculture in the region could have a significant long-term impact on water quality in underlying aquifers. For example, the puddling of soil and the flooding of fields during the cultivation of paddy rice will inhibit the diffusion of oxygen to the subsurface. In the long term – and the timescales are unknown – this could affect the redox status of an underlying aquifer and thereby indirectly affect the solubility and mobility of redox-sensitive metals and metalloids such as iron, manganese and arsenic as well as other redox-sensitive species such as nitrate, nitrite and sulphate. This would be especially important in the alluvial aquifers of the delta areas with their shallow water tables. Such effects could be exacerbated if groundwater pumping enhanced the downward migration of organic-rich, oxygen-demanding soil water (potentially contaminated with animal and human waste) to the subsurface. The generation of increasingly reducing groundwaters has recently been said by one group to be responsible for at least part of the Bangladesh groundwater arsenic problem. This is analogous but less extreme to the situation found near landfills and beneath urban areas such as Hanoi.

Unlike in temperate regions where the concentration of soil organic matter in agricultural soils is gradually declining due to enhanced oxidation as a result of agricultural activities, the reverse could arise in densely populated, lowland areas with a shallow unsaturated zone and paddy cultivation. The oxidation of organic wastes from animals and humans in such environments is difficult. The implications of this are potentially broad, long-term and poorly understood.

Elevated chloride concentrations of groundwater beneath cities are also generally an indication of the impact of infiltrating wastewater, and might also be expected beneath the irrigated area. The 1994 and 1995 sampling of groundwater showed elevated but still not very high (100 mg l^{-1}) concentrations of chloride. The modest concentrations may be the result of mixed influences of the high-chloride wastewater and large volumes of low-chloride water recharging from the bed of the Red River.

3. Project structure

The present project as proposed is divided into several activities and groups of tasks. However it is our view that the project needs to have clearly defined Phase 1 in which the likely extent, scale and severity of problems associated with mining and wastewater use and impacts on soils, crops and groundwater is assessed. While individual studies were described in the seminar, the extent of some of the activities and their actual or potential impacts was not clear. For example, the total land area irrigated by wastewater from Hanoi and Ho Chi Minh City combined was estimated by one participant at 6000 to 8000 ha, a tiny fraction of the total land area irrigated for rice.

Phase 2 could then focus on the areas of greatest concern identified in Phase 1. Where important information gaps are found, then new studies should be undertaken to collect the required data.

3.1 INFORMATION REQUIREMENTS

3.1.1 Soils and crops

The scale and nature of any heavy metal pollution is unclear. One-off studies of particular sites give little indication of the extent of any problems and so some kind of stratified random survey is required. Since the joint Australia/Vietnam/Thailand project is looking mainly at vegetable crops, it is recommended that this study only look at the rice crop. It is recommended that the stratification should be on the basis of the likely extent of contamination, for example, that it should be stratified into:

- Cultivated areas close to known metal mines
- Peri-urban areas where crops are grown
- Areas receiving wastewater irrigation
- Background cultivated areas (none of the above).

Such areas should be identified across the whole of Vietnam. Within each such area, one or more sites should be randomly selected for sampling of both soil and crop when the crop is mature. Detailed sample location should be noted using GPS.

The scale of the survey in terms of numbers of samples depends on the resources available. We recommend that at least 30 sites be chosen within each of the above strata.

The rice samples should be analysed for Cd, Zn, Pb, Cu, Ni and Cr and preferably Ca and Mg. The soil samples should be analysed for acid-extractable and phyto-available metals. Before any such analyses are undertaken, the laboratory carrying out the analyses should have an adequate QA procedure in place, i.e. it should be able to demonstrate that it has carried out analyses with acceptable accuracy (based on the analysis of recognised standard materials) and that it has regular QA procedures in place to ensure that this standard continues to be met during the survey analyses.

Such a survey would: (i) identify any contaminated soils and rice along with their spatial distribution; (ii) enable the relationship between soil contamination and crop uptake to be established, and (iii) highlight whether further action was necessary.

3.1.2 Groundwater

As a component of Phase 1 of the project, and to provide the necessary background on groundwater for Activity 2 of the proposed project as written, the following information will be required:

- Types, sizes and distribution of industries and their effluents;
- Characteristics of the urban wastewater – volumes, variability, chemical (inorganic and organic) and bacteriological quality;
- Physical infrastructure – canals and canalised rivers, lined or unlined;
- Irrigation methods, pumping from canals, distribution, field application;
- Cropping regimes, fertiliser and pesticide usage;
- Existing groundwater quality data.

If the groundwater quality were a key focus of the project eventually developed, then a somewhat different stratified random sampling approach to provide an overall distribution of quality would be required.

If the project is largely soils and crop oriented, then tracing the food chain links and health impacts, one question always asked is the relative importance of the intake in food and water. For activity 2c, therefore, in developing sampling programmes, the source of drinking water will need to be identified and regularly sampled to allow this distinction to be made, even if groundwater pollution by heavy metals is unlikely to occur. Rural or peri-urban domestic water supplies from groundwater are likely to be much shallower than the large-scale, urban public supply boreholes in the municipal wellfields, and therefore more vulnerable to the impact of wastewater irrigation at the land surface. The extent to which such sampling would be extended to other parameters remains to be decided, but it would certainly need to include the parameters which define the major hydrochemical environment – pH, DO/Eh, EC, major ions, trace metals of interest and ammonium.

3.2 MANAGEMENT OF THE PROJECT

The project envisages a multi-disciplinary team to develop management approaches that are suitable and can be adopted. The current emphasis in the proposal as written is on management at the farm level, which is clearly required, and options from the field study in Thailand were presented. However, it is a wider issue of waste management in the environment and the feasibility of selective collection and treatment of industrial wastewaters may need to be investigated. Experience from elsewhere (Mexico, India, Pakistan and others) suggests that collection and treatment of small volumes of wastewater from large numbers of dispersed, small informal industrial premises is, while technically feasible, difficult to impose by regulation as the industries do not separately have the financial capacity to install suitable treatment.

The project needs a partner or partners to cover this – to be able to characterize the industrial wastewaters, their trends of growth, the present environmental legislation and any proposed new legislation and the management options for improving wastewater quality. The same considerations apply to the mining and artisanal industrial sources referred to earlier. National partners/collaborators to cover the wastewater generation, environmental legislation and management options are needed.

Soil environments affected by copper recycling activities, Dai Dong village, Van lam District, Haoi Hun Province, Vietnam

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Abstract

Copper (Cu) recycling is a cottage industry in Dai Dong village. This activity causes soil contamination. In order to be able to evaluate the seriousness of this problem, the authors investigated the immediate neighborhood of the village. Soil and surface water samples were collected in the area surrounding the village along four transects orientated southeast, northwest, northeast and southwest. Samples were taken at distances of 0, 50, 100, 150, 200 and 300m from the village. Measured Cu contents were high. The highest Cu contents were found along the southeast orientated transect with soil Cu concentrations ranging from 237.8 mg kg^{-1} at distance of 300m to 375.02 mg kg^{-1} near the village. The lowest content of copper was found along the northeast orientated transect with soil Cu concentrations of 97.18 mg kg^{-1} at 300m from the village and 167.87 mg kg^{-1} near the village. Soil total and available Cu contents decrease significantly with increasing distance from the village. The ratio between total and available copper is 3:1. On a wider scale, the total soil Cu concentration in an area of 0.6 km radius around village is estimated to be over 60 mg kg^{-1}.

Introduction

Recycling of heavy metals has been on the increase in many small villages around Hanoi and in other areas of Vietnam. Due to the high economic return from this activity, outputs have increased without any regard for the environment. This carries with it the potential for future environmental damage and contamination of the soil, surface and groundwater.

Dai Dong village belongs to Hung Yen District, Haoi Hun Province, at a distance of about 12 km from National Highway No 5. The village covers an area of 7,000 ha and has an estimated resident population of 8,275. The village household economy is based on agriculture, with main crops being paddy rice, corn, sweet potato, and vegetables. Dai Dong village has been recycling Cu for > 60 years. Currently, 45 households or approximately 33% of the village are recycling Cu. The total Cu output for the village is estimated at 360 t yr^{-1}. With the rudimentary equipment and technologies adopted and absence of emissions and disposal controls it may be expected that the area within and adjacent to Dai Dong village is significantly contaminated with Cu.

During the Cu recycling and manufacturing process adopted in Dai Dong village there are two stages that can cause environmental pollution. The first is when the copper scrap is heated to a temperature of 1500^{o}C. Copper fumes escape and contaminate air, soil and water resources. The second stage is at the preparation of the final product when polishing and 'shaping' take place. Fine Cu cuttings are lost and not recovered and cause direct contamination of the soils and water.

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Sampling method

Soil samples were taken at a depth of 0-20 cm at 0, 50, 100, 150, 200 and 300m distance along four transects orientated Southeast (SE), Northwest (NW), Northeast (NE) and Southwest (SW) from the centre of the village. Surface water samples were taken at the same site as soil samples. Total-Cu and available-Cu were determined using colorimetric methods. In addition, pH_{KCL}, Organic Matter Content (OMC), soil texture and CEC were determined using standard analytical methods.

Main properties of soil

Soils used in the study are alluvial, formed by river sedimentation. Soils have a clay fraction of 58% and a sand fraction of 42% dry soil weight. In addition, soil CEC ranges from 15.57-19.5 meq $100g^{-1}$ dry soil.

Results and Discussion

Soil pH_{KCl} are relatively stable ranging from pH 4.91 – 5.89 irrespective of sampling location (Table 1). Soil OMC ranged from 2.27 to 3.40 % in the surface 0-20 cm. The highest OMC value is found along the NE orientated transect approximately 50m from the village.

Table 1. pH_{KCl} in the top soil (0-20cm)

Transect Orientation	Distance from the village (m)						
	0	50	100	150	200	300	Mean
SW	5.24	5.22	5.52	5.25	5.20	5.49	5.34
NW	5.13	5.59	5.63	5.48	5.07	5.56	5.41
SE	5.46	4.91	5.25	5.74	5.09	5.26	5.29
NE	5.13	5.89	5.63	5.48	5.07	5.56	5.46
Mean	5.24	5.40	5.51	5.49	5.11	5.47	5.37

Table 2. Total organic matter content (OMC) % in the soil at 0-20 cm depth.

Transect Orientation	Distance from the village (m)						
	0	50	100	150	200	300	Mean
SW	2.27	2.94	2.37	4.03	3.51	2.53	2.94
NW	2.37	2.48	2.37	2.99	2.06	2.27	2.42
SE	3.42	3.10	2.27	2.06	1.55	2.43	2.47
NE	2.63	5.06	3.05	2.58	2.89	1.86	3.01
Mean	2.67	3.40	2.52	2.92	2.50	2.27	2.71

Soil Cu concentration

Total soil Cu ranged from 237.81 - 375.02 mg kg^{-1}, 124.62 - 160.7 mg kg^{-1}, 149.78 - 232.1 mg kg^{-1} and 97.18 - 168.07 mg kg^{-1} for the SW, NW, SE and NE orientated transects, respectively (Figures 1 a-d). Available soil Cu although approximately 30% of Total-Cu shows a similar spatial distribution. Copper contents in soils are high, well over the critical standards set by the Department of Science and Technology in Hanoi.

Figure 1a-d. Soil Total-Cu and Available-Cu concentrations (mg kg^{-1}) in relation to transect orientation.

Figure 1a. SW sampling transect

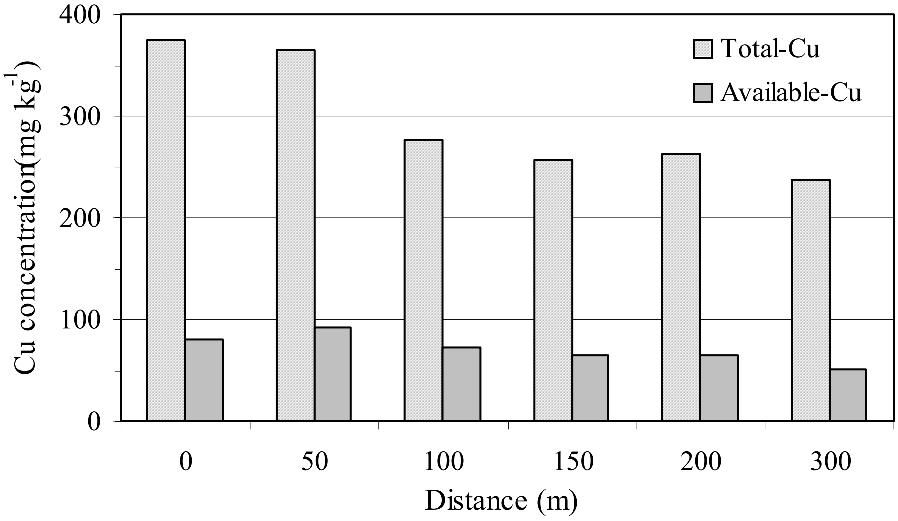


Figure 1b. SE sampling transect

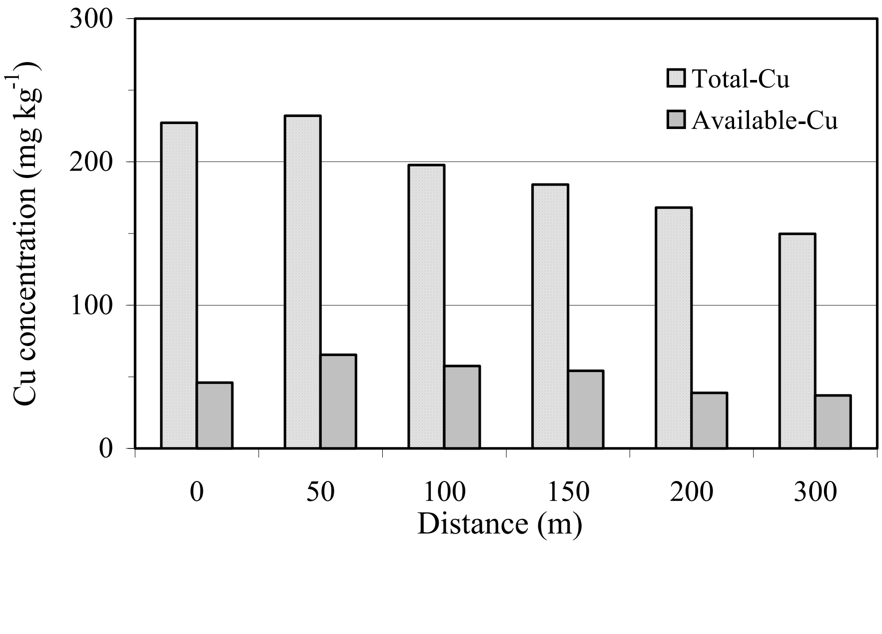


Figure 1c. NW sampling transect

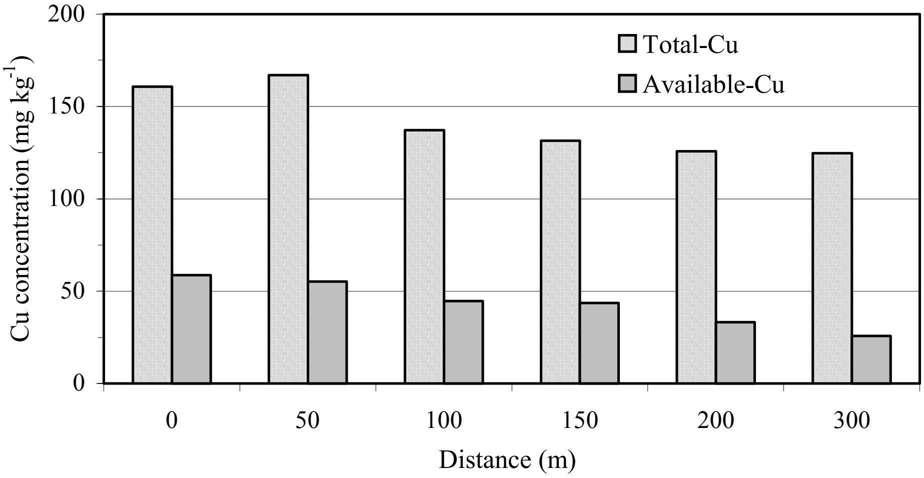


Figure 1d. NE sampling transect

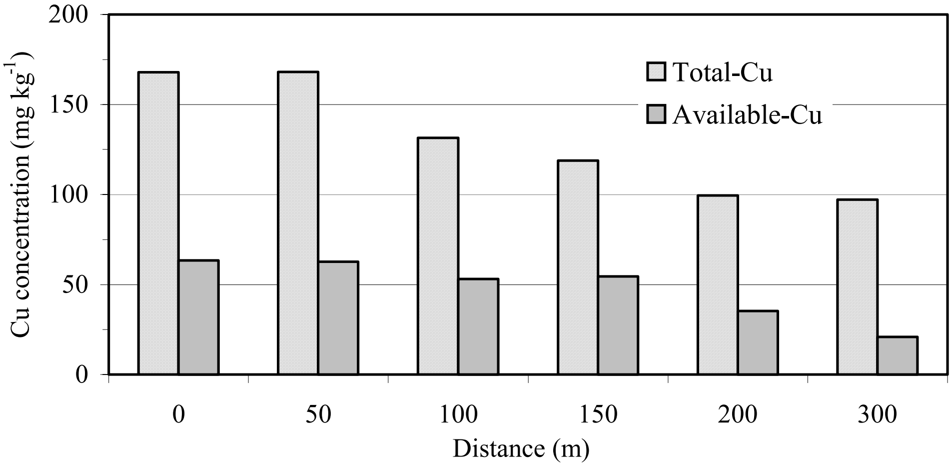


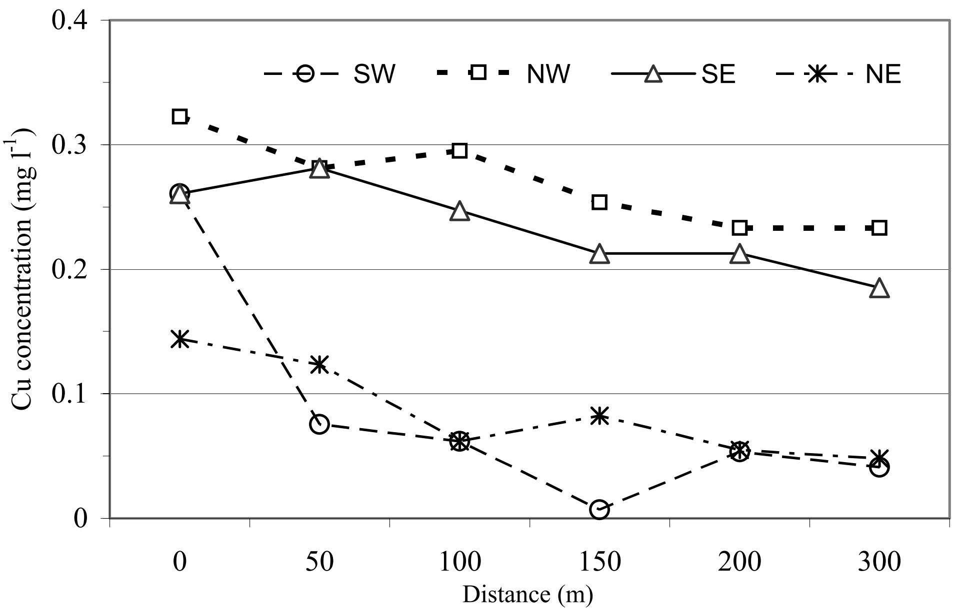
Table 3. Vietnamese provisional maximum permissible concentrations for total Cu in the soil

Soil pH	Maximum Permissible concentration (mg kg^{-1})	Soil pH	Maximum Permissible concentration (mg kg^{-1})
3.5	< 15	6.0	< 120
4.0	< 20	6.2	< 180
4.5	< 25	6.5	< 250
5.0	< 40	7.0	< 260
5.5	< 60	7.5	< 270
5.7	< 80	8.0	< 280

Copper concentrations in (Cu^{2+}) in surface water

Surface water samples were collected at the same sampling points as the soils. The assay results for these water samples are presented in Figure 2.

Figure 4. Concentration of Cu in surface water samples (mg l^{-1}) collected adjacent to Dai Dong Village, Hung Yen District, Haoi Hun Province, Vietnam.



Copper in surface water averages ranges from 0.0083-0.2698 mg l^{-1}. In addition, surface water Cu concentrations decrease significantly with increasing distance from Dai Dong village. Further, pH of the water samples collected ranges from pH 7.0-7.4. This significantly affects the Cu-solubility which is higher under acidic conditions. The highest copper values in surface water samples were observed along the NW orientated sampling transect.

Conclusions

Soil total and available Cu concentrations decrease with increasing distance from Dai Dong village. Soil Cu concentrations at all locations sampled significantly exceed the Vietnamese provisional maximum permissible concentrations for Total-Cu in the soil. The agricultural soils adjacent to Dai Dong village therefore may be considered to be contaminated and remediation measures should be implemented.

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The sustainability of land use and problems of the soil environment as a result of rice cultivation in the Red River Delta

Dr. Nguyen Xuan Cu[1]

Abstract

This research was carried out on fluviosols in the Red River Delta of Vietnam. The main purpose of the research was to evaluate the sustainability of paddy rice production in the Red River Delta based on analysis of land use systems, crop yields and changes in soil qualities over time. The main factors affecting the sustainable land use are also defined. The results show that rice cultivation is changing from traditional to modern techniques of production. The combination of traditional experiences and new technologies has been essential for sustainable development of agriculture in the past few decades. Consequently, trice yields have increased gradually from 2.94 t ha^{-1} in 1985 to 3.42 t ha^{-1} in 1990, 4.44 t ha^{-1} in 1995 and 5.43 t ha^{-1} in 1999.

In terms of land use systems, the area of specific use is changing very quickly with a decrease of annual crops and paddy rice. On the other hand, 'special use' and residential areas have increased. The area under annual crops and paddy rice is expected to decline to approximately 718,764 ha and 565,843 ha by the year 2010, respectively as compared to 621,793 ha and 575,869 ha in the year 2000.

At present the production of rice and the use of fertilizers do not pollute paddy soils. Residues of pesticides are generally found in soils but only at trace levels. However, it is suggested that soil contamination is observed in some areas surrounding industrial and urban areas or traditional 'handicraft' production villages. In addition, rice cultivation systems have affected many properties of the soil environment. Primarily, soil humus, nitrogen and phosphorus levels have increased. However, both total and available potassium, and soil pH have decreased. Soil acidification and decreasing potassium and cultivation areas are identified as the main causes affecting sustainable development of rice production systems in the Red River delta in the future.

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Wastewater Management and Water Environment in Vietnam

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Abstract

Vietnam covers an area of 329,566 km², with a population of about 78 million. Approximately 23 % of the population is living in urban areas. There are 61 provinces/cities with 623 towns and cities. Environmental problems have brought difficult challenges for Vietnam. This is against a background of a poor country, serious degradation of the environment, long-term harmful effects on the environment and nature caused by many years of war, urgent social problems including poverty, diseases, illiteracy and malnutrition. All need to be addressed at the same time whereas investment sources are very limited.

Vietnam is undergoing industrialization and urbanization. The associated socio-economic development causes strong pressure on natural resources and the environment. Environmental pollution is becoming an urgent problem. Municipal and industrial wastewater is the main cause of water pollution in the cities and this problem is increasing. Wastewater and rainwater are not treated. The survey data of water quality of the rivers which run through urban areas in 1996 - 2001 show that the concentrations of BOD_5 *, COD,* NH^+_4*; ,* NO^-_3 *are 2 - 4 times higher than permissible values. Further, total coliform is a hundred times higher than the permissible value. In several samples traces of pesticide chemicals were also found. In other samples the concentration of lead and mercury was several times higher than the permissible value. Some rivers were heavily impacted by wastewater resulting in a concentration of* BOD_5 *and COD 5-7 times higher than the permissible value for class A water supply (domestic water) and 3-4 times higher than the permissible value for class B (non-domestic water supply).*

Water supply capacity has increased from 1.95 million $m^3\ d^{-1}$ *in 1990 to nearly 3 million* $m^3\ d^{-1}$ *in late 2001. There is a very low percentage of the population with access to adequate sanitation, especially in rural, peri-urban and poor urban areas. Urban sewerage and drainage systems are still inadequate and are degrading. In most cities and towns floods and inundation occur in the rainy season. Existing sewer networks in cities have been built for surface water drainage only.*

The percentage of the population served by water supply is 60-70%, with an average per capita usage of 40 - 50 $l\ d^{-1}$ *(equal to 40 - 50% of the standard demand). Non-revenue water ranks from 30 to 70 % in the cities. Up to the year 2000, about 25 million people from rural areas had access to clean water supply (42% of the total rural population).*

In order to give directions for sewerage and drainage activities the Vietnam Government has approved the Orientation for the Development of Urban Sewerage (ODUS) with long-term objectives to 2020 and immediate objectives to 2005.

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An increase in resources from the state budget for the construction and rehabilitation of sewerage and drainage systems and capacity building for companies engaged in the management of operation and maintenance of the systems has led after 3 years of implementing ODUS to a significant increase in the number of urban sewerage and drainage projects funded by ODA. Starting with the Hanoi Sewerage and Drainage project (Phase I) the construction of which commenced in 1998 with ODA funds mainly from Japan and with a total budget of USD 200 million, there have now been 10 out 61 cities and provincial towns of Vietnam with ODA funded sewerage and drainage projects with a total budget of over USD 1 billion from the Governments of Japan, France, Denmark, Belgium, Switzerland and international financial institutions like the World Bank and the Asian Development Bank. Projects are in various phases of implementation. Centralized wastewater management has been the norm in municipal engineering circles for more than 100 years. Based on the "Pipe it away first, then think about what comes next" philosophy, centralized management is the structure of choice in most cities and countries. However, there are a number of disadvantages to centralized wastewater management systems.

Combining all kinds of wastewaters and occasionally run-off 'storm' water leads to a highly complex mixture and a wide variety of pollutants widely varying in composition and concentration. Thus, effective removal of the pollutants becomes very difficult. The costs for the installation of sewer systems are almost an order of magnitude higher than the cost of building treatment facilities. In many cases, delays of water investment projects often occur due to lack of money. Very high operation and maintenance costs are also a big challenge for the municipal authorities, especially when cities are in the river delta and flat coastal areas, where pumping stations are required and sewers are installed with limited slope. Inadequate operation and maintenance of the network of sewers may lead to sewer clogging, local flooding, pipe leaks, and, as a consequence, to pollution of soil and groundwater, or increases of the hydraulic loading of the treatment plant. Pipes and tanks of higher capacity are needed. These are the reasons that wastewater management projects in most of cities and towns are facing delays.

But approaches may be changing. Most small communities have found conventional systems to be hugely expensive and have begun to investigate decentralized concepts. The decentralized concept is based on a simple premise that wastewater should be treated (and reused, if possible) as close to where it is generated as is practical. CEETIA has been developing suitable low-cost technologies for decentralized wastewater and fecal sludge treatment. In the CEETIA laboratory a study is carried out on the treatment of domestic wastewater using a baffled septic tank with anaerobic filter. This could be the most feasible option for on-site wastewater treatment in residential areas of Vietnam. The data indicates that baffled septic tanks with or without anaerobic filter could effectively treat black sewage in Vietnamese conditions.

Removal efficiencies for COD from 43.24 - 94.92 % (average 74.85%), for BOD from 47.13 - 90.87 % (average 71.47%), for SS from 37.40 - 97.18 % (average 71.14%) have been achieved. This could help in the improvement of wastewater management practices in Vietnam. Decentralized schemes of wastewater management are proposed for medium and small cities in Vietnam.

Key Words: BOD, decentralized wastewater management, wastewater treatment, water pollution.

Note by the editors

The papers before you are presentations made by participants at the *Seminar on environmental and public health risks due to contamination of soils, crops, surface and groundwater from urban, industrial and natural sources in South East Asia.*

The seminar was held in Hanoi, Vietnam, from 10 – 12 December 2002. It was jointly organized by UNESCAP and IWMI and hosted by the National Institute for Soils and Fertilizers of Vietnam. In addition to contributions by invited participants from China, Cambodia, Lao PDR, Thailand and Vietnam, presentations were also made by staff of the British Geological Survey, under a contract with UNESCAP. The BGS contribution is included in this volume as the keynote address.

Apart from reviewing the current status of pollution in the region, the meeting was to announce an IWMI led 4-year program at the sub-regional level to assess pollution levels (based on analytical data), the uptake of heavy metals/metalloids by crops and potential food chain contamination, subsequent potential impacts on the health of rural and urban populations and the sustainable use of soil and groundwater resources, and identify pollution sources and causative processes with a view to developing countermeasures and formulating requisite regulations and legislation.

The resources for this 4-year program, entitled "Protecting food security, human health and environmental integrity in rice-based agricultural systems from the detrimental impacts of heavy metals/metalloids", are expected to come from various sources simultaneously. While UNESCAP may address groundwater issues, other potential partners were and are invited to express their interest in covering the remaining sectors, including agriculture, industry, public health, etc. This multi-sectoral activity is expected to result in the collaboration of government departments with international agencies, NGOs as well as the private sector to develop a level of decision making based on reliable and balanced information that will ensure the sustainability of soil and water resources safe for rural, peri-urban and urban populations.

Contamination of water and soils as a result of natural processes, human activity and industrial and agricultural development is an ongoing process though we may not always have been aware of the damaging concentrations of contaminants in the waters we drink and the soils we grow our produce on. Often, what seemed useful and beneficial over the ages has recently been found to have a serious polluting character. Phosphates in washing powders, the over-use of natural fertilizers, the worldwide occurring still fairly high-grade heaps and ponds of mine tailings from which quietly heavy metals are leached that disappear into the local drainage, the wastewaters produced by industrial estates and tourist resort areas, there are many more examples of economically necessary human activities that have an unwanted polluting by-product.

Natural processes also play a role. Outcropping arsenic rich sulfide minerals and rocks produce anomalous and polluted local environments and the natural weathering process is responsible for the release into the drainage system of a multitude of elements, some of which may be serious pollutants. As with most potential disasters, being aware of the risks and being able to recognize it and to measure its impact is a battle halfway won. Planning and executing remedial measures is the next step.

The papers presented at the seminar all go some way in addressing the contamination of water and soils and the effects this may have on the health of people and on the produce we grow. From country papers to very specialized research reports, they cover a wide spectrum of facts, views and opinions, covering such subjects as ammonia, arsenic and cadmium pollution and the removal techniques that may be successful for some of these pollutants.

The reader will find that some of the papers, mostly those of a general nature are easily read. Others, certainly the papers concerned with the presentation of the results of laboratory research are more complicated and may be difficult to understand for those without a scientific background. All papers though have a distinct relevance to the subject matter discussed at the seminar and deserve their place in this volume.

The papers have been grouped according to their content and subject matter in the following categories:

- *Water quality*
- *Heavy metals and pesticides in soils and water*
- *Arsenic contamination and removal techniques*
- *Wastewater management*

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