## Abschlussbericht VNM 08/006

Initiierung eines Vietnamesisch-Deutschen Netzwerkes von Experten zur Bewertung von Arsen in der Nahrungskette und zur Entwicklung, Optimierung und Einsatz von Filtertechniken zur Entfernung von Arsen aus belastetem Grundwasser in ländlichen Regionen des Deltas des Roten Flusses, Vietnam



Maidong, 9. Dezember 2010:

Carsten Bahr von der Firma GEH und Trang Pham von der Hanoi University of Science, Center for Environmental Technology and Sustainable Development, an einer im Projekt installierten Filtereinrichtungzur Entfernung Arsen aus dem Grundwasser

(Filterrohr mit Filtermaterial der Firma GEH, Vorfilterung in Sandbecken, gesamter Filterblock errichtet von Le Van Chieu, Hanoi University of Science, Center for Environmental Technology and Sustainable Development)

## Vietnamesische Partner:

Hanoi University of Science, Center for Environmental Technology and Sustainable Development

Hanoi University of Science, Faculty of Biology, Genetic Department Vietnamese Academy of Science and Technology, Institute of Chemistry National Institute of Occupational and Environmental Health

## Deutsche Partner

Karlsruher Institut für Technologie, Institut für Mineralogie und Geochemie
Karlsruher Institut für Technologie, Institut für Geographie und Geoökologie
Karlsruher Institut für Technologie, Institut für Regionalwissenschaft
Technische Universität Berlin, Institut für Technischen Umweltschutz
Ruhr-Universität Bochum, Klinik für Psychiatrie, Psychotherapie, Psychosomatik und Präventivmedizin
Ruhr-Universität Bochum, Lehrstuhl für Siedlungswasserwirtschaft und Umwelttechnik
Universität Trier, Ökotoxikologie/Toxikologie und Institut für Biogeoanalytik und Umweltprobenbanken
Gesundheitsamt Stadt Köln, Infektions- und Umwelthygiene
GEH Wasserchemie GmbH Co KG Osnabrück
AHG Allgemeine Hospitalgesellschaft AG Düsseldorf
Psytest, Psychologische Testsysteme, Herzogenrath

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#### 1. Beschreibung der durchgeführten Arbeiten und Ergebnisse

Anhang 1 beinhaltet den Zeitplan gegenseitiger Besuche. Folgende Ergebnisse wurden erzielt:

- Aufbau eines funktionierenden interdisziplinären Netzwerkes Vietnamesischer und Deutscher Wissenschaftler über das Thema "Ursachen und Folgen von Arsen in der Nahrungskette".
- Durchführung von fünf größeren Workshops in Vietnam (dreimal in Hanoi) und Deutschland (zweimal, Karlsruhe, Bochum) zum Austausch des Stand des Wissens und zur Diskussion von Lösungswegen (Vorträge s. beigelegte DVD). Programme des Eröffnungsworkshops und des Abschlussseminars sind dem Abschlussbericht beigefügt, ebenso ein Film (auf DVD) des Eröffnungsworkshops.
- Zwei Feldkampagnen in drei verschiedenen Dörfern (Phan Phuc, Mai Dong, Nghia Dan) wurden im November 2008 und Februar 2010 zur Untersuchung von Arsen in der Nahrungskette durchgeführt. Hierbei entstanden zwei wissenschaftliche Arbeiten (s. beigelegte DVD). Hieraus ergab sich, dass eine ganzheitliche Betrachtung der Arsenaufnahme über das Trinkwasser und die Nahrung aber auch der Lebensgewohnheiten (Alter, Arbeitsplatz, Geschlecht, Einkommen...) nötig ist, um das Gesamt-Risiko einordnen zu können. Ein hieraus resultierender Flyer zur Aufklärung der betroffenen Bevölkerung über Arsen in der Nahrung ist in Bearbeitung.
- Zwei Feldkampagnen wurden zu den gesundheitlichen Auswirkungen der Arsenbelastung wurden April 2009 und September 2010 in Mai Dong und Nghia Dan organisiert. Hierbei wurde den vietnamesischen Projektpartnern computergestütztes Programm zur Untersuchung von neurologischen Funktionen von der Firma Psytest, Herzogenrath im Wert von 5.000 € kostenlos überlassen. Es konnte gezeigt werden, dass somatoforme Störungen, Symptome der Depression und Beeinträchtigungen von neuropsychologischen Funktionen wie Aufmerksamkeit und fluide Intelligenz einen Zusammenhang zur Arsen Belastung aufwiesen (Bericht in Anhang 2).
- In den Jahren 2009 und 2010 besuchte eine vietnamesische Gastwissenschaftlerin f
  ür jeweils rund einen Monat die Deutschen Partner und f
  ührte Absorptionsversuche von Arsen an Filtermaterial sowie Arsenanalysen an entsprechendem Probenmaterial durch. Derartige Analysen wurden auch in Vietnam durchgef
  ührt (Anhang 3)

- 2010 wurden durch das Projekt im Dorf Mai Dong zehn einkommensschwachen Familien Filtersysteme zur Entfernung von Arsen gebaut. Hierzu und für weitere Untersuchungen stellte die Firma GEH insgesamt 600 kg Filtermaterial kostenlos zur Verfügung (Wert 2640 €). Das gewonnene Wasser aus diesen Filtersysteme wird nun auch über das Projektende hinaus kontinuierlich auf Arsen analysiert, wozu die Firma GEH weitere 1300 € bereitstellt (Anhänge 4 und 5).
- Im Januar 2011 wurde in Chuyen Ngoai, Ha Nam Provinz, eine soziologische Befragung zur Akzeptanz und Nutzung von dezentralen Wasserreinigungssystemen durchgeführt. Es zeigte sich, dass in dem untersuchten Gebiet rund et 40 % der Bevölkerung ausschließlich Grundwasser als Trinkwasserquelle nutzen. Derzeit werden von fast allen Haushalten einfache Sandfiltern eingesetzt, die mit dezentralen Filtersystemen gekoppelt werden können, wie in einem anderen Ort (Mai Dong) von der Projektgruppe gezeigt wurde. Auch der Ausbau von Regenwassertanks bietet sich als einfache Maßnahme zur Verringerung der Arsenbelastung an (Berichte in den Anhangen 6).
- Anhang 7 beinhaltet den Projektbericht der vietnamesischen Partner an das MOST in Vietnam. Hier wurden teilweise zusätzliche Untersuchungen in Absprache mit den deutschen Partner aber ohne deren direkte Beteiligung durchgeführt
- Die Ergebnisse des Projekts wurden auf dem IWRM Kongress in Karlsruhe im November 2010 vorgestellt und veröffentlicht (Anhang 8, Norra et al. 2010: Development and optimization of measures against the contamination of the food chain by arsenic from polluted groundwater resources in rural areas of the Red River Plain in Vietnam, In: Steusloff (Hrsg.): IWRM Karlsruhe 2010 Conference Proceedings, 191-199. KIT Scientific Publishing).

#### 2. Bericht über die beabsichtigte Verwertung der Ergebnisse / bisherige oder zukünftige Kooperation mit der Industrie

Es ist von der Projektgruppe geplant einen Antrag auf Förderung im Rahmen des BMBF CLIENT Programms im August 2011 zu stellen. Hierbei soll neben Entwicklung und Anpassung effektiver Arsenfiltermethoden zur Arsenentfernung unter Berücksichtigung der Filterreststoffverwertung auch die Abwasseraufbereitung in den betroffenen ländlichen Gebieten verbessert werden. Dies ist notwendig, um den Eintrag von organischer Substanz in den Untergrund zu verringern, wodurch die Entstehung reduzierender Bedingungen im Untergrund begünstigt und damit die Arsenfreisetzung gefördert werden kann. Weiterhin sollen Anaerobtechniken weiterentwickelt und angepasst werden, die die an organischen Verbindungen reichen Abwässer für die Energieerzeugung nutzbar machen. Dadurch kann der Bedarf an Kohle zum Kochen verringert werden und die damit verbundene Staub-Belastung verringert werden. Die Kombination der Technologien greift nicht nur punktuell in den Wasserkreislauf in den betroffenen ländlichen Gebieten ein, sondern zielt darauf ab, ihn seiner Gesamtheit nachhaltig zu sanieren. Das Projekt schließt zudem die langfristige Evaluierung der Auswirkungen dieses Technologieeinsatzes auf die Gesundheit ein und bewertet Veränderungen mit Bezug auf die Wasserqualität. In diesen Projektantrag werden neben den beteiligten Firmen GEH, Psytest und Allgemeine Krankenhausgesellschaft weitere Firmen zur Anaerobtechnik und biologischen Abwasserreinigung integriert.

Für die Firma GEH haben sich im Rahmen dieses Projektes wertvolle Erfahrungen hinsichtlich des Vermarktungspotentials ihres Filterwirkstoffes und deren Anpassung an vietnamesische Verhältnisse ergeben.

Die beteiligte privatwirtschaftlich geführte Allgemeine Krankenhausgesellschaft konnte Erfahrungen über die Wirkung von Arsen im so genannten subtoxischen aber trotzdem gesundheitsrelevanten Konzentrationsbereich gewinnen.

Seitens des Instituts für Regionalwissenschaft ist es geplant, die durchgeführten Untersuchungen in einer Promotion weiterzuführen und diese im Mai 2011 anzumelden (Arbeitstitel "Factors influencing the diffusion of point of use Water treatment innovations in developing countries: A comparative case study")

Die gewonnenen wissenschaftlichen Erkenntnisse werden nun sukzessiv international veröffentlicht.

### 3. Bewertung der Zusammenarbeit mit Ihrem Partnerinstitut

Die Zusammenarbeit mit den vietnamesischen Partnern war äußerst erfolgreich und bildet ein hervorragendes Fundament für nachfolgende Projekte. Mit der Etablierung erster Filtersysteme und deren Monitoring in einem betroffenen Gebiet konnten bereits sehr konkrete Maßnahmen realisiert werden, die weit über die ursprüngliche Zielsetzung des Projektes hinausreichen. Dabei wurde dieses Projekt um die umfängliche aber notwendige Reiseaktivität zu ermöglichen parallel von der DFG unterstützt.

#### 4. Projektbezogene Publikationen, Patentanmeldungen

Boie, I. 2009: Arsenic contamination in rural areas of the Red River Delta in Vietnam, Diplomarbeit, KIT, Karlsruhe

Kellermeier, E. 2010: Arsenic in the food chain in rural areas of the Red River Delta in Vietnam, Diplomarbeit, KIT, Karlsruhe

Norra et al. 2010: Development and optimization of measures against the contamination of the food chain by arsenic from polluted groundwater resources in rural areas of the Red River Plain in Vietnam, In: Steusloff (Hrsg.): IWRM Karlsruhe 2010 Conference Proceedings, 191-199. KIT Scientific Publishing

## Anhang 1: Zeitplan der gegenseitigen Aufenthalte

2.11. – 8.11.2008:	Kick-off Meeting in Hanoi und Besuch vietnamesischer Partnerinstitutionen sowie Feldbegehung durch deutsche Partner.durch deutsche Partner vom 2.11. bis zum 8.11.2008
8.11. – 14.11.2008:	1. Feldkampagne zur Analyse der Arsenbelastung der Nahrungskette, Schwerpunkt Boden-Pflanze Transfer
11.4. – 21.4.2009:	2. Feldkampagne zur Untersuchung neuropsychiatrischer, neuropsychologischer und allgemeinmedizinischer Folgen der Arsenbelastung der betroffenen Bevölkerung
13.7 26.7.2009:	Besuch deutscher Partnerinstitutionen durch vietnamesi- sche Partner und Workshop in Karlsruhe (16. – 17.7.2009)
27.7 11.9.2009:	Aufenthalt einer vietnamesischer Gastwissenschaftlerin in Deutschland (Frau Vi Thi Mai Lan) am Institut für Minera- logie und Geochemie des Karlsruher Instituts für Techno- logie und am Fachgebiet Wasserreinhaltung der TU Berlin
18.1. – 17.2.2010:	<ol> <li>Feldkampagne zur Analyse der Arsenbelastung der Nahrungskette, Schwerpunkt Bilanzierung Arsenaufnahme</li> </ol>
3.4. – 11.4.2010:	Vietnamesisch-deutscher Workshop (9.4.) und Besuch vietnamesischer Partnerinstitutionen sowie Feldbegehung durch deutsche Partner.
18.5. – 7.6.2010:	Besuch deutscher Partnerinstitutionen durch vietnamesi- sche Partner und Workshop in Bochum (25.5.2010)
12.9. – 27.9.2010:	4. Feldkampagne zur Analyse genetischer Prädisposition der humanen Arsentoxitizitätstoleranz.
2.11. – 4.12.2010:	Aufenthalt einer vietnamesischer Gastwissenschaftlerin in Deutschland (Frau Vi Thi Mai Lan) am Institut für Minera- logie und Geochemie des Karlsruher Instituts für Techno- logie.
7.12. – 17.12.2010:	Vietnamesisch-deutscher Workshop (10.12.) und Besuch vietnamesischer Partnerinstitutionen sowie Feldbegehung durch deutsche Partner.
2.1. – 16.1.2011:	5. Feldkampagne zur soziökonomischen Erhebung der Einstellung von Dorfbewohner zur Arsenbelastung des Grundwassers und dessen Nutzung

#### Anhang 2

## Mental health burden and neurobehavioural findings of chronic arsenic exposure in the Vietnamese field study

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#### BACKGROUND

Arsenic exposure in humans is commonly known to lead to peripheral polyneuropathies with parasthesiaes. However, as arsenic enters the blood-brain-barrier through an undefined mechanism in already low concentrations, organic arsenic compounds are capable to induce central nervous disorder. Acute clinical central nervous symptoms are vertigo, nausea and vomiting with further psycho-organic symptoms of an "encephalopathy" like mental confusion, delirious states, drowsiness and loss of consciousness. Acute and long-term observations if present include subthe fluctuating superior neuropsychiatric deficits in orientation, concentration, memory, as well as emotional instability, anxiety, organic paranoid psychosis, headaches and sleep disturbances. The only long-term study on arsenic poising (milk in infancy) was able to show marked developmental neurotoxicity like mental retardation, EEG abnormalities, further different neurological diseases and a fivefold increase in mortality for various central nervous diseases. Further, neuropsychological dysfunctions in humans are described in the domains of intelligence, learning and memory, attention, visual, spatial and acoustic processing pointing to a dysfunctional integrity of the human brain correlated with arsenic exposure.

#### AIM OF THE STUDY

There are hardly any larger systematic population-based studies of neurobehavioural testing in arsenic endemic areas - in particular for subclinical or chronic neurological and psychiatric effects of arsenic neurotoxicity (including low-level arsenic exposure).

Subjective and social consequences of arsenic exposure regarding cognitive and neurofunctional requirements of daily living (e.g. driving or working abilities) have not been investigated so far. The aim was to develop sophisticated psychobiological indicators for physical and mental health of arsenic neurotoxicity that can also be implemented for control of success of arsenic free potable water and food.

#### METHODS

In close cooperation with the Vietnamese partners a battery of neuropsychiatric and neuropsychological diagnostic procedures was developed, including intense exchange of medical knowledge and training for the specific Vietnamese situation in order to assess subtle health consequences of arsenic neurotoxicity. These methods included established neurological and psychiatric tools in clinical examination (neuropsychiatric status, psychometric evaluation), easy to handle on site, as well as instruments for examination of subjective mental health burden and quality of life (semi-structured interview, questionnaire). Neuropsychological testing instruments were also adapted to the Vietnamese situation and included intellectual abilities (intelligence and profile of primary intellectual functions), attentional functions (alertness and subfunctions), visual scanning in visual guided attentional functions, divided attention), visual and verbal learning and memory with translated test instruments, psychomotor speed and fine-motor coordination.

In April 2009, the pilot study was performed in two areas of the Red River delta including 66 individuals form MaDong (As high) and 72 from Nghia Dan (As low). Neuro-medical examinations were performed by Vietnamese doctors, and the interviews and questionnaires were supported by trained personnel from the Vietnamese institutes also taking the human samples (urine, hair, nails) - under supervision of the German colleagues. Further genetic sampling of saliva probes in the same inhabitants of the two villages was performed in a second field visit in autumn 2010.

#### RESULTS

Neuro-psychiatric examination revealed subclinical neurological findings with significant sensory impairments but also impairment of motor reflexes, cranial nerve functions and as well as some mental functions accompanied by significant increase of headaches and mood disturbances in the high As region. Of notice, analysis of the self-report instruments on mental health issues points to a general enhanced burden in the two regions whereas findings of depressive symptoms were predominately seen in the high As region, thus referring to some particular deficit with potentially social consequences, too. Moreover, symptoms of somatization were significantly correlated with the level of As in hair.

Neuropsychological functions were also impaired in the whole group of all tested individuals. However, special domains like attention (divided attention) and intelligence (fluid intelligence) showed significant correlations with As in hair. Taking extreme groups of all individuals As levels in hair, reaction times (alertness, divided attention) in subjects with high As levels were increased, and several intelligence functions (correct solutions, long-term memory) were reduced as opposed to those with low As levels.

DNA-analysis of genetic samples has been finished recently and identification of relevant polymorphisms is currently underway (Ruhr University Bochum, Germany).

#### CONCLUSIONS

These preliminary results already suggest differences in the neuropsychiatric and mental health status in the two As regions with serious implications for public health status in Vietnam. Ideally, the findings of this pilot will be completed by counselling and information on arsenic-associated neuropsychotoxic deficits and preventive strategies; a basis for such an approach would be a larger follow-up field study of sustainable effects that derive from arsenic removal strategies of contamined rural sites.

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### ADSORBENTS AND ADSORPTION OF ARSENIC FROM WATER MEDIUM.

Division for Environmental Chemistry, Institute of Chemistry, Vietnam Academy for Science and Technology

#### 1. Introduction:

Many groundwater sources in rural areas in Vietnam being used for domestic purposes are contaminated with high arsenic concentration. Groundwater sources contaminating with arsenic are mostly the wells belong to individual farmer family in rural areas and diffusely distributed .

For a safe use, arsenic must be removed from drinking water to protect the health of water consumers.

In addition to arsenic, the numerous water sources are characterized by variable concentration of other constituents (Fe, Mn, P, and organic matter), different ratio of As(III) to As(V), which will make difficult for the removal performances of the treatment system .

Several arsenic treatment technologies have been developed and applied in practice including precipitation, membrane filtration, ion exchange, adsorption and phyto-filtration. An arsenic removal adsorber seems to be mostly appropriate for small – scale applications in this situation.

Adsorbents used for removing arsenic from water are rather abundant based on aluminium, ferric, manganese oxides or mixture thereof.

Arsenic removal performance of an adsorber depends on the individual adsorbent used, the non- arsenic constituents present in water source (e.g. phosphate, hardness, organic matters), pH, in particular the As(III)/As(V) (in turn, this ratio is affected by pH and oxidation – oxidation potential).

Due to the better adsorbility of most adsorbents to As(V) than to As(III), it wishes that beside of high adsorption capacity, the adsorbent would possess oxidation ability (best with dissolved oxygen) to convert As(III) to As(V) for prevent the supplement adding external oxidants to treatment system.

Arsenic adsorption usually presents a slow kinetical process, it requires several hours, even days establishing the adsorption equilibrium. The slow kinetical behavior of the adsorption process is related to the kinetical mechanism, mainly the internal transport and the surface complex formation on the adsorbent solid. The slow process will diminish the adsorbility of original materials used (low dynamical adsorption capacity). Designing an adsorber for arsenic removal from water is always facing with the presence of the non- arsenic constituents and the capacity lost under flow condition due to slow kinetical process.

For practical applications, a further difficulty is arising for adsorbent regeneration because of strong binding of arsenic to solid surface in form of a chemical complex. In conventional

manner, chemicals are used to regenerate the spent adsorbents by a rather complexes operations and it is not easy for a nonprofessional operator as a farmer using the treatment system.

In general, the people living there have low potential to pay money for water supplies.

- This specific feature requires appropriate treatment methods with respect of:
- Safety of the water quality.
- Low capital and running costs.
- Easy operation and maintaining.
- Researches and technology developments for arsenic removal have been therefore focused on:
- Creation of suitable adsorbents characterized by reasonable cost, processing oxidation ability, easy regeneration and readily available.
- Design of the adsorber with a minimal correction for individual application.
- Monitoring the performance of adsorbers installed during discontinuous operation.

#### 2. Research activities:

#### 2.1 Adsorbent preparation:

Synthetic adsorbents for arsenic were prepared on the basis of manganese and ferric oxides. The products were obtained by converting Mn(II), Fe(II) with suitable chemicals such as potassium permanganate or by electrochemical precipitation.

As results, four adsorbents were manufactured:

CDM1, CDM2: manganese dioxide by chemical precipitation

EDM manganese dioxide by electrochemical precipitation.

NC-F20: magnetic ferric oxide with nanostructure.

Beside of synthetic adsorbents, natural manganese ore (pyrolusite) was also used for investigation.

#### 2.2 Adsorbent characterization:

The products are characterized by different methods: SEM, XRD, BET, PZC and magnetic properties. Some characteristics of products are summarized in table 1.

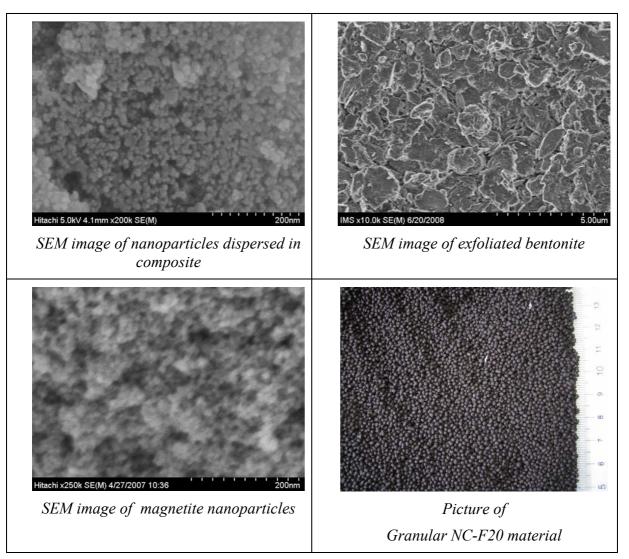
Product	CM1	CM2	EDM	NC-F20
Surface area $(m^2/g)$	75	43	55	145
Modification	$\delta$ - MnO <sub>2</sub>	Ramsdellite	$\alpha$ - MnO <sub>2</sub>	Nano
PZC (range)	$\approx 6$	$\approx 6$	$\approx 6$	$\approx 7$
Representative size, nm	1000-2000	5000-10000	5000-10000	10-12

Table 1. Some characteristics of synthetic adsorbents.

NC- F20 was granulated and specified by:

- Capacity for arsenic removal: 30- 35 g As/kg
- $Fe_3O_4$  content: > 70 %.
- Specific surface area: 135 145 m2/g

- Bulk density: approx. 0.8 1 kg/liter
- Granular size: 1 1.2 mm
- Mean particle size: 10.02 nm.



### 2.3 Adsorbility evaluation:

The adsorbility of products was evaluated by measuring the adsorption isotherm for As(III) and As(V) at different pHs values. Isotherm data were treated by Langmuir isotherm equation to obtain the maximal adsorption capacity (table 2).

$$a = a_m \cdot \frac{K \cdot C}{1 + K \cdot C} \tag{1}$$

a: adsorption capacity corresponding to equilibrium concentration C.

a<sub>m</sub>: maximal adsorption capacity of adsorbent.

K: Langmuir adsorption constant.

C: equilibrium concentration of arsenic in solution.

For example, the maximal adsorption capacity of different manganese dioxide adsorbents was given in table 2.

Capacity	acity a <sub>m</sub> of CMD1		a <sub>m</sub> of CMD2		a <sub>m</sub> of EMD	
pH	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)
pH = 5,0	1,000	0,500	0,714	0,357	0,833	0,417
pH = 6,0	0,769	0,435	0,588	0,322	0,667	0,370
pH = 7,0	0,625	0,400	0,476	0,303	0,526	0,345

*Table 2. Adsorption capacity*  $a_m$  (g/kg) of manganese dioxide.

#### 2.4 Arsenic adsorption in column:

To evaluate the adsorption column performances, the Adam- Bohart model describing the breakthrough curve is used:

$$t = \frac{a_o \cdot H}{C_o \cdot v} - \frac{1}{k \cdot C_o} \ln \left( \frac{C_o}{C_b} - 1 \right)$$
(2)

Equation (2) can be converted into form:

$$t = \frac{a_o}{C_o.v} (H - L) = \frac{a_o}{C_o.v}.\eta$$
 H (3)

with

$$L = \frac{v}{k.a_o} \ln\left(\frac{C_o}{C_b} - 1\right) \tag{4}$$

 $a_o$ : statical adsorption capacity corresponding to initial (influent) concentration  $C_o$ . L: the mass transfer zone. k: formal kinetical constant. H: the height of adsorbent layer.  $C_b$ : break-through concentration (10 µg/l for arsenic as standard value); v: flow velocity of water through column; t: working (service) time.  $\eta$ : the utilization degree of column.

The performance or the working time of an adsorber is dependent upon the adsorption capacity ( $a_0$ ), arsenic quantity entering the column ( $C_0v$ ), the adsorbent mass in column (contained in H), the breakthrough concentration  $C_{ob}$  and the lost of adsorbent mass (contained in L).

Mass transfer zone is characterized by a length of column, in which the adsorbate concentration will decreases from  $C_0$  to  $C_b$ . The length of column corresponding to mass transfer (or dead zone) will be wasted during operation. One of most impacted on the mass transfer zone is the kinetical constant (k), the lower the adsorption rate the higher the length of transfer zone. Mass transfer zone is also influenced by the quality of adsorbent  $(a_0)$  and operational parameters (water flow velocity v, concentration of adsorbate  $C_0$ ,  $C_b$ ).

In ground water, several non-arsenic constituents exist, which can impact the adsorber performances by different mechanism. The frequent contaminant is phosphate, it can form chemical complex with the functional group on the solid surface as arsenic because of the similarity of chemical structure. The presence of phosphate (and the others) in water will badly impacts the adsorber performances.

All parameters influencing the arsenic adsorption on individual adsorbent and in each water source should be investigated to optimize the process. It is time – consuming and not easy task.

For practical applications, the assessment is limited on the influence of initial arsenic concentration ( $C_0$ ), water flow velocity (v), contaminants (hardness, phosphate, organics) on  $a_o$  and L. The obtaining results could be used for designing an adsorber.

Experimentation for the determination of  $a_0$  and L was implemented by the construction of the arsenic breakthrough curves at variable adsorbent layers H (figure 11) using an available adsorbent (MF – 97, a natural manganese ore, pyrolusite form, MnO<sub>2</sub> >65 %). From the breakthrough curve, the working time corresponding to the length of layer was determined and  $a_0$ , L were calculated by using eq.(3). The linearity for the relationship of the working time and adsorbent layer was shown in figure 12.

Results of dynamical adsorption investigation are presented in table 3.

Influence of exp. Conditions			$a_o (\mu g/cm^3)$
Concentration C <sub>o</sub>	$C_o = 55 \mu g/l$	15	5.03
V = 6 bed volume/h	$C_o = 104 \mu g/l$	19	7.36
	$C_o = 116 \mu g/l$	33	6.54
V = 3 bed volume/h	$C_o = 220 \mu g/l$	35	9.19
	$C_o = 310 \mu g/l$	39	9.98
Flow rate v	$Q = 3.V_{h't}/h$	39	9.98
$C_{o} = 310 \mu g/l$	$Q = 6.V_{h't}/h$	42	9.39
$PO_4^{3-}$ - Influence	$PO_4^{3-} = 0 mg/l$	39	9.98
$C_0=310\mu g/l,$	$PO_4^{3-} = 2 mg/l$	41	6.62
v= 3 bed volume/h	$PO_4^{3-} = 5 mg/l$	42	3.29
Influence of Hardness (H) and or ganic matter COD (Mn)	$H=100 mgCaCO_3/l$ $COD (Mn) = 1 mg O_2/l$	39	9.98
$C_0 = 310 \mu g/l$ , v= 3 bed volume/h	$H=500 \text{mgCaCO}_3/l$ $COD (Mn) = 20 \text{ mg O}_2/l$	39	9.73

Table 3. Dynamical adsorption characteristics of system MF-97.

#### 4. Conclusions:

- Four synthetic adsorbents were prepared by chemical or electrochemical precipitation and characterized by SEM, XRD, PZC, BET methods.
- Adsorption capacity for arsenic was evaluated by measuring the isotherm of As(III) and As(V) under static conditions at different pHs.
- Dynamical adsorption behaviors influencing by flow rate, principal contaminants in water as well as operational parameters were investigated to determine the dynamical adsorption capacity, the mass transfer zone and the column utilization degree.

#### Anhang 4:

## GEH Water Filters for Arsenic Removal from Drinking Water in the Red River Delta

(Status report for ViGerAs-project by GEH Wasserchemie GmbH, Carsten Bahr)

Adsorption filters provide the technically simplest and most reliable technology for arsenic removal, offering significant advantages over iron flocculation, ion exchange and membrane filtration processes. Adsorbents based on ferric hydroxide provide the highest capacity for arsenic removal as shown by application experience in recent years. Along with synthetically manufactured granular adsorbents, numerous materials which are found in nature or derived from side products or waste materials have been proposed for use as arsenic adsorbents. While these materials are often lower in price, they also have the disadvantage of relatively low adsorption capacity. GEH granular ferric hydroxide was developed in the 1990's in Germany at the Technical University of Berlin as the first commercially available iron-based granular adsorbent. GEH is a pure ferric oxide hydroxide which is in full conformance with the quality requirements of European Standard EN DIN 15029. It is certified for use in drinking water treatment in many countries of the world (e.g. ANSI/NSF Standard 61 in the United States) and has been used successfully for many years worldwide.

In countries utilizing for the most part central water supply (e.g. in Europe and the U.S.), GEH is used in large filtration units made of plastic or stainless steel. These systems are normally used in continuous operation at throughput rates in the range of 10-100 m<sup>3</sup>/h. In applications requiring lower supply rates (e.g. 50 L/d) and discontinuous operation, point-of-use (POU) treatment units are used. Simple, low-maintenance operation is of primary importance in POU filtration units, particularly when used in rural areas. These small filtration units must be dimensioned such to ensure optimum operating conditions, i.e. with a filtration flow speed not exceeding 20 m/h and an empty bed contact time (EBCT) of at least 3 minutes. Figure 1 depicts the basic design of a small GEH filter and summarizes the operational parameters.

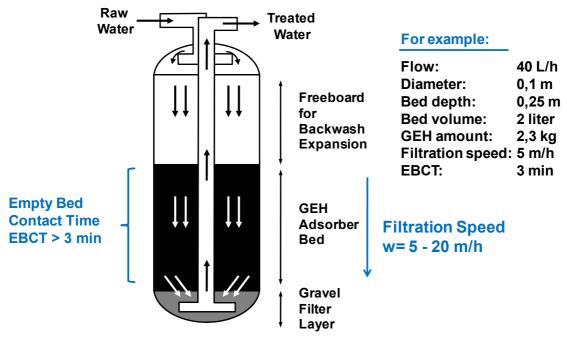


Figure 1: Design of a small-sized GEH filter system

In general it should be noted that GEH adsorbers remove arsenic only and do not effect iron removal, if necessary, from the water treated. In areas with iron-laden, chemically reduced groundwater, filtration in sand beds has proven to be the simplest method for removal of iron (as well some of the arsenic) in practice to date. However, when the groundwater treated is heavily contaminated with arsenic, sand-bed filtration normally does not remove enough arsenic to attain permissible levels for drinking water. In such cases it is advisable to divert a portion of the sand-filtered water through a GEH adsorber specifically for use as drinking water - e.g. for drinking or cooking. Water for other household uses does not require this treatment.

GEH adsorbers require minimum maintenance and can be operated or shut down over any time intervals as desired. However, during periods of non-operation, drying out of the adsorber bed must not be permitted. Regular backflushing of the adsorber bed may be required as a maintenance measure if the groundwater treated contains high levels of suspended particulants, as they can accumulate in the GEH adsorber and reduce throughput. Analyses of arsenic content in the treated water are conducted at regular intervals to ensure high quality. This is normally done by on-site tests conducted by trained personnel. The adsorption capacity and therefore the service life of the adsorber bed are highly dependent on the composition of the groundwater, i.e. its arsenic content, pH level etc. and the operating conditions (figure 2).

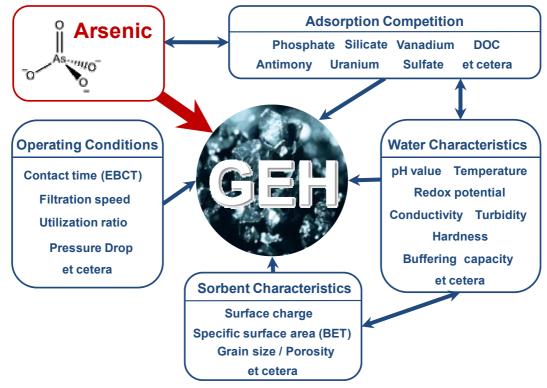


Figure 2: Factors affecting the adsorption capacity of GEH

Replacement of the adsorbent material is recommended once per year, depending on the dimensioning of the unit. When groundwater with very high arsenic levels is treated, two or more adsorbers can be used in series to further ensure consumer safety. With regard to hygiene, GEH adsorbers do not cause problems as they are not conducive to microorganism growth as is the case in activated charcoal filters. However when the groundwater treated may contain microbial contamination, it is generally advisable to boil it before use, even if after GEH treatment. If the testing conducted on treated water shows arsenic levels above permissible limits, the adsorbent material in the bed must be replaced. Following use, the exhausted GEH adsorbent contains approximately 2-10 g/kg. This arsenic is securely bound by the GEH adsorbent and is not eluted out under pH neutral and oxidative conditions, as has been shown by leaching tests (e.g. the toxicity leachate procedure of EPA Test Method 1311). However, like the used sand from the sand filtration beds, exhausted GEH adsorbent is a potentially hazardous waste material and should be collected for disposal in landfills. Regeneration of saturated GEH adsorbent with sodium hydroxide, while feasible under certain conditions, is not done in practice as it is not economical.

The pilot GEH adsorbers installed by the project partner CETASD in fall 2010 are now providing valuable information on adsorption capacity, operational reliability and consumer acceptance by rural users. The breakthrough behavior of the filters will be monitored during the next 12 months. Additionally, GEH Wasserchemie will deliver 600 kg adsorbent media to CETASD for further pilot testing.

#### Anhang 5

## Evaluation of arsenic filter systems applied at Mai Dong village

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Mai Dong is a commune belongs to Kim Dong district, Hung Yen province with the total area of 6.31 km<sup>2</sup> and the population of 5,565 people. People here are living based on agriculture. Except the Hung Yen town, almost families in Mai Dong are using ground water and rain water for cooking all around the year. Depended on the volume of the storage tank in each family, the stored rain water are just enough for about 4 - 6 months and the rest of the year people are using water from the bored wells with the very simple and individual sand filters. The investigated data showed that the current situation of existing sand filter systems in the local are unadequate for iron and arsenic removal for drinking purpose.

3 new enhanced sand filter systems had been constructed and 7 renovated existing household sand filter systems by replacing yellow sand since September 2010 applied for testing the performance of iron and arsenic removal. 10 cartridges of Granular Ferric Hydroxide (GEH Wasserchemie GmbH & Co. KG) had also been installed after sand filter systems for improving of arsenic removal for drinking water.

The new enhanced sand filter systems are consisted of 4 main stages: 1. Aeration using the perforated ejector; 2. Settling tank with the central column; 3. Rapid sand filter; 4. GEH cartridge and Storage tank. The system was designed as follows:

(1) Aerator consisted of the PVC column (50 cm, diameter of 9 cm) perforated with 60 holes with the diamter of 5 mm. 5 perforated (4mm diameter) dishes made of PVC are installed on a pilar inside of the column. The dishes are used for distributed the water flow through. Water is pumped through the aerator with the flow rate of 1 m<sup>3</sup>/h and attracted air through the holes on the column wall and air is supplied for the oxidation of Fe<sup>2+</sup> into Fe<sup>3+</sup> in the form of iron hydrooxide. Water is impacted on the wall and dishes improved the oxidation process of odor and CO<sub>2</sub> removal and increasing pH. The co-precipitation of arsenic is also occured in this stage.

(2) Reaction column and settling tank conisted of PVC funnel (12cm heigth, 20cm diamter) conected with the PVC column (80 cm height, 9 cm diameter) installed veritcally in the settling tank. Water after the aerator is collected into the funnel. The oxidation reaction of  $Fe_2^+$  is continuing occured and precipitated in the form of ironhydrooxide and settled in the bottom of column and settling tank. The hydraulic contact time of 40 minutes is designed for the maximum removal of iron concentration of 20 g/l.

(3) Rapid sand filter is designed with the yelow sand column of 1 m height. Yellow sand was screened through the sieve with the diameter of 1-3 mm. The volume of the sand filter is designed with the retention time of 30 minutes and flow rate of 3 m/h.

(4) GEH catridge is manufactured with PVC cyclinder column (60 cm height, 9 cm diamter). The GEH material is filled with the height of 40 cm and weight of 2 kg. The designed filter rate of 2m/h or 10 l/h with the EBCT of 4 minutes.

The preliminary investigated results from 10 sand filter systems showed that:

Ground water contained relatively high iron and arsenic and ammonium with the value of 7.1 mg/l, 195  $\mu$ g/l and 11.1 mgN/l, respectively.

Iron in ground water could be removed down to the value of less than 1 mg/L but arsenic could not be removed completely in the existing simple sand filter systems. With the presence of iron concentration from 1-10 mg/L, arsenic could be removed with the rate of 20-90% and treated water is not satisfied the National Technical Regulation on Drinking Water Quality (QCVN 01:2009/BYT).

All enhanced sand filter systems (both 3 new and 7 renovated ones) could completely removed iron in ground water. Arsenic removal efficiency depended on the content of iron. The correlation between As removal rate and iron content in ground water showed the linear relation. The 3 new sand filter systems showed the average arsenic removal rate of 71-78% which is improved of 33% higher than those in 7 old sand filter systems. Arsenic concentration in outlet of 10 GEH cartridges showed the values under the QCVN 01:2009/BYT for drinking water and the investment cost is about 20 VND/L of treated water.

The investigation of sand filter systems and GEH cartridges are still continuing. It is supposed that the performance of iron and arsenic removal can be improved due to the accumulation of iron hydroxides on the surface of sand filter layer.

Ammonium concentration in outlet of sand filter systems is still high (from 0.2-12 mgN/L) 2 - 8 time higher than standard for drinking water. It is proposed to implement the ammonium removal stage with suggested measures of slow sand filter or the combination of biotrickling filter or etc.





Some photos of the enhanced sand filter systems with GEH column for iron and arsenic removal with household scale in Mai Dong village, Hung Yen province.

## Anhang 6

## " Adoption of point-of-use water treatment for mitigation of arsenic contamination in rural areas of the Red River Delta, Vietnam"

#### Antje Wegner, Institut für Regionalwissenschaft, KIT

#### 1. Introduction and objectives of the survey

Since about ten years it is known that groundwater in the Red River Delta is highly contaminated with arsenic. The presumption, leading to in-depth analysis in Vietnam for example by EAWAG, was obvious because of similar geological and hydro-geological characteristics in the Red River and the Bengal Delta. Hazards emanating from geogenic arsenic in soil and groundwater gain scientific attention worldwide, since contaminated aquifers can be found in China, India and Bangladesh as well as in Taiwan, Mexico, Argentina and Chile. The issue has been subject to manifold investigations. Research has been done in order to investigate the extent and probable causes of elevated Arsenic levels in groundwater and soil but scientific evidence about the factors influencing the success of mitigation efforts is scarce. Even over short distances often high variations of arsenic levels are observed which points to the need for a comprehensive survey to take into account water supply and treatment for each single household as well as awareness and knowledge. The majority of studies still focuses on the different factors which determine the mobility of arsenic in the environment and approaches for its mitigation. In contrast less is known about social, cultural and economic factors influencing the exposure of individuals and the diffusion and use of mitigation efforts in the long run.

Due to the elevated arsenic levels in the groundwater, which might cause severe health problems, new drinking water technologies and filter techniques have to be introduced to the households in the rural Red River Delta. A variety of (low cost) mitigation options on household level like sand-filters is available and has partly been implemented during the last years often pushed by interventions of scientific and non-governmental actors. Whereas the VIG-ERAS-project primarily focused on the technical feasibility of filter-techniques so far, only little attention was paid to social, economic and psychological factors influencing the adoption and dissemination of sand-filters and other kinds of water treatment. Hence the use and acceptance of different arsenic mitigation options were assessed by empirical data gained in face-to-face interviews.

The survey which was recently carried out in January 2011 in Chuyen Ngoai, Ha Nam province, aims at revealing:

- a) which water resources and treatment methods are commonly used,
- b) which arsenic mitigation strategies are already applied and how they differ in terms of operability, usability and acceptance,
- c) the level of awareness and knowledge about water quality and in particular about arsenic contamination and its potential harmful consequences for health,
- d) and if the usage of water resources, water treatment methods and arsenic mitigation strategies differs amongst certain groups in the village.

The information delivered by the face to face interview in each household is complemented by water samples for each household taken before and after sand-filtering as well as by a hair sample. These data on the one hand indicates the actual exposure of a single household to arsenic and on the other one allows to assess the efficacy of sand-filters.

#### 2. Site of investigation

In Vietnam mainly two regions are affected by arsenic contamination: the large alluvial deltas of the Mekong River in south and the Red River in the north (Berg et al. 2007). Especially in Ha Nam province, which belongs to the administrative region of the Red River Delta and comprises besides the capital Hanoi 10 other provinces, significant contamination and early symptoms of arsenic posing are found (Nguyen et al. 2009, Dang et al. 2004). Thus the region has been subject of interventions. This province, where the site of investigation Chuyen Ngoai is located, has a population of 786.000 inhabitants living on 860,2 km<sup>2</sup> and is thus the smallest province according to population size (GSO Vietnam 2009).

#### 3. Description of the field work

The survey was prepared in cooperation with Hanoi School of Public Health in autumn and conducted in January 2011 in Chuyen Ngoai, Ha Nam province. The village in Duy Tien district is located closely to the Red River. 150 households in seven different hamlets ("thon") were included in the sample, four of them lying beyond the dyke.

Prior to the main field work a quick test for arsenic in several households and two pretests for the questionnaire were carried out during a short visit in Chuyen Ngoai to check whether this is an appropriate site for investigation. Additionally contact to local authorities was established to get the permission for the research, a list of households and ensure collaboration during the field campaign.

In parallel the questionnaire was revised and interviewers were recruited and instructed. In the field interviewers worked in pairs and each one was accompanied by local staff to introduce them to the households. In order to provide an incentive for the interviewees to take part in the survey a small present and 20,000 VND were given to each household. While one interviewer conducted the interview with a member of the household the other one took water samples from the tube-well of the respective household – one before and one after sand-filtering.

The questionnaires covers different topics ranging from socio-demographic information about equipment of household, land ownership and livestock, to water sources and treatment by sand-filters or other filter techniques. The section about use of sand-filters, other filter-systems and rainwater tanks contains detailed questions about construction and maintenance of these facilities as well as an assessment of costs, perceived efficacy and improvement of water quality by each kind of water treatment. Additionally the respondents were asked about their knowledge about arsenic contamination, its impact on health and potential mitigation options. The questionnaire ends with a brief section about information and communication behavior in health and water related issues.

#### 4. Analysis of the empirical results

The data was structured in two datasheets and analysed by SPSS 18. One datasheet is based on households as unit of reference and the other one on the individual household members.

#### 4.1. Description of the sample

In sum the sample comprises 626 persons belonging to 150 households located in 7 different hamlets. Four of these hamlets are lying beyond the dyke. 46% of the household members

are male and 53% female. The **household structure** of the sample in Chuyen Ngoai is representative for rural areas in Ha Nam province according to household size and age. On average 4,32 persons are living in one household. Single-person-households are very uncommon in the village and only every eighth households consists of two persons. On the contrary three quarters of the households comprises from three to six persons. In comparison with the data for the rural areas of Ha Nam provided by the GSO Population and Housing Survey 2009 the households in Chuyen Ngoai are larger than the average in rural Ha Nam. This is especially due to the extremely low percentage of single-person-households in the considered hamlets.

The size of the households is mainly determined by two factors: on the one hand often three generations are living in one household, on the other hand two thirds of the households have children (under 18 years old) half of those even two or more.

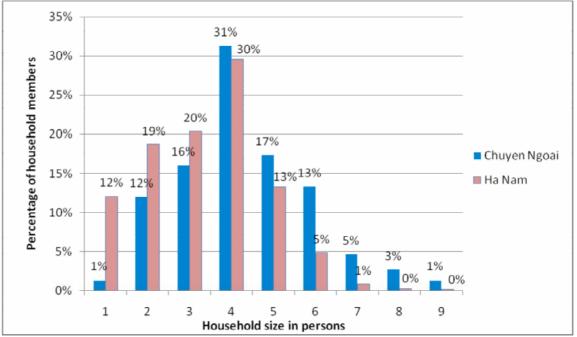


Fig. 1 Household size in Chuyen Ngoai\* and rural areas of Ha Nam Province\*\*

\* Data for Chuyen Ngoai results from survey (N=150)

\*\* Data from Population and Housing Survey Vietnam 2009 (GSO 2010), percentages calculated from absolute numbers

In general the **age** pattern of the sample corresponds to that of the provincial level. In comparison to the rural areas in Ha Nam the younger age groups (up to 10 years) are slightly under-represented (see figure 2). Nearly every second inhabitant of Chuyen Ngoai is younger than 30 years old whereas just 13% exceed the age of 60. Although the age distribution still reflects a considerable growth rate and quite young age distribution, the declining percentage of the age groups younger than 15 years points to the growing desire to limit family size to two children.

The analysis of **educational levels** indicates a considerable educational expansion amongst the age groups younger than 30 years. All degrees from intermediate school fall upon this group. Likewise the percentage of persons which has finished the third level of secondary school or holds a university or college degree reaches its peak between the age of 20 to 30. The changing structure in education level strongly impinges on **occupation and employ-ment** of the respondents. Due to the age distribution and educational expansion every fifth of the inhabitants states to be a student. Nevertheless farming remains the main livelihood

strategy for a great share of the inhabitants (44%) and even for those of pensionable age. Every tenth earns his living as a worker, others act as craftsmen, small traders or communal staff.

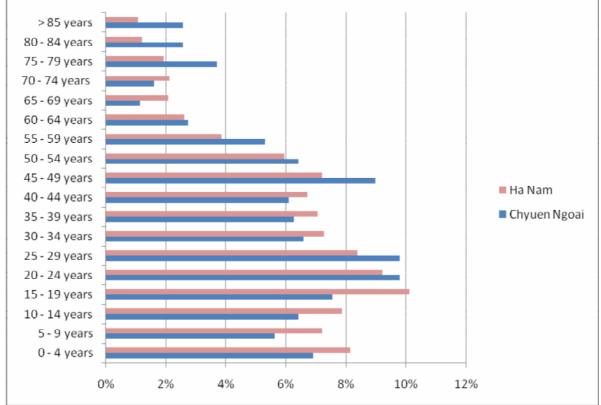


Fig. 2 Percentage of age groups in Chuyen Ngoai\* and rural areas of Ha Nam Province\*\*

\* Data for Chuyen Ngoai results from survey (N=150)

\*\* Data from Population and Housing Survey Vietnam 2009 (GSO 2010), percentages calculated from absolute numbers

#### 5. Arsenic contamination of tube-well water in Chuyen Ngoai

Survey data about socio-economic status, knowledge and awareness of the inhabitants has been complemented by data about the level of arsenic contamination in the tubewell water of the households. For each household a water sample has been taken before and after sand-filtering and was analysed by the Centre for Environmental Technology and Sustainable Development (CETASD) at Hanoi University of Science and Technology.

Arsenic concentration ranges between 8 and 579  $\mu$ g/l in the raw water and 0 to 163  $\mu$ g/l after filtering. Like in other villages where are arsenic levels have been monitored in Vietnam so far the concentrations vary spatially even within different hamlets. Figure 3 outlines the range of arsenic levels before and after filtering within and between the hamlets of Chuyen Ngoai.

The amount of arsenic should be reduced by sand-filtering. The efficacy of the sand-filter can be assessed by the reduction of the arsenic level before and after sand-filtering. In the mean the level is decreased to only 10 percent of the starting concentration. Independently from the concentration of arsenic in the raw water after filtering most of the samples (89,2%) show a level less than 50ppb, which has been the threshold value in Vietnam before 2002. However only every fifth households sticks to the current WHO threshold value of  $10\mu$ g/L, meaning that in spite of extensive use of filters many respondents are exposed to high arsenic levels over a longer period of time. The accumulation of arsenic in the human tissue is not

only influenced by the level of arsenic and absolute duration of the uptake but also by its continuity over the year. Thus the water use behavior during the year needs to be considered.

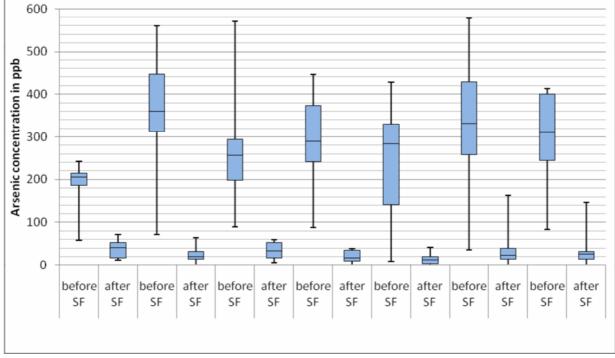


Fig. 3 Arsenic level in ppb before and after sand-filtering in hamlets of Chyuen Ngoai

The boxplot displays minimum and maximum values as well as quartiles. Data from survey (N=150)

5.1. Water use behavior – sources and treatment facilities

Although half of the respondents own a tank to store rainwater during the dry season only a minority of 12 households is using it all year round as the exclusive source for drinking water. Additional 51% of the village dwellers use their tube-well as well as rainwater for drinking whereas the remaining two fifth cover their water demand exclusively by their tube well.

Sources of drinking water	Ν	Percentage of households*
Rainwater	88	58,7%
Tube-well water	138	92,0%
Tube-well and rainwater	76	50,7%
Exclusively rainwater	12	8,0%
Exclusively tubewell	62	41,3%
Water treatment facilities	N	Percentage of households*
Tubewell	150	100,0%
Sand-filter	149	99,3%
Aeration unit	11	7,3%
Settling tank	23	15,3%
Other filter system	23	15,3%
- Korea King	16	10,7%
- Other	7	4,7%
Rainwater tank	77	51,3%
Total	150	

\*multiple answers possible Data from survey (N=150)

One result about the sources of drinking water and the used water treatment facilities is striking: almost all people (99%) in the sample are using sand-filters and maintain them quite regularly. Whether proper maintenance necessarily correlates with a good efficacy of the sand-filter has to be proved by analysis of water samples. Besides sand-filters half of the interviewed households own rainwater tanks and 15% even another filter-system. In some cases the sand-filter is coupled with an aeration unit (7%) or a settling tank (15%). Settling tanks remove arsenic by the principle of passive precipitation and sedimentation of iron(hydr)oxide particles. The removal rate is similar to those of the sand-filter (Luzi et al. 2004).

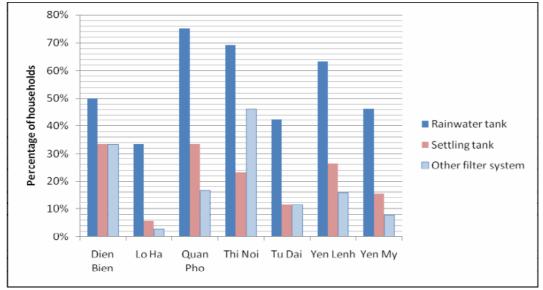


Fig. 4 Percentage of used water treatment by hamlets

5.2. Use of water sources during the year

Since other water sources like surface water from rivers or ponds, water from private or public taps is not available in Chuyen Ngoai the analysis focuses on tube well and rainwater. Besides the question whether people do have access to water resources and treatment facilities it is important to consider whether the household is able to provide enough safe water the whole year round for all members of the household. Half of the households use tube-well water all year round and only a minority of 20% less than six month a year. Drinking and cooking with rainwater is not an option which is available at any time of the year. Nevertheless about two fifth of the households are able to cover their water demand for at least six month and 15% even throughout the year. Furthermore the data from the survey does not reveal any correlation between the volume of rainwater tank which is available per person in a household and number of month in which tube well water is used for drinking and cooking. Additionally, the number of month in which the household members drink rainwater only weakly depends on the volume of the rainwater tank (r=0.236, p<0.05). Thus the volume of the tank seems not to be the limiting factor in rainwater storage and use.

Data from survey (N=150)

#### 5.3. Analysis of sand-filter use

The survey provides sufficient information for a detailed analysis of usability and efficacy of sand-filters because all households in the sample - except one use sand-filters. Usually sand-filters are constructed as two superimposed tanks made of brick and concrete. Whereas the upper tank contains the filter-material the water is stored in the underlying one (Luzi et al. 2004). Often a combination of different filter-materials like black or yellow sand, gravel or charcoal is used in the upper tank.

In the survey each respondent was asked about the material they use, the thickness of the layer in cm and the order of the material in the filter. People in Chuyen Ngoai mostly use black or yellow sand in their filter but the thickness of the material varies considerably. Every tenth filter only contains a thin layer of 20 cm or less but the majority of 62% puts a layer of 20 to 60 cm in the upper tank and the remaining quarter even up to over 100 cm. In sum the level of arsenic after sand-filtering in two of three cases decreases to less than 10 percent of the concentration in the raw water but the reduction rate neither correlates with the thickness of all layers together nor with the thickness of the sand layers in particular.

#### 5.4. Diffusion of water-related innovations

The installation of tube wells, sand-filters and rainwater tanks might be considered against the background of processes of innovation diffusion. "An innovation is an idea, practice or object perceived as new by an individual or other unit of adoption" (Rogers 2003: 36). Whereas this proves to be true for tube wells and sand-filters, rainwater might also be interpreted as a traditional source for drinking water which is perceived as advantageous in the light of unsafe tube well or surface water.

If the cumulated frequency of constructed facilities is displayed for each year it becomes obvious that the result does only very roughly resemble the typical S-shaped curve with a "period of relatively rapid adoption sandwiched between an early period of slow take up and a late period of slow approach to satiation" (Geroski 2000: 604) as often shown in diffusion studies. On the contrary the frequency distribution in figure 5 is characterized by several peaks for example in the years 1995/96, 2000 and 2004. This accumulation might point to some interventions to promote the use of tube wells and sand-filters. In three of four cases the sand-filter was constructed in parallel with the well. That is why constructors of tube well are turned out to be promising agents for sand filter diffusion.

Rainwater storage instead has been used by some households for over fifty years, long before the tube wells and sand filters began to spread in the village. Astonishingly the diffusion did not really speed up. In spite of a remarkably increase in the number of rainwater tanks installed in the last ten years satiation still seems not within sight although 99% of the households are endowed with tube wells and sand filters. Whether the newly discovered interest in rainwater storage results from an increased awareness about contaminated groundwater or could be traced back to some particular interventions requires additional information.

#### 5.5. Knowledge and awareness

Since knowledge and awareness are often considered as essential prerequisites to form an attitude towards an issue and thus evoke health preventive behavior it should be scrutinized how the issue of arsenic contamination is perceived by the respondents.

Although the inhabitants of Chuyen Ngoai use sand-filters and store rainwater, knowledge about arsenic contamination and other water related problems is astonishingly scarce – in particular against the background of high adoptions rates for sand-filters and the high level of arsenic in the tubewell water. Almost two thirds of the households state that they have heard about the problem of arsenic contamination and most of these respondents believe that arsenic affects health but only a minority knows in detail about the health consequences.

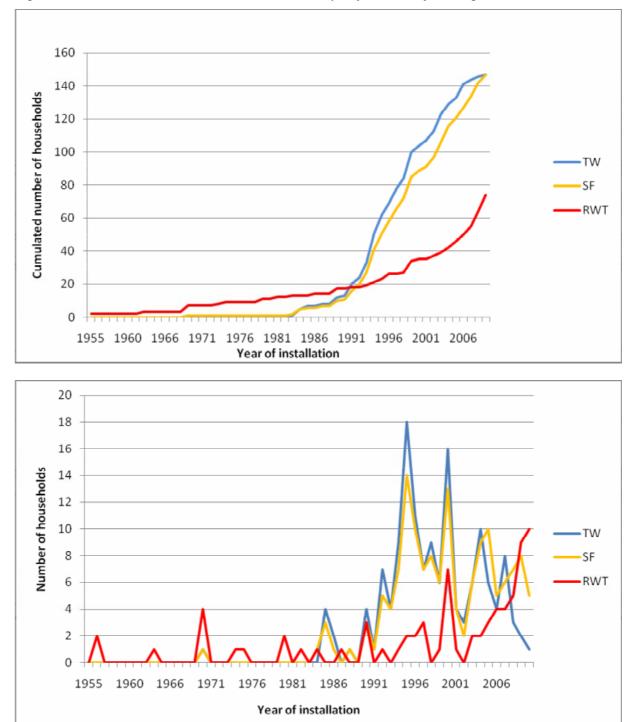


Fig.: 5 Number of installed TWs, SFs and RWTs per year in Chyuen Ngoai\*

\* TW = tube well SF = sand filter RWT= rainwater tank Data from survey (N=150)

On the contrary the results of the survey reveal that in the perception of the respondents for the majority there should be a need to engage themselves in arsenic mitigation measurements for several reasons:

- about half of the respondents believe that arsenic has an (negative) impact on health,
- half of the interviewees are worrying that their family might be affected by diseases due to arsenic contamination,
- 10% of the interviewed households even know people showing symptoms of arsenicosis,
- two fifth of the respondents think that their water is at least slightly contaminated by arsenic, additionally 13 per cent are not sure about the level of arsenic in their groundwater
- and some of the tube-wells in the village even have been tested before the survey and show elevated arsenic levels.

Detailed analysis to identify households which are in particular exposed to health consequences due to arsenic is still outstanding. Furthermore it will be scrutinized whether these households show similarities with reference to their social-economic status, level of knowledge, awareness or information and communication behavior. Additionally, first descriptive analysis about the location of households using different strategies for water treatment point to the fact, that the diffusion of filter technologies is influenced by social networks and learning.

#### 6. Conclusion

In general the survey re-enforces the assumption that the arsenic removal by sand-filters could rather be regarded as a fortunate side-effect than an intended decision for acquirement and use. The analysis of water-samples underscores that simple one step sand-filtering is not a sufficient method to provide safe water in accordance with the WHO threshold value. Two starting points for potential mitigation measurements can be identified: first, the construction of rainwater tanks and the promotion of this water source – a promising approach against the background of the positive attitude towards rainwater as source for drinking water – and second, efforts to raise awareness and knowledge about the health impact of arsenic contamination by transfer of in-depth information.

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#### Anhang 7: Projektbericht der vietnamesischen Partner

#### Project title:

### Assessment of arsenic in the food chain and on the development, optimisation and implementation of filter techniques to remove arsenic from contaminated groundwater in rural areas of the Red River Delta in Vietnam

#### **Duration:**

1/2009 - 12/2010

#### Vietnamese partner

Center for Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science (HUS)

Prof. Dr. Pham Hung Viet

#### Other personnels involving in the project:

Assoc.Prof. Le Van Cat	Institute of Chemistry, Vietnamese Academy for Science and Technology (VAST)
Dr. Dang Thi Minh Ngoc	National Institute of Environmental Health
Dr. Pham Thi Kim Trang	Center for Environmental Technology and Sustainable Devel- opment (CETASD), Hanoi University of Science (HUS)
MSc. Vi Thi Mai Lan	Center for Environmental Technology and Sustainable Devel- opment (CETASD), Hanoi University of Science (HUS)
Dr. Le Van Chieu	Center for Environmental Technology and Sustainable Devel- opment (CETASD), Hanoi University of Science (HUS)

#### I. Tasks have been implemented by Vietnamese partners

#### 1. Assessment of arsenic exposure from drinking water and foods

## \* Water and food sampling at arsenic contaminated site (study site) and nonexposed site (control site): April, 2009

Mai Dong village and Nghia Dan village were chosen for study and control sites, respectively. Both villages belong to Hung Yen, a flat provine locates by the Red river.

- Samples of raw groundwater (before sand filters), sand filtered water, drinking water (water after boiling), tea water and rain water were collected from 24 households in Mai dong village and 20 households in Nghia Dan village

- Vegetable and rice used for daily meal of households were sampled for the assessment of daily arsenic intake from foods.

## \* Analysis

- Arsenic contents in collected water and rice samples were analyzed by using HG-AAS at CETASD

- Other 24 elements in water samples were measured by ICP/MS at IMG (July 2009)

- Total arsenic concentrations in vegetable samples are being analyzed by ICP/MS at IMG (November 2010)

# 2. Assessment of the risk of chronic arsenic poisoning in by using bio- indicators (2009)

- Samples of hair, nail (finger and toe nails) and urine were taken from people of households at which water samples had been collected. There were 66 persons in Mai dong and 72 persons in Nghia Dan giving permission for taking their hair, nail and urine samples
- Implementation of interviews at households and each person who gave samples on water and food using habit

- The total arsenic concentrations in hair and nail samples were determined by using HG-AAS and ICP-MS, arsenic species in urine samples were measured by HPLC-ICP/MS

## 3. Assessment of human health risk of people exposed to arsenic (2009)

- Clinical health and neurological mental health checks were carried out on individuals giving human samples at both study and control sites.

# 4. Study on arsenic accumulation in vegetables/plants irrigated with arsenic contaminated groundwater

Vegetable, irrigation water and soil samples were taken from Binh Nghia village (Hanam province) where farmers have been using arsenic contaminated groundwater for irrigation of the crops, Van Noi village were chosen as the control site since groundwater used for irrigation has not been contaminated by arsenic (sampled in January 2010).

Samples have not been analyzed.

# 5. Development, optimisation and implementation of filter techniques to remove arsenic from groundwater in Mai dong

\* Application of some adsorbents based on iron and manganese for arsenic removal:

- Assessment of the efficiency of absorbents MF-97 (based on manganese) and NC-F20 (based on iron oxide) to remove arsenic from groundwater in Mai Dong

## \* Assessment of the efficiency of available sandfilters and and project's filter systems for arsenic removal (April – October 2010)

- 30 interviews were carried out with 30 households to get idea of their awareness of arsenic in drinking water and using and maintaince of sandfilters
- Groundwater samples before and after sand filter treatment from 26 households were collected in order to study the effects of other chemical compositions such as iron, phosphate, silicate on arsenic removal.
- 3 new filter systems were installed at 3 households with high arsenic contamination in groundwater and different levels of iron content (<5 >10 mg/L). This systems conclude an aerosol, a settling component, sand filter and a cartridge filled with GEH material which are expected to fully remove arsenic to meet the guideline of 10 µg/L of WHO and MOH Vietnam on arsenic in drinking water.
- 7 other households were chosen to install GEH cartridges after their available sandfilters in order to compare our project's system and available sandfilters at the village.

## **II. Building capacity**

- 2 workshops were held in Vietnam in November 2008 and April 2010 with the participation of scientists from Germany, Switzerland and Vietnam.
- A trip for Vietnamese partners for visiting German Institutions and participating the workshop held at IMG was organised in July 2009.
- A personnel from CETASD, HUS was appointed to take the mission of analysis of water, nail and vegetable samples at IMG, Karlsruhe Uni. in July, 2009 and November, 2010 and study the arsenic adsortion onto GEH materal at the Department of Water Quality Management, TU Berlin in August, 2009.

## Development and optimization of measures against the contamination of the food chain by arsenic from polluted groundwater resources in rural areas of the Red River Plain in Vietnam

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## Abstract

In Vietnam, the health of 10 million people living in rural areas of the Red River Delta (RRD) is acute endangered by Arsenic contaminated water. This calamity is caused by the establishment of numerous tube wells during the last century. These wells show arsenic concentrations from 100  $\mu$ g/L up to more than 400  $\mu$ g/L, which is far too high in regard to the WHO limit value of 10  $\mu$ g/L and in regard to the recommended daily human uptake of 2  $\mu$ g/kg body weight. The uptake of high arsenic amounts can cause general health problems such as black foot disease and cancer but a high incidence of mental diseases, too.

Many Vietnamese people already show symptoms and it will become more severe in the near future.

This project aims to investigate the various aspects of the uptake of Arsenic by human beings and the toxicological consequences as well as the development and establishment of adapted mitigation techniques and quality control methods. Therefore an interdisciplinary team was formed covering subjects from environmental medicine to water management and filter technology. In its first phase from 2008 to 2010, this program is funded as initial project<sup>1</sup> by the International Bureau of the German Ministry of Education and Research (BMBF), the German Research Foundation (DFG) and the Vietnamese Ministry of Science and Technology (MOST).

### Catchwords

Arsenic, food chain, toxicology, neurotoxicology, groundwater pollution, drinking water quality, filter techniques, mental disorder, Vietnam, Red River Delta

## 1 Background and Challenge

The contamination of groundwater with arsenic from geogenic sources is a severe problem throughout the world. Using this groundwater as drinking water can cause arsenicosis as already early reported from countries like Taiwan [1], Chile [2], Mexico [3] or Argentina [4]. These casualties have been known for a long time, but only a limited number of people were affected. Following the discovery of the arsenic calamity in the densely populated Bengal Delta [5] the topic came into the focus of the scientific world leading to intensive investigations. Other regions with elevated arsenic levels in groundwater have since been identified, primarily in relatively young alluvial deposits, such as the densely populated deltas of Mekong and Red River in Cambodia and Vietnam, where numerous tube wells have been established during the green revolution [6, 7, 8, 9, 10, 11].

In Vietnam, the health of 10 million people living in farms of the Red River Delta (RRD) is acute endangered by Arsenic contaminated water [6, 7, 11]. The release of Arsenic is caused by chemical redox processes in the underground from where the water is extracted. During the last decades, numerous new wells have been drilled resulting in an intensive use of groundwater for drinking and irrigation purposes (fig. 1). Those waters contain often more than 100 up to more than 400  $\mu$ g/L Arsenic. The current limiting value proposed by the WHO for drinking water is 10  $\mu$ g/L and for Arsenic uptake by food is 2  $\mu$ g/kg

<sup>&</sup>lt;sup>1</sup> Name of the initial project: VIGERAS - Initiation of a Vietnamese-German network of experts for the assessment of Arsenic in the food chain and on the development, optimisation and implementation of filter techniques to remove Arsenic from contaminated groundwater in rural areas of the Red River Delta, Vietnam.

bodyweight. Uptake of higher amounts of Arsenic by human beings causes illnesses such as skin cancer, black food disease and mental disorders. Many Vietnamese in the affected areas in the RRD show symptoms of those illnesses and many more will show those symptoms in future if no counter measures are taken. However, only little is known about the health effects on the neurological system [12] and of arsenic in levels of subtoxic concentrations, which could be manifested in mental disorders or an impaired development during childhood, e.g. of intelligence. Furthermore, arsenic toxicity can be influenced by genetic polymorphisms, nutrition and general environmental pollution. These are all factors still not sufficiently investigated.



Figure 1: left side – self made filter system at Van Phuc; right side – sewage pond at Maidong

A major pathway of Arsenic uptake by humans is by drinking water. Although in the affected areas self made filter systems using sand are sometimes established, they can not guarantee Arsenic free water. In the particular case of the shown filter system the resulting concentrations of Arsenic in drinking water are still more than twice the WHO threshold value [13]. These filter systems are made mainly to extract dissolved Iron from the groundwater. However, groundwater is also intensively used for the irrigation of rice and wheat fields, which are the main crops cultivated in that area. The volume of water used for the irrigation of a specific crop varies considerably depending not only on climatic factors, but also on the permeability of soil. The water demand of rice is particularly high [14]. Though the potential risk is evident, studies on the impact of irrigation with high Arsenic groundwater on soil and crop attracted some attention only during the last couple of years [15, 16, 17].

Over the years, various processes have been postulated in order to explain high arsenic concentrations in the aquifers and they are still subject of dispute. The reductive dissolution of different iron oxides, which are common in sedimentary environments, is widely accepted as a key process for the release of arsenic into groundwater [18, 19, 20, 21]. However, the reduction of iron oxides alone cannot explain the wide range of groundwater

arsenic concentrations encountered in similarly reducing aquifers [22]. What is clear is that the microbially driven decomposition of organic material plays an important role for the onset and the maintenance of reducing conditions in aquifers [23, 24, 25, 26]. A characteristic feature of Vietnamese villages in the Red River Delta are the numberless sewage ponds through which organic compounds enter environmental systems (fig. 1). Despite its importance, not enough is know about the nature and the origin of organic carbon [25]. Different sources of organic carbon have been proposed over the years: peat layers or confining sediment layers rich in total organic carbon (TOC) [24, 27, 28], recharge from ponds and rivers commonly high in dissolved organic carbon (DOC) and anthropogenic sources [19, 27, 29]. Further processes under discussion, which could have an influence on the arsenic concentration in groundwater are competition with other dissolved ions like phosphate [39] or bicarbonate [19, 31] oxidation of pyrite [32] or precipitation and dissolution of secondary mineral phases (e.g. siderite, magnetite, amorphous phases incorporating arsenic) [33, 34, 35]. It was also suggested that arsenic released in the surface soil by redox cycling could be transported downwards towards sandy aquifer [36].

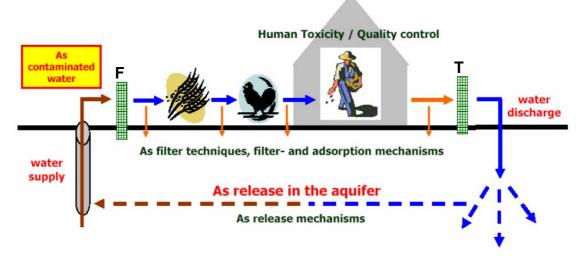
There is still much disagreement about underlying causes of the patchy arsenic distribution commonly observed in affected areas. Pronounced differences in arsenic levels can be found within distances of 100 m [37, 38, 39]. Recent studies in portions of the Red River Delta have also revealed significant differences even within short distances of 10 - 20 m [9]. Several explanations have been proposed for the complex spatial distribution of arsenic, including differences in the subsurface lithology, mineralogy, geochemistry, local hydrology, and the abundance of organic material [22, 40, 41]. Considerable uncertainty remains, however, and too little is known to predict with confidence how arsenic concentrations will evolve over time and to what extent aquifers currently providing potable water can be relied on in the future [42]. However, this patchy and till now not predictable distribution of high Arsenic concentrations in groundwater resources is highly endangering its usability as potable water and irrigation water by the rural population of Vietnam.

#### 2 Objectives

The overall aim of this program is to place clean and healthy water at the disposal for the rural population of the Red River Delta in Vietnam. From this, following project milestones can be defined:

• Comprehensive capacity building and scientific exchange in the various fields concerning arsenic contamination of water resources and food chain. Training of Vietnamese partners on assessing health consequences of Arsenic contamination of the food chain.

- Investigation of distribution processes of Arsenic in the environment, the food chain and in selected human tissue in dependency of different Arsenic concentrations in groundwater as depicted in figure 2. Identification of major transfer pathways of Arsenic from groundwater into the human body.
- Selection, development and establishment of optimized filter and treatment techniques (fig. 2) and adaptation of those techniques to the specific economic and cultural situation in Vietnam.
- Development and establishment of medical indicators for control of success of reduction of Arsenic exposition of human beings.
- Development and establishment of a sustainable water management system for the rural areas of the Red River Delta.



#### As flux through rural housholds

Figure 2: Arsenic flux through rural households of the Red River Delta, Vietnam. F is representing adapted filter systems for arsenic and T is representing a treatment system for waste water. The development of F and T are aims of the presented program.

The final results of this program shall be made available to the local population at a pilot farm in the rural region of the Red River Delta, where specific filter systems will be installed as demonstration projects, help in water supply issues will be offered and health support will be provided. This general concept is shown in figure 3.

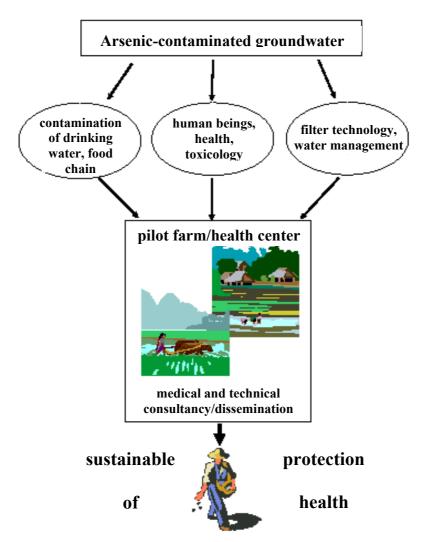


Figure 3: General project concept with the objective to establish a pilot farm where necessary information will be made available for the local population.

Figure 1 depicts the necessary technological inventions to filter (F) Arsenic from groundwater resources for various uses as irrigation and drinking water and to clean (T) the waste water to minimize the dispersion of dissolved organic carbon compounds, which have the potential to contribute to reducing conditions in the aquifer.

The results of this initial project will be compiled in a final report acting as basis for the design of the future program phases. The health centers of the rural villages in the Red River Delta shall be used for dissemination of the results. In future phases of the program, the local water authorities will be involved in the establishment of a water management system providing clean water for the population.

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## Anlagen auf CD

- Film des Eröffnungsworkshops
- Vorträge beteiligter Wissenschaftler
- Diplomarbeiten von Inga Boie und Eva Kellermeier
- Abschlussbericht