

Environmental Analytical Research in Northern Vietnam – A Swiss-Vietnamese Cooperation Focusing on Arsenic and Organic Contaminants in Aquatic Environments and Drinking Water

Walter Giger^{a*}, Michael Berg^a, Hung Viet Pham^b, Hong Anh Duong^b, Hong Con Tran^b, The Ha Cao^b, and Roland Schertenleib^a

Abstract: A long-term education and research partnership has been established between the Swiss Federal Institute for Environmental Science and Technology (EAWAG) and two university institutes in Hanoi. Here we give a summary report on environmental analytical investigations conducted in cooperation with the Hanoi University of Science focusing on (i) arsenic contamination in ground and drinking water, (ii) volatile organic compounds (VOCs) including disinfection by-products and chlorination practice in drinking water, (iii) analysis and occurrence of organophosphorus pesticides in rice growing areas, and (iv) chlorinated phenols and other chlorinated pollutants in wastewater of a pulp and paper mill. Arsenic concentrations ranged from 1 to 3050 µg/l (average 159 µg/l) in groundwater from the city of Hanoi and surrounding rural areas. The high arsenic levels indicate that several million people consuming untreated groundwater might be at a considerable risk of chronic arsenic poisoning. Water produced by the Hanoi waterworks is partly affected by arsenic, but VOCs and disinfection by-products were below international guideline limits. However, the current chlorination practice was found to be critical regarding water quality issues. Chlorinated pollutants were particularly abundant in wastewater effluents of pulp bleaching, suggesting that point-of-source treatment options should be implemented. The high pesticide concentrations measured in rice fields (>500 µg/l) were rapidly flushed into ambient surface waters, where beneficial organisms could be affected.

Keywords: Arsenic · Groundwater · Organophosphorus pesticides · Trihalomethanes · Wastewater

Introduction

We report here on a project promoting professional knowledge in environmental analysis, drinking water production technology and wastewater treatment in Northern Vietnam. It is based on a cooperation

between the Swiss Federal Institute for Environmental Science and Technology (EAWAG) and the Hanoi University of Science. The Government of Switzerland, through the Swiss Agency for Development and Cooperation (SDC) launched its support of environmental science and training in the Hanoi area in 1993. The 'Chemistry of the Environment Project', a cooperation between the Swiss Federal Institute of Technology Zurich (ETHZ) under the guidance of vice-president Prof. Fritz Widmer and the Chemical and Environmental Engineering Department of the Hanoi University of Science, ran from 1993 to 1996. The Swiss funding supplied laboratory equipment and analytical instruments, while the Vietnamese government was responsible for constructing a new university building with laboratories and class rooms (see Fig. 1). It should be noted that Vietnam is one of

the 17 priority countries, where SDC is conducting activities focused on sustainable development processes.

The involvement of EAWAG began in 1998 with the program called 'Capacity Building for Environmental Science and Technology in Northern Vietnam' (ESTNV) and has recently moved into a second phase lasting until 2007. Capacity building is accomplished by applied research projects in environmental chemistry and environmental engineering, as well as in pilot-scale and scaling-up studies for enhancing drinking water quality, wastewater treatment and solid waste management. Senior Vietnamese researchers and graduate students were educated in project planning and performing research including a strong emphasis on analytical quality control and elaborate data interpretation. The partners in Hanoi are two institutes committed to ad-

*Correspondence: Prof. W. Giger^a

Tel.: + 41 1 823 5475

Fax: + 41 1 823 5311

E-Mail: giger@eawag.ch

^aSwiss Federal Institute for Environmental Science

and Technology (EAWAG)

Überlandstrasse 133

CH-8600 Dübendorf

^bCentre for Environmental Technology and

Sustainable Development (CETASD)

Hanoi University of Science

Vietnam National University

334 Nguyen Trai Street

Hanoi, Vietnam



Fig. 1. Inauguration ceremony of the new CETASD research building in February 1998 by the Swiss ambassador in Vietnam (Dr. Jürg Leutert) and the former rector of the Hanoi University of Science (Prof. Dao Trong Thi).

dressing environmental issues in northern Vietnam, namely the Centre for Environmental Engineering of Towns and Industrial Areas (CEETIA) belonging to the Hanoi University of Civil Engineering and the Centre for Environmental Technology and Sustainable Development (CETASD) being part of the Hanoi University of Science. Both centers made substantial progress during the first ESTNV phase. Considering that the topic of this CHIMIA issue is environmental analysis, this article describes activities conducted at CETASD in cooperation with EAWAG.

The educational and research output from 1998 to 2003 resulted in five master theses, two dissertations, five international publications [1–5], two book chapters [6][7], and seven Vietnamese publications [8]. The research topics investigated are of significant environmental relevance for Vietnam. Table 1 gives an overview of the chemical investigations undertaken.

Arsenic Contamination of Groundwater and Drinking Water in the Red River Delta

The arsenic contamination of water resources in the city of Hanoi and in the surrounding rural districts was discovered in 1998 during an investigation on water contamination by heavy metals [2]. Fig. 2a shows the arsenic concentrations measured in samples collected in September 1999 from the upper aquifers in tubewells of the rural districts. With an average arsenic concentration of 159 $\mu\text{g/l}$, the contamination levels varied from 1–3050 $\mu\text{g/l}$ in rural groundwater samples, which were collected from private small-scale tubewells. In the most affected district, groundwater used directly as drinking water had an average of 430 $\mu\text{g/l}$ arsenic. Table 2 summarizes the arsenic concentrations measured in three

Table 1. Chemical research projects of the Swiss-Vietnamese co-operation program on Environmental Science and Technology in Northern Vietnam (ESTNV, 1998–2002)

Analytes	Samples	Analytical methods	Refs
Arsenic and other heavy metals such as iron and manganese	GW, DW, SED	Atomic absorption spectroscopy Atomic fluorescence spectroscopy	[2]
Volatile organic compounds including trihalomethanes	GW, DW	Head-space, GC/MS	[1]
Ammonium, nitrate, bromide, DOC, alkalinity	GW, DW	Various standard methods for water analysis	
Organophosphorus pesticides	SW	Solid-phase microextraction GC/MS	[3]
Chlorinated phenols	IWW, SW	Solvent extraction, GC/MS	[8]
Adsorbable organic halogen (AOX)	IWW	Combustion, coulometric titration	[8]
Polycyclic aromatic hydrocarbons	SED	Soxhlet extraction, GC/MS	

GW: groundwater; DW: drinking water; SW: surface water; IWW: industrial wastewater; SED: sediment; GC/MS: gas chromatography/mass spectrometry

sample series of the 68 private tubewells. Our results indicate that several million people of the Red River delta are at a considerable risk of chronic arsenic poisoning [2][8][9].

Table 2. Arsenic concentrations in groundwaters of rural districts around Hanoi. N is the number of analyzed samples and the districts A to D are indicated in Fig. 2a. Groundwater samples were collected from private tubewells between September 1999 and May 2000.

District	N	Arsenic concentration [mg/l]	
		Average	Range
A	47	31	1–220
B	48	67	1–230
C	55	127	2–3050
D	45	430	9–3010
All districts	195	159	1–3050

Natural groundwater contamination by arsenic has become a crucial water quality problem in many parts of the world, particularly in the Ganges delta (Bangladesh and West Bengal, India) [10–12]. Our findings of so far unknown but highly alarming arsenic contamination in groundwater resources of the Red River delta contribute to the current discussion of whether the high arsenic levels in Bangladesh have to be considered exceptional. Chronic levels of 50 μg arsenic per liter can already cause health problems after 10–15 years of exposure. The development of the disease is strongly dependent on the exposure time and the resulting accumulation in the body. The first health symptoms are characterized by a noticeable skin pigmentation, which can lead to skin cancer. The subsequent health problems affect the cardiovascular and nervous system. After 15–30 years of exposure, victims often develop lung, kidney, or bladder cancer.

The Vietnamese capital Hanoi, situated in the upper part of the 11,000 km² Red River delta, is inhabited by 11 million people. Together with the Mekong delta, the Red River delta has become one of the most populous and agricultural productive regions of South East Asia. In the last 7–9 years, a rapidly growing rural population has stopped using surface water or water from shallow dug wells. Instead, it has become popular to pump water using individual private tubewells. The exploitation of groundwater in the city of Hanoi began 90 years ago and has since been expanded several times. Today, eight major well fields are operated by water treatment facilities which process 450'000 m³ of water per day [1]. Due to naturally anoxic conditions in the aquifers, the groundwaters contain large amounts of iron and manganese that are removed in the Hanoi drinking water plants by aeration and sand filtration [1]. The urban water treatment plants exclusively exploit the lower aquifers in 30–70 m depth, whereas private tubewells predominantly pump groundwater from the upper aquifer in 12–45 m depth [2]. Based on geological analogies to the Ganges delta, we expected elevated arsenic concentrations in the aquifers of the Red River basin. Thus, the scope of our study was to survey arsenic levels in the aquifers of Hanoi and surrounding rural areas. Over a period of 15 months all major drinking water plants of

Hanoi and 68 private tubewells in the adjacent rural districts were investigated, covering an area of approximately 700 km². Fig. 2a shows color-coded arsenic concentrations measured in the rural districts in September 1999. Most tubewells yielded arsenic concentrations above the current WHO guideline of 10 µg/l and the concentrations varied greatly within the studied area. In the southern part (district D), the majority of the wells' arsenic concentrations exceeded the Vietnamese standard of 50 µg/l. Alarming concentrations of 1000–3000 µg/l were measured in the south on both sides of the Red River. Our results indicate that the sources of contamination are distributed over a large area. Table 2 presents the averages and ranges of concentrations measured in the rural districts (three sample series: September and December 1999, May 2000).

Raw waters (lower aquifer) and treated waters from the eight water treatment plants of Hanoi were analyzed seven times between March 1999 and July 2000. The concentrations of September 1999, depicted as split rectangles in Fig. 2b, show that some raw groundwaters contained more than 300 µg arsenic per liter. Although arsenic concentrations were substantially reduced by the treatment, the levels in finished waters still exceeded the Vietnamese limit in 50% of the samples. The data in Fig. 3 demonstrate that this was observed

during the whole 15-month study period. The high concentrations of up to 430 µg/l found in raw groundwater were, in general, substantially reduced in treated water yet average concentrations of 25–91 µg/l remained. Interestingly, most tap water samples collected at individual homes contained arsenic concentrations below 50 µg/l (range 7–82 µg/l, average 31 µg/l), suggesting that additional arsenic removal occurs in the distribution system, possibly by adsorption to iron oxide surfaces in the pipes.

Although there is no direct evidence for an anthropogenic origin of arsenic in the subsurface in and around Hanoi, the possibility of pollution through landfill leakage, agricultural fertilizers, or mining wastes carried by the Red River cannot be excluded. However, the widespread arsenic occurrence in the investigated aquifers points to natural geogenic sources similar to the situation in the Ganges delta. Sediment-bound arsenic most probably originates from erosion and weathering processes, which result in the enrichment of arsenic onto ferric oxyhydroxides followed by fluvial transport and sedimentation. Several studies have suggested that elevated arsenic levels in groundwater are caused by reductive dissolution of arsenic-rich iron oxyhydroxides occurring as dispersed phases in the aquifer rocks ([11] and references therein).

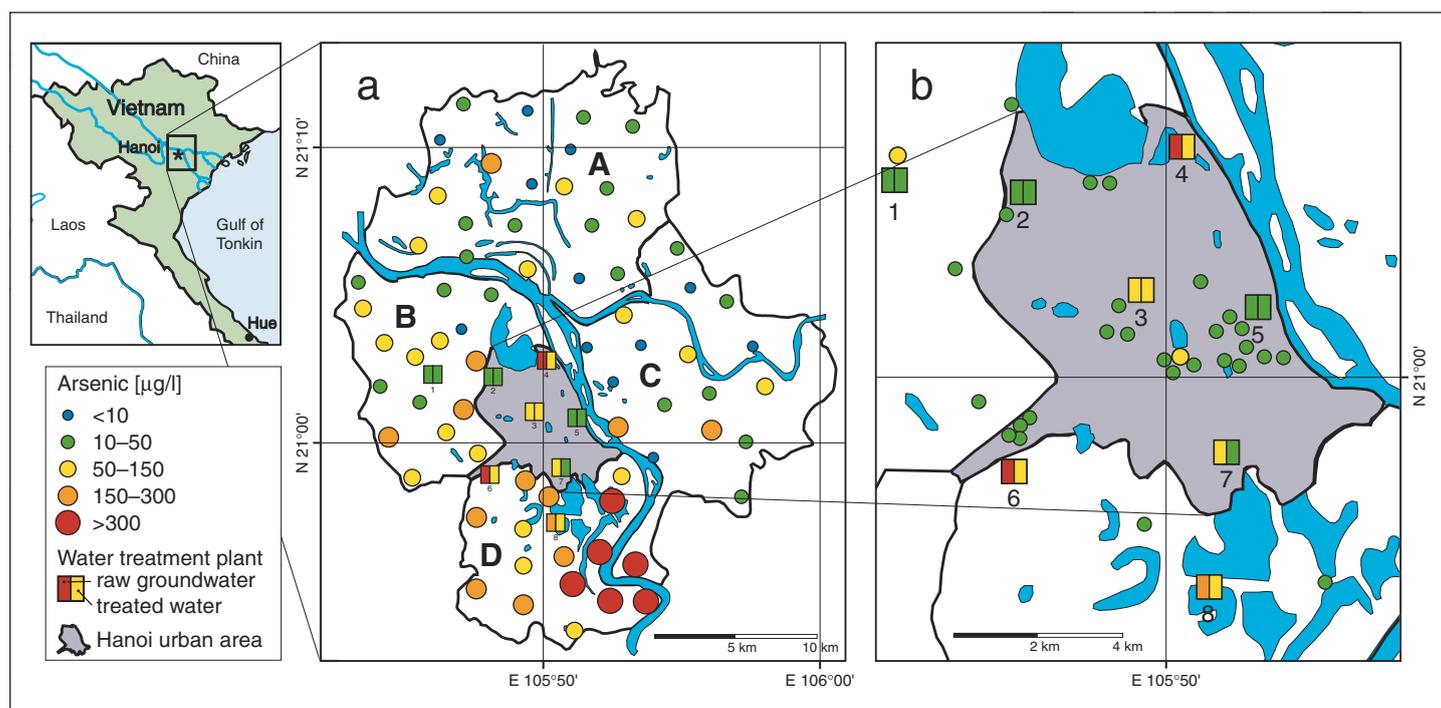


Fig. 2. Arsenic concentrations in the Hanoi area in September 1999. (a) In the rural districts A to D arsenic concentrations were measured in groundwaters pumped from the upper aquifer by private tubewells (dots). (b) In the city of Hanoi, arsenic concentrations were analyzed in raw groundwater (lower aquifer) and treated water of the eight major water treatment plants (split rectangles), as well as in tap water of supplied households (dots). The numbers 1 to 8 refer to the following water treatment plants. 1: Mai Dich, 2: Ngoc Ha, 3: Ngo Si Lien, 4: Yen Phu, 5: Luong Yen, 6: Ha Dinh, 7: Tuong Mai, 8: Phap Van. (Reproduced with permission from *Environ. Sci. Technol.* **2001**, 35, 2621–2626. Copyright 2001 Am. Chem. Soc.)

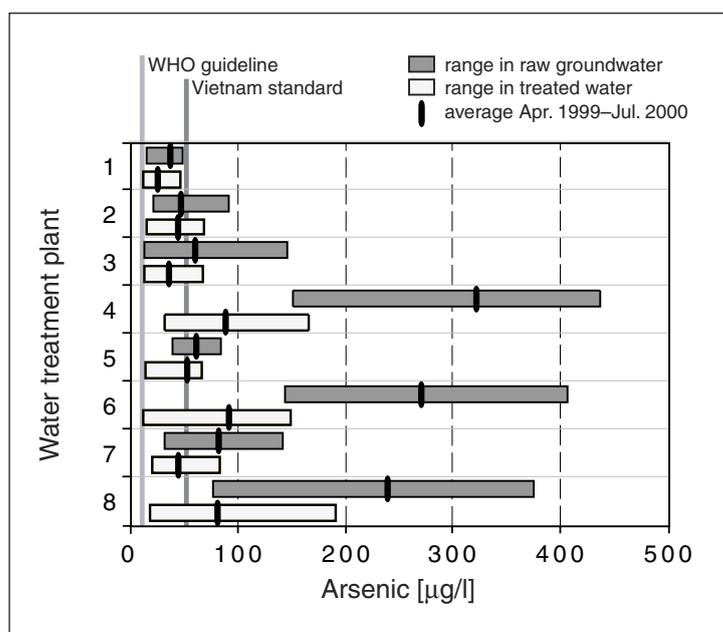


Fig. 3. Arsenic concentrations in raw waters from the lower aquifer and treated waters of eight water treatment plants in the city of Hanoi. Seven sample series were analyzed from March 1999 through July 2000 (7 x 16 samples). The numbers 1–8 of the water treatment plants refer to Fig. 2. (Reproduced with permission from *Environ. Sci. Technol.* **2001**, *35*, 2621–2626. Copyright 2001 Am. Chem. Soc.)

The anoxic conditions in the Red River sediments are driven by natural organic matter (NOM) present in the subsurface [13]. In fact, in sediment bore cores we have found peat layers with NOM concentrations of 15% total organic carbon. Dissolved oxygen is rapidly consumed by microbiological mineralization of NOM, resulting in the formation of bicarbonate and inorganic nitrogen species. This is consistent with the generally high alkalinity (31–810 mg/l) and high nitrogen concentrations (10–48 mg N/l) measured in the studied groundwaters [13]. Inorganic nitrogen was mainly found in its reduced ammonium form that reached particularly high levels of 48 mg N/l in the most severely arsenic contaminated district D. As a result of the low redox potential, As(v) is reduced to the more soluble As(III) that we have found to contribute to 50–100% of the total arsenic in the groundwaters.

In order to explain the significantly different arsenic levels of district A and district D (Fig. 2a), the different geological settings and actual hydrogeological conditions of these areas must be considered. Due to frequent riverbed migrations in the past, the aquifers are not fully separated and are in some locations connected through sand lenses. Even without the pumping of groundwater, recharge in the upper two aquifers can partly originate from Red River bank filtration. However, Hanoi's high

demand of water is causing a significant lowering of the groundwater table. This is particularly severe in the districts B and D where depression cones go down as far as 30 m. Under these conditions bank filtrates from the Red River must be of major importance and strongly influence the aquifers in the Hanoi area.

The results of this survey reveal that eleven million people of the Red River delta are exposed to a risk of chronic arsenic poisoning [2]. No disease symptoms have been diagnosed so far. This could possibly be attributed to the fact that in Vietnam, arsenic contaminated groundwater has only been used as drinking water for the past 7–10 years. Experience shows that it can take ten or more years before the first arsenic poisoning symptoms become apparent. Compared to Bangladesh one might further speculate that the general nutrition of the Vietnamese population is much better and could have a retarding influence. Nevertheless, the expected number of arsenic-related health problems in the future should not be underestimated. With a view to attaining early mitigation measures, EAWAG [14] and CETASD, with support from SDC, are addressing this issue with the Vietnamese Government and with specialists of other research and development organizations, such as UNICEF, WHO and the Danish Agency for Development Assistance.

Trihalomethane Formation by Chlorination in Water Supplies

Chlorination has been of crucial importance for improving the microbiological safety of drinking water since the beginning of the 20th century. Among the commonly applied disinfectants, chlorine has many advantages, because it is effective against many microorganisms, inexpensive, relatively easy to use and maintains a disinfection residual in the drinking water distribution system. The undesired formation of chloroform and brominated trihalomethanes caused by water chlorination was first reported in 1974 [15]. The reason for this problem is the fact that, in addition to inactivating pathogens, chlorine reacts with natural organic matter (NOM) in water to produce so-called disinfection by-products (DBPs) such as trihalomethanes (THMs), including CHCl_3 , CHCl_2Br , CHClBr_2 , CHBr_3 , and other halogenated compounds. The occurrence of THMs and other DBPs became the subject of many research projects, because the results of toxicity tests and epidemiological evidence suggest that these substances might have adverse health effects [16].

The total concentration of THMs and the relative distribution of individual THM species in chlorinated water strongly depends on the properties of the raw water, on the operational parameters of the chlorination in the water treatment plant, and on the residual chlorine in the distribution systems [17]. Aimed at minimizing the cancer risk, USEPA, WHO, and many European countries introduced regulations for THMs in drinking water. The standard maximum allowable concentrations for total THMs in drinking water range from 10 to 100 $\mu\text{g/l}$.

In Vietnam, chlorination is applied in almost all water treatment plants. The minimum residual chlorine in water at the outlet of water treatment plants and in the distribution system is required to be 0.8 and 0.3 mg/l, respectively [1]. It should be noted that using boiled water for consumption is a traditional habit of many Vietnamese people. Boiling water has a good germicidal effect and happens to simultaneously remove volatile compounds such as THMs.

Until now, there is no official Vietnamese guideline for THMs in drinking water, and no monitoring data for THMs were available [1]. We selected the eight major water treatment plants (WTPs) in the urban area of Hanoi for our investigation on THMs in drinking water based on two reasons. Firstly, Hanoi being the second largest city of Vietnam is experiencing a strongly increasing water demand for domestic and industrial use, which is triggered by the fast

development of the city infrastructure and the rapid growth of the urban population (3.5 Mio in 2001). The second reason concerns the chemical composition of the groundwater resources exploited for water production. The aquifers below Hanoi are characterized by varying hydrogeological conditions, even within short lateral and vertical distances. Due to anoxic conditions in the aquifers, the groundwater is rich in iron and manganese [2]. However, groundwater pumped from several locations is of significantly differing chemical composition, which is strongly influenced by varying ratios of bank filtrates from the Red River as well as lateral and vertical infiltration [2][13]. Based on a preliminary investigation of THM precursors (reflected by DOC and UV254 absorption, bromide concentration, and chlorine demand (indicated by ammonium and ferrous content)), we inferred that substantial variations in trihalomethane formation would occur in the eight Hanoi WTPs, although the WTPs apply very similar treatment procedures, *i.e.* aeration, settling, sand filtration, and chlorination using a dose of ≤ 1.5 mg/l chlorine.

This research is documenting the current situation with regard to THM formation (see Fig. 4) and disinfectant residual in the water supply of urban Hanoi [1]. The results and recommendations provided should guide the Vietnamese authorities in improving chlorination efficiencies and in defining guidelines for DBPs in drinking water. In addition, chlorination experiments with natural groundwater were carried out

in the laboratory to evaluate the maximum THM formation potential and THM yields for various chlorine doses (see Fig. 5). Based on these data, a relationship between chlorine exposure and THM formation was established. The results of the laboratory experiments can be used to adjust the chlorine doses, which are needed for the individual raw waters in order to achieve efficient disinfection and acceptable levels of THMs in the drinking waters of Hanoi.

The occurrence and the fate of trihalomethanes (THMs) in the water supply system of Hanoi was investigated from 1998 to 2001 [1]. The chlorination efficiency, THM speciation, and THM formation potential (THMFP) were determined in the water works and in tap water. With regard to THM formation, three types of groundwater resources were identified (see Fig. 4): (I) high bromide, (II) low bromide, and (III) high bromide combined with high ammonia and high dissolved organic carbon (DOC) concentrations. Under typical treatment conditions (total chlorine residual 0.5–0.8 mg/l), the total THM formation was always below WHO, EU, and USEPA drink-

ing water standards and decreased in the order type I > type II > type III, although the THMFP was >400 mg/l for type III water. The speciation showed >80% of bromo-THMs in type I water due to the noticeably high bromide level (≈ 140 mg/l). In type II water, the bromo-THMs still accounted for some 40% although the bromide concentration is significantly lower (<30 mg/l). In contrast, only traces of bromo-THMs were formed ($\approx 5\%$) in type III water, despite the high bromide levels (>240 mg/l). This observation could be explained by competitive kinetics of chlorine reacting with ammonia and bromide. Based on chlorine exposure estimations, it was concluded that the current chlorination practice for type I and II waters is sufficient even for 2-log inactivation of *Giardia lamblia* cysts. However, in type III water the applied chlorine is masked as chloramine with a much lower disinfection efficiency. In addition to high levels of ammonia, type III groundwater is also contaminated by arsenic, which is not sufficiently removed by the water treatment [2]. N-nitrosodimethylamine (NDMA), a potential carcinogen suspected to be for-

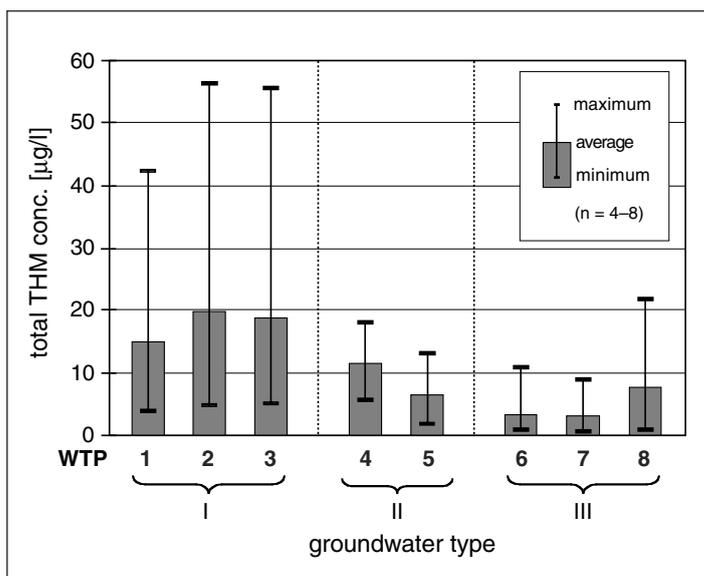


Fig. 4. Averages and ranges of total trihalomethane (THM) concentrations measured in finished waters of the Hanoi water treatment plants. The numbers 1 to 8 of the water works refer to Fig. 2. The different groundwater types are indicated by I–III. (Reproduced with permission from *Water Research* 2003, 37, 3242–3252. Copyright 2003 Elsevier Science)

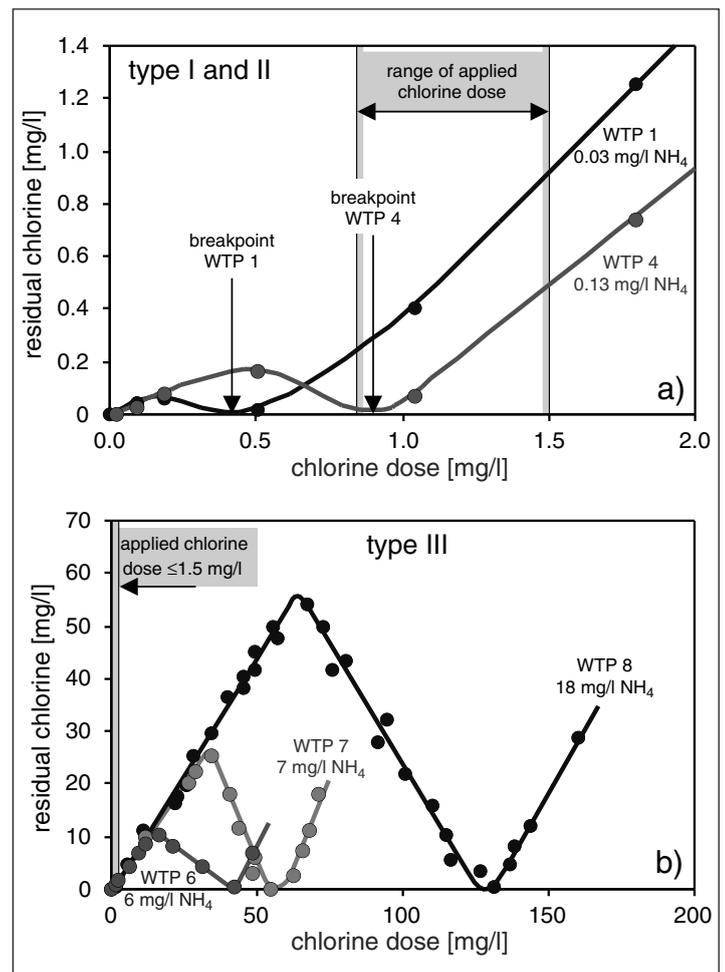


Fig. 5. Breakpoint curves and applied chlorine dose for a) WTP 1 and 4, and b) WTP 6–8. The range of the chlorine dose applied in the WTPs is indicated. (Reproduced with permission from *Water Research* 2003, 37, 3242–3252. Copyright 2003 Elsevier Science)

med during chloramination processes [18], was below the detection limit of 0.02 $\mu\text{g/l}$ in type III water.

The following conclusions and recommendations can be drawn from the findings obtained through this study.

a) Based on estimations of chlorine exposure, the chlorine dose of 0.8–1.5 mg/l applied for disinfection by the Hanoi water works is inefficient for water type III, and critical for water type I and II if ammonium concentrations exceed 0.1 mg/l.

b) It is recommended that a steady chlorine dose of 1.5 mg/l (instead of 0.3 mg/l) for water type I and II is maintained if ammonium concentrations are below 0.15 mg/l.

c) Due to the high ammonium levels of ≥ 15 mg/l in water type III, chlorine is mainly transformed to chloramine which is a considerably less efficient disinfectant than chlorine (~ 100 times). The chlorine doses of 10–30 mg/l necessary to reach a 2-log inactivation of *Giardia lamblia* cysts in WTPs 6–8 might cause substantially higher THM concentrations and possibly form NDMA. A satisfactory quality of drinking water derived from water type III therefore requires multistage treatment for removal of Fe, Mn, NH_4 , and DOC. In addition, a primary disinfection stage should be implemented.

d) Chlorine, THM and oxygen concentrations decreased in the distribution system of water type III (WTP 6). In this water, oxygen is possibly consumed by nitrification of ammonia in the reservoir and the distribution system, resulting in anaerobic conditions. Low oxygen conditions are unfavorable with regard to several water quality issues such as corrosion, taste, and odor.

Determination of Polar and Nonpolar Organophosphorus Pesticides in Aquatic Environments

Using polyacrylate coated fibers, a solid-phase microextraction (SPME) method was developed for the simultaneous determination of eleven commonly applied organophosphorus pesticides (OPs) and triazine herbicides representing a broad range of polarity [3]. The method was optimized and validated for both SPME adsorption and desorption processes. Water samples of only 1.3 ml were necessary for automated or manual SPME. With regard to the significantly different polarity of the target pesticides, optimum adsorption conditions were reached by addition of 4 mol/l NaCl to the water sample and with a SPME fiber exposure of 50 min at 60 °C. Desorption from the SPME fiber was best at 280 °C. The

method detection limits (MDL) were 3–35 ng/l, depending on the pesticide's polarity. By applying deuterated compounds (*e.g.* d_{10} -diazinon, d_5 -atrazine) and similarly-structured compounds (*e.g.* chlorthion, prothoate) as internal standards, high recoveries of 75–104% (RSD 1–9%) were achieved for spiked OP concentrations of 50–100 ng/l.

There has been a substantial amount of research employing SPME for the analysis of organic pollutants in environmental samples [19]. Organo-chlorine pesticides and OPs in water samples were determined by direct aqueous SPME at levels of nanograms per liter. As reported in these publications, the SPME efficiency for polar compounds such as dimethoate, dichlorvos, or desethylatrazine was always very low due to their high solubility in water, which leads to low recovery rates. The SPME method described here is very efficient for polar and nonpolar pesticides. We have thoroughly evaluated all parameters involved in the SPME analysis of OPs and tri-

azine herbicides in aqueous water samples by gas chromatography and mass spectrometry (GC/MS) [3]. The developed SPME method is highly robust and suitable for the simultaneous quantification of polar and apolar organophosphorus pesticides, as well as atrazine and its major metabolite desethylatrazine. Water samples of only 1.3 ml are required for the direct aqueous SPME method. Excellent method detection limits of 3–9 ng/l, 20–35 ng/l, and 277 ng/l were achieved for apolar, polar compounds, and the highly polar dimethoate, respectively. Considering its very low $\log K_{ow}$ value of only 0.7, and the difficulties encountered by any other analytical technique reported in the literature, the direct quantification of dimethoate from water samples can be considered highly satisfactory.

The presented SPME method was applied to analysis of organophosphorus pesticides and triazine herbicides in various water samples collected in the provinces Vinh Phuc, Hanoi, and Thai Binh, known as large rice-growing areas situated along the



Fig. 6. Aerial view of a typical rice-growing area in Northern Vietnam. It is evident that the waters in the rice fields are closely connected to the river.

Red River (Fig. 6). The most abundant pesticides were fenitrothion, diazinon, and fenobucarb with average concentrations in the three provinces of 250 to 700 ng/l, 150 to 250 ng/l, and below 10 to 280 ng/l (see Fig. 7), respectively. Atrazine was only found at trace levels below 10 ng/l.

In the irrigation channels, the two most abundant pesticides fenitrothion and diazinon had maximum concentrations of 980 and 196 ng/l, respectively. In the ponds, highest concentrations were 175 ng/l for fenitrothion and 117 ng/l for diazinon. Extremely high fenitrothion concentrations of up to 510'000 ng/l were measured in water of flooded rice fields after pesticide application. However, fenitrothion concentrations decreased rapidly (*i.e.* within 3–5 days) to levels below 5'000 ng/l, mainly due to flushing with unpolluted water and sorption to soil sediments. Nevertheless, such high fenitrothion concentrations in rice paddy water are of concern, because this insecticide will eventually not only eliminate targeted insects but also harm beneficial organisms living in the aqueous environment.

Chlorinated Phenols in Wastewaters from Pulp and Paper Production

Our research on the contamination by chlorinated pollutants in wastewater from the Bai Bang Paper Company, the largest integrated pulp and paper mill in Vietnam, was conducted in 2000 to 2001. In this study, concentrations of chlorophenols (CPs) and other parameters such as adsorbable organohalogen (AOX), total organic carbon non-purgeable organic carbon and volatile organic compounds were determined at various locations throughout the wastewater system including bleached effluents and receiving water of this pulp and paper company [8]. As can be seen in Fig. 8, CPs were detected at highest concentrations in the hypochlorite stage (E and H-stages) of the bleaching process. The most toxic compound, pentachlorophenol, was detected at relatively high concentrations of several $\mu\text{g/l}$ in the bleaching effluent. The total discharge of chlorophenols to the bleaching effluent was 336 g/ton air dried pulp. The variation profile in concentrations of chlorophenols throughout the wastewater system was similar to that of adsorbable organohalogen (AOX), suggesting that chlorophenols can be used as a suitable parameter for monitoring the discharge of chlorinated organic matters in bleach effluents. The removal efficiency of chlorophenols in a laboratory-scale con-

ventional activated sludge reactor was similar to that reported in other studies, while a newly developed technology based on powder activated carbon showed high removal efficiency. High elimination of chlorophenols using powder activated carbon technology suggests the need to develop this method for a potential wastewater treatment plant in the future.

In addition, the results presented in Fig. 8 clearly demonstrate that the highly polluted wastewater derived from black liquor, C-, E-, and H-stages should be collected and treated in separate lines, rather than mixed with less polluted wastewater and treated thereafter.

On-going and Future Studies

The Swiss and Vietnamese authorities have decided that the ESTNV cooperation should be continued for another four years

period (2003–2007). Based on the achievements of the first phase, research studies in the field of environmental chemistry in aquatic systems and drinking water treatment technology will be implemented with expected outputs of providing policy makers with reliable data and propose adequate technical solutions. Quality assurance and quality control of sampling, laboratory analysis as well as scientific report writing will be of high priority. CETASD will carry out the following pilot research projects: a) Research on Hanoi drinking water treatment options, b) arsenic contamination in groundwater in the environments of Hanoi, assessment and mitigation, and c) the occurrence and behavior of antibiotics in wastewater of hospitals and of pharmaceutical industries (for details see Table 3). In addition, both Vietnamese institutes CETASD and CEETIA will be supported in improving their institutional management by organizational development profession-

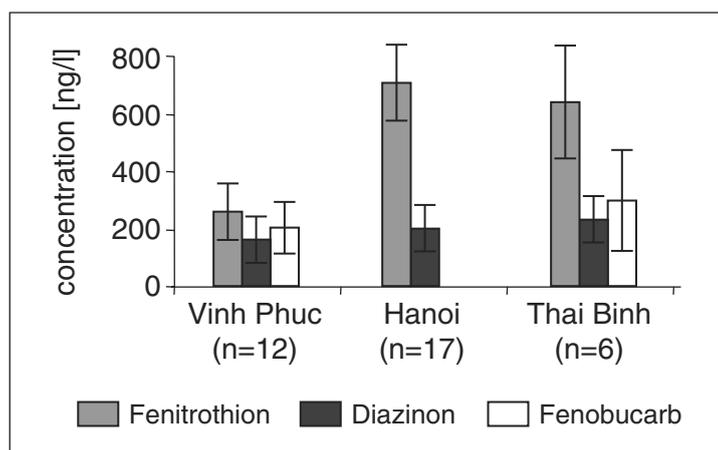


Fig. 7. Average concentrations of organophosphorus pesticides in three provinces of the Red River delta.

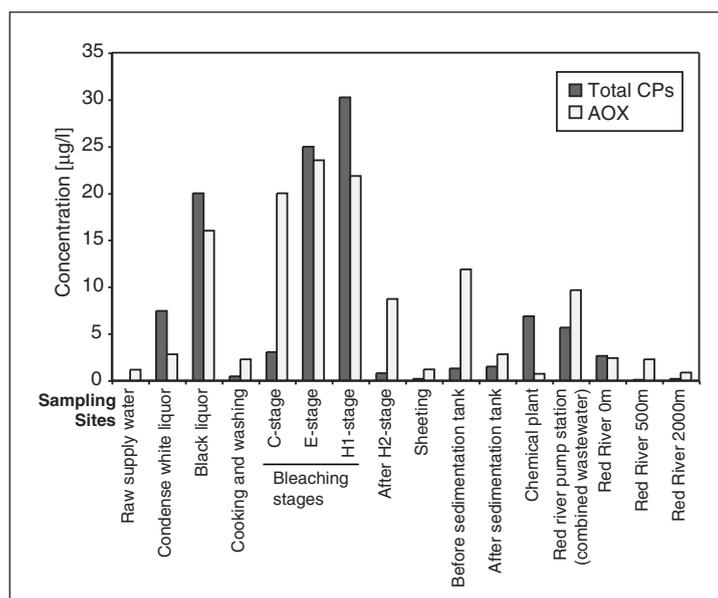


Fig. 8 Chlorophenol and adsorbable organic halogen (AOX) concentrations in the major wastewater lines of the pulp and paper mill BAPACO and downstream in the Red River.

Table 3. Planned chemical and engineering projects for the second phase of ESTNV (2003–2007)

Topics	Environmental compartments	Objectives
A) Elevated concentrations of geogenic ammonium, nitrate, phosphate, heavy metals (Fe, Mn, As, etc.) and dissolved organic compounds (DOC) in Hanoi groundwater	groundwater drinking water	<ul style="list-style-type: none"> – establishing feasible treatment solution on a laboratory scale. – scale-up experiments in cooperation with engineers for developing drinking water treatment options
B) Arsenic contamination in groundwater aquifers in the environment of Hanoi, assessment and mitigation	groundwater drinking water treatment, biological samples (hair, nails, urine), sediments	<ul style="list-style-type: none"> – understanding geochemical influences affecting spatial and seasonal variation of arsenic in the groundwater – studying the correlation between arsenic concentration of the groundwater and its impact on human health – developing low cost arsenic removal systems on household scale – evaluation of low cost field analytical methods like biosensors
C) Occurrence and fate of antibiotics in wastewaters of hospitals, of pharmaceutical industries and of aquacultures	hospital wastewaters industrial wastewaters aquacultures	<ul style="list-style-type: none"> – establishing quality controlled analytical methods – comparison to the situation in Switzerland – correlation of chemical analyses with antibiotic resistances

als. The general goal is to sustainably build up until 2007 Vietnamese capacities for performing research and development projects in environmental science and technology in an independent way.

Acknowledgements

These studies were funded by the Swiss Agency for Development and Cooperation (SDC) in the framework of the Swiss–Vietnamese Cooperation Project ESTNV (Capacity Building in Environmental Science and Technology in Northern Vietnam). We gratefully acknowledge the support of the members of the SDC coordination office in Hanoi, especially Olivier Chave, George Capt, Urs Herren, Dang Mai Dung, Barbara Böni and Walter Meyer. We also acknowledge the help and interest of a large number of CETASD and EAWAG scientists, among them Le Van Chieu, Pham Ngoc Ha, Nguyen Hung Minh, Vu Duc Nam, Nguyen Thuy Ngoc, Pham Thi Kim Trang, Alfredo Alder, Jakov Bolotin, Hervé Gallard, Urs von Gunten, Ursula Heusi, Stephan Hug, David Kistler, Eva Molnar, Hansrudolf Siegrist, and Caroline Stengel. Finally we thank Rolf Gloor and the Institute Bachema for beneficial quality evaluation and support in education and training.

Received: August 16, 2003

- [1] H.A. Duong, M. Berg, M.H. Hoang, H.V. Pham, H. Gallard, W. Giger, U. von Gunten, *Water Research* **2003**, *37*, 3242.
- [2] M. Berg, H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib, W. Giger, *Environ. Sci. Technol.* **2001**, *35*, 2621.
- [3] H.M. Nguyen, H.V. Pham, W. Giger, M. Berg, *Anal. Sci.* **2001**, *17*, a375.
- [4] M.P. Espino, D.S. Aga, H.M. Nguyen, H. Singer, M. Berg, S.R. Müller, *Kimika* **2001**, *17*, 13.
- [5] T.C. Schmidt, H.A. Duong, M. Berg, S.B. Haderlein, *Analyst* **2001**, *126*, 405.
- [6] H.V. Pham, H.C. Tran, T.H. Cao, V.H. Hoang, M. Berg, R. Schertenleib, in 'Arsenic Exposure and Health Effects, Vol. 5', Eds. W. R. Chappell, C. O. Abernathy, R. L. Calderon, Elsevier, Oxford, UK, **2003**.
- [7] H.C. Tran, T.H. Nguyen, M. Berg, H.V. Pham, in 'Arsenic Exposure and Health Effects, Vol. 5', Eds. W.R. Chappell, C.O. Abernathy, R.L. Calderon, Elsevier, Oxford, UK, **2003**.
- [8] H.M. Nguyen, N.H. Pham, H.V. Pham, W. Giger, M. Berg, *J. of Analytical Sciences of the Vietnam Analytical Sciences Society* **2000**, *5* (3), 39; H.A. Duong, M.H. Hoang, H.V. Pham, M. Berg, W. Giger, *J. of Analytical Sciences of the Vietnam Analytical Sciences Society* **2000**, *6* (2), 31; H.A. Duong, H.V. Pham, H. Gallard, M. Berg, *J. of Analytical Sciences of the Vietnam Analytical Sciences Society* **2000**, *6* (4), 63; H.V. Pham, H.C. Tran, T.C. Nguyen, M. Berg, W. Giger, R. Schertenleib, *Bulletin of Geology and Minerals of Vietnam* **2001**, *57*; H.C. Tran, V.T. Vu, H.V. Pham, V.H. Hoang, *Bulletin of Geology and Minerals of Vietnam* **2001**, *81*; D.N. Vu, T.N. Nguyen, T.L. Vo, T.H. Cao, H.V. Pham, R. Schertenleib, W. Giger, M. Berg, Proceedings of the 2nd Conference on Environmental Science and Technology, Hanoi University of Science, **2002**, pp. 30; H.A. Duong, H.V. Pham, N.T. Lam, Proceedings of the 2nd Conference on Environmental Science and Technology, Hanoi University of Science, **2002**, pp. 53.
- [9] M. Berg, *EAWAG News* **2002**, 53e, 12.
- [10] P.L. Smedley, D.G. Kinniburgh, *Appl. Geochem.* **2002**, *17*, 517.
- [11] R.T. Nickson, J.M. McArthur, P. Ravenscroft, W.G. Burgess, K.M. Ahmed, *Appl. Geochem.* **2000**, *15*, 403.
- [12] M. Berg, S. Hug, J.R. van der Meer, J. Zorbrist, *Aqua Press International* **2002**, *4*, 15.
- [13] J.M. Trafford, A.R. Lawrence, D.M.J. Macdonald, V.D. Nguyen, D.N. Tran, T.H. Nguyen, BGS Technical Report WC/96/22, British Geological Survey, Keyworth, UK, **1996**.
- [14] www.eawag.ch/arsenic
- [15] T.A. Bellar, J.J. Lichtenberg, R.C. Kroner, *J. Am. Water Works Ass.* **1974**, *66*, 703.
- [16] P.C. Singer, in 'Safety of Water Disinfection: Balancing Chemical and Microbial Risk', Ed. G. F. Craun, ILSI Press, Washington, DC, **1993**.
- [17] M. Palacios, J.F. Pampillon, M.E. Rodriguez, *Water Research* **2000**, *34*, 1002.
- [18] W.A. Mitch, D.L. Sedlak, *Environ. Sci. Technol.* **2002**, *36*, 588.
- [19] J. Beltran, F.J. Lopez, F. Hernandez, *J. Chromatogr. A* **2000**, 885, 389.