PRODUCTION SITE - WATER, SOIL - FOOD - RESIDENTS A CASE STUDY OF THE CRAFT SETTLEMENTS IN NAM DINH, VIETNAM

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ABSTRACT

Family manufactures and other small companies are the typical metal trading producers in the settlements of the province Nam Dinh (Vietnam). The average life expectancy is reported with about 65 years for Vietnam, but the administrative authorities draw for the craft settlements in Nam Dinh province an average life expectancy of less than 55 years, accompanied by a high rate of cancerous, neurotic and pulmontic deseases.

Geochemical investigations show hot pot-like high contents of heavy metals in soils (especially Cu, Pb, Zn), in sediments of watercourse (especially Cu, Pb, Zn, Cr, Mn, Cd) and in sediments of ponds (Cu, Pb, Zn up to 17200 mg/kg, Cr^{6+} up to 15400 mg/kg, Mn, Cd, Ni).

Especially the melter are exposed to dust aggregates (iron bearing ash spheres with a remarkable amount of a diameter < 2 μm; Al-grains with sharp edges, which could enhance inner injuries).

The crucial dimension of pollution´s feedback to the residents is reflected in plants (Cd, Pb, Zn), in hairs of employed inhabitants and in comparison to Hanoi residents (Cd, Cu, Pb, Zn).

The high contents of various heavy metals in the hair of inhabitant and in plants indicate the toxic dimension of pollution on people and on vegetables in the study area.

It is necessary to continue the investigation of pollution, especially in water, dust, plants and the hair of inhabitants, to determine the real toxic dimension of pollution, to recognize the most common path of pollutant and to design an in - situ system for the attenuation of pollution in this region.

Keywords: *Anthropogenic impacts, Clay minerals, Heavy metals, , Sediment, Soil, Pollution Pathway, Vietnam.*

INTRODUCTION

Nam Dinh is one of the most densely populated province in the Red River delta region (about 3000 - 4000 people per sq km in the craft oriented settlements). This trade-oriented district is an economical and political important territory for the North of Vietnam generally (economical index, degree of employment etc.). Family manufacturing and other small companies are the typical craft trading producers in the settlements of this administrative province.

The small family production without any treatment system has created various environmental effects such as sediment, water, and soil pollution. It also causes serious community health problems.

The average life expectancy for Vietnam is about 65 years of age, but for the settlements involved with the metal working trade, the average life expectancy is less than 55 years of age and is accompanied by a high degree of cancerous, neurotic, and pulmonic diseases.

The objective of the present work was to identify the contamination pathways concerning the metal production in the craft villages of Nam Dinh Province and the impact of the pollution on the community health in this region.

STUDY AREA

The Nam Dinh region is a part of the Red River delta with its characteristic alluvial landforms. It is situated ca. 100 km SE of Hanoi, on the right bank of the Red River. The study area is bound by the Song Dao in the West, by the Song Ninh Co in the East (both branches of the Red River) and by the Red River in the North.

The climate of the region is a humid tropical type. It is divided into four seasons: the spring is cold and wet, extends from February to April; the summer is warm with heavy rainfall and storms, and extends from May to August; the autumn is pleasant and dry, and extends from September to November; the winter is cold, and extends from December to January. June is the hottest month with temperature up to 39 ^{0}C and January is the coldest month with temperature under 15 ^{0}C. Usually 70 - 80 % of the total annual rainfall occurs during June, July and August. The intensity and the duration of the rainy season affect strongly on the mobilization of the pollutant in this region.

In the Province there are 71 traditional craft villages with different production branches. Most of workshops are loccated right at the living areas, yards or garden. The statistical data concerning raw material used in 9 villages with metal production (mechanic, casting, plating etc.) (Dao Huy Quy et al 2000).

METHODOLOGY

Sampling

Sediment samples were taken from the drainage networks and ponds of the settlements and the Van Chang River. The drainage structures and ponds in each settlement guided the sampling. Each sample was usually a mixture of materials, collected from 3-4 locations adjacent to each other. The samples were collected manually with the help of a plastic scraper and a plastic spatula from the uppermost 5-30 cm of the sediments of the river channels. They were dried at ambient room temperature and stored in the dark.

Soils samples were taken from areas adjacent to the settlement drains, from the Van Chang River channel and from family gardens in order to find out the contaminant pathway ′production-soil`. Additionally, soil samples were collected from some agricultural areas in which the flooding of wastewater occurs during heavy rainfall and in which farmers utilize wastewater for irrigation. Soil samples were collected with the help of a hand-boring machine. The depth of drilling was 1 meter. In each location 4 soil samples were taken: 0-25 cm *(sample a)* 25-50 cm *(sample b)*, 50-75 cm *(sample c)*, and 75 - 100 cm *(sample d)*. Sampling tools were washed and cleaned with water before the next sample was collected.

Plant and snail samples were collected and analyzed in order to find out the influence of the pollutants on the biological material. The plant samples are mixtures of different types plants that grow on the riverbanks and drainage banks and are used by the farmers as vegetables or as fodder. The plants were taken out with the root, washed with clean water, and dried immediately at ambient room temperature. Further more hair of inhabitants was collected and analyzed. Hair from inhabitants of Hanoi was used as control sample.

Sample Preparation and Analytical Techniques

After drying at ambient room temperature, the soil and sediment samples were sieved to obtain the < 2 mm fraction. The < 2 mm fraction was used for analysis. To determine the element distribution in the fine soil fraction, some selected samples were further separated into faction < 2μm by Attenberg sedimentation. This faction was used for analysis too. The analysis was carried out in laboratories at the Institute of Geological Sciences, Institute of Chemistry and Biochemistry and Institute of Hygiene and Environmental Medicine (Greifswald University) and at the Institute of Geological Sciences, Institute of Chemistry (National Center of Sciences and Technology, Hanoi).

The determination of pH values in soil and sediment was done after Lewandovski et.al., 1997. The suspension is prepared by addition from 12 g of material and 25 ml 0.01M $CaCl_2$-solution.

After intensive stir, the solution is already for pH- measurement. The moisture and the humus were estimated after Lewandovski et.al., 1997.
The soil and sediment samples were analyzed by ICP-AES and AAS after digestion by the Koernigswasser method. To control the accuracy of the analysis, one International Standard Sample *pacs - 1* was prepared and analyzed using the same procedure *(s.Tab.1)*.

Table 1. Accuracy of the analytical data with reference to certified values of the international Standard Reference sample pacs- 1 (SD standard deviation, RSD relative standard deviation)

Element	Concentration (mg/kg)		S.D.	±R.S.D. (%)
	Certified values	Measured values		
PO4		3230	64.1	1.92
S04		38555	112	0.29
As193	211	192	1.9	1.0
Zn		818	0.7	0.08
Pb220	404	384	3.0	0.8
Co228	17.5	18.6	0.2	1.1
Cd226	2.38	1.5	0.2	14.3
Ni231	44.1	36.6	0.4	1.0
Mn		366	2.4	0.6
Cr	113	75	0.59	0.79
Cu	452	427	2.07	0.48

RESULTS AND DISCUSSION

Assessement of Contamination Pathways: Production-Sediment-Soil

Metal Contents in Sediment

The mean concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in sediment are given in *Tab. 2*. All the sediment samples contain high values of Cd, Cr, Cu, Mn, Pb and Zn. The sediment samples from the Van Chang River show high concentrations (maximum values by sample LA44) of Zn (15 000 mg/kg), Ni (12 000 mg/kg), Cr (10 200 mg/kg), Pb (681 mg/kg), and Cd (6.6 mg/kg). The sediment sample from Dong Coi pond (LA23a) shows extremely high concentrations (maximum values) of Cr (15 440 mg/kg) and Zn (17 210 mg/kg). It is clear, that concentrations of heavy metals in lake and river sediments in the study areas are higher than the standard values of Holland (Denneman, CAJ and Robberse, JG 1993).

Metal Contents in Soil

The mean concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in soil are given in *Tab. 2*. Soil in the farmer garden (settlement Van Chang, samples *LA 14* and *LA 6*) contains the highest values of Cd, Cu, Mn, Pb and Zn: Cu (up to 490 mg/kg), Pb (up to 580 mg/kg), and Zn (up to 7 200 mg/kg). However, a vertical tendency of element distribution in soil samples (from sample a to sample d) cannot clearly be seen. The elements Co, Ni, and Cr do not increase in comparison to the local geological background. The concentrations of heavy metals in the soils of Dong Coi only lightly increase in comparison with the local background. The elements Co, Ni, and Cr do not increase. It is observed, that the concentrations of elements increase in the fine soil fraction *(Fig. 1)* due to the fact that the heavy metals tend to concentrate both within, and on the surface of soil particles. Hence, the fine fraction with expandable layers has larger contact surface area, which leads to the increase of metal sorption intensity (Scheffer&Schachtschabel, 1992).

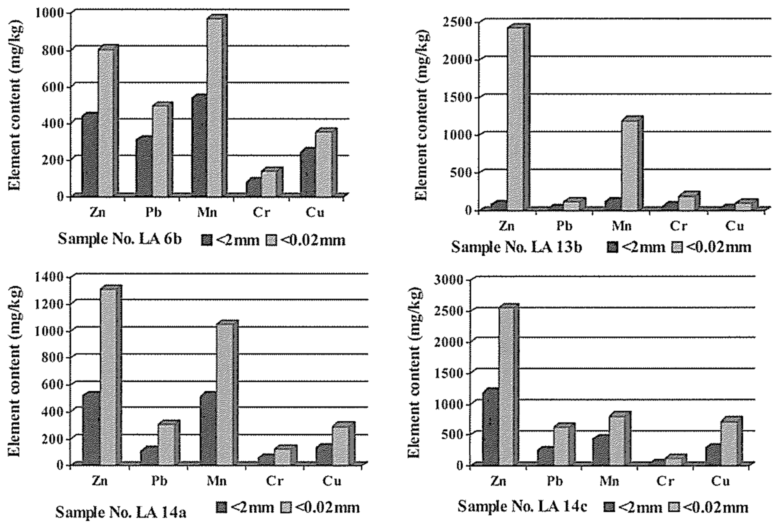

Fig. 1 Distribution of heavy metal in different soil fractions.

Metal Enrichment

To quantify the enrichment of heavy metals in soil and sediment through anthropogenic activity in the study area, enrichment factors were calculated after Ansari et al. 1999 for analyzed elements in relation to the local geological background values *(Tab. 2)*. It is shown that the sediments in the rivers, in the drains and in the lakes of Van Chang and Dong Coi are highly enriched with Cd, Cr, Cu, Ni, Mn, Pb and Zn in relation to the local geological background concentrations. The enrichment factors are 8.8 for Cd, 54.8 for Cr, 14 for Cu, 91 for Ni, 6 for Mn, 5.5 for Pb and 43.7 for Zn. The high enrichment factors for Ni, Cr, Zn, Pb, Cd and Cu indicate that the sediments in watercourses of the study area are heavily polluted with heavy metals. It is clearly, that untreated wastewater from metal manufacturing companies in the settlements of Dong Coi and Van Chang flowing directly in to the watercourses is the reason for this metal pollution.

The enrichment factors in soils are smaller than those in sediments. The soils of Van Chang are enriched by factors of 3-4 for Zn, Cu and Cd; 2.2 for Pb, and 1.5-1.1 for Ni and Mn. The soil of Dong Coi shows very low enrichment factors: 2 for Cu, 1.5 for Cd and 1.2-1.1 for Pb, Zn, Mn and Cr. These enrichment factors also show the dimension of the influence of wastewater on soil in Van Chang and Dong Coi.

Table 2. Mean concentration and enrichment factor of heavy metals in soil and sediment of the study area.

Soil VanChang n= 35	Zn	Pb	Cd	Co	Ni	Mn	Cr	Cu
Mean concentration	402	89	3	12	32	395	67	88
Geological local background	101	40	1	15	37	320	64	28
Enrichment factor	**4**	**2,2**	**3**	**<1**	**<1**	**1,2**	**1,**	**3,1**
Soil Dong Coi n=18								
Mean concentration	121	45	1,5	16	42	473	71	60
Geological local background	101	40	1	15	37	320	64	28
Enrichment factor	**1,2**	**1,1**	**1,5**	**1**	**1,1**	**1,5**	**1,1**	**2**
Sediment n= 11								
Mean concentration	4811	245	4,4	7	4210	1849	3946	431
Geological local background	110	45	0,5	15	47	309	72	31
Enrichment factor	**43,7**	**5,5**	**8,8**	**0.5**	**91**	**6**	**54,8**	**14**

The Pathway Production-Environment-Inhabitant

To determine pathway production-environment-inhabitant, plant, water snail and hair samples were collected and analyzed. The plant samples were digested at the Institute of Hygiene and Environmental Medicine by the temperature-pressure-digestion method using microwave model MDS-2000, and were estimated of heavy metals by ICP-AES and AAS at the Institute of Geological Sciences (Greifswald University). The snail shells were prepared at the institute of Chemistry and Biochemistry, Greifswald university, Germany. The results are given in *Tab. 3a* and *Tab. 3b*. and Tab. 3c.

Table 3a. Heavy metal contents in the snail samples

Sample No	Element concentration (mg/kg d.m)			
	Cu	Pb	Cd	Zn
LA SC1	9.14	1.04	0.038	8.30
LA SC2	15.32	0.86	0.049	13.75
LA SC3	16.72	0.61	0.030	10.80
LA SC4	9.36	0.99	0.087	15.18
LA SC5	11.92	0.59	0.026	26.18
LA SC6	20.61	1.43	0.020	9.72
LA SC7	11.81	0.80	0.010	17.23

Table 3b. Heavy metal concentrations in plants in the study area (mg/kg d. m.).

Plant samples	P2O5	S	Zn	Cd	Ni	Mn	Cr	Cu
LA4f	7237	3312	146	300	<5	42	<5	12
LA8f	5962	11110	107	5	<5	40	<5	18
LA10f	5197	4579	90	<1	12	473	57	44
LA11f	7102	2874	52	<1	<5	48	<5	10
Norm values for fodder*			**3,5-50**	**1,0**	**0,1-2,7**	**300**	**0,02-14**	**5-20**

Table 3c. Heavy metal concentration in hair of inhabitants in the study area (mg/kg d. m.)

Hair samples	P205	S	Zn	Pb	Cd	Co	Ni	Mn	Cr	Cu
LA25 Hvc	990	43351	282	70	2	<5	9	81	15	36
LA26 Hhn	788	46607	245	(4)	<1	<5	<5	42	(0,7)	12
Children < 12 years n=5				2.50	0.25					8.70
Worker 30-50 years n=13				17.00	1.20					18.50
Old people >70 years n=3				3.00	0.50					9.10
Normal values**			**150-250**					**4**	**1**	**15-25**

* In Lebensmittelrichtwerten (ZEBS 1990) und Grenzwerten der uttermittelverordnung (Futtermittel VO 1988)

** In Seeger 1993

Data for snail samples show a total concentration range of 9.14 - 20.61 mg/kg d.m for Cu; 0.59 - 1.43 mg/kg d.m for Pb; 0.020 - 0.087 mg/kg for Cd and 9.72-26.18 mg/kg for Zn. The general trend of the mean concentration of trace elements in the shell materials of snail is

Zn>Cu>Pb>Cd (Tab. 3a). After a investigation of Giusti and Hao Zhang (2002) the most trace elements are more enriched in the soft tissue than in the hard part of the mussels they analyzed. It is shown that some plant samples *(LA 4f* and *LA 8f)* contain high values of Cd and other heavy metals like Cu and Zn (Tab. 2b). These samples were collected on the bank of a lake NE of the Van Chang settlement and on the bank of the Van Chang river, where waste water flows in directly. It may be considered that waste water influences the heavy metal concentrations in these plants.

The digestion of hair samples was done at the Institute of Hygiene and Environmental Medicine and at the Institute of Chemistry and Biochemistry (Greifswald University). The estimation of heavy metals was done by ICP-AES and AAS at the Institute of Geological Sciences too (Greifswald University). Additionally, to recognize any external influence like dust on the analytical results, each hair sample was divided into three parts and was prepared by three different procedures before digestion: (1) without any further treatment; (2) washing with distillated water and (3) washing with triton X-100. No strong tendency in the difference of the analytical results was noticed. The average heavy metal values in the inhabitant hair are given in Tab.3c.

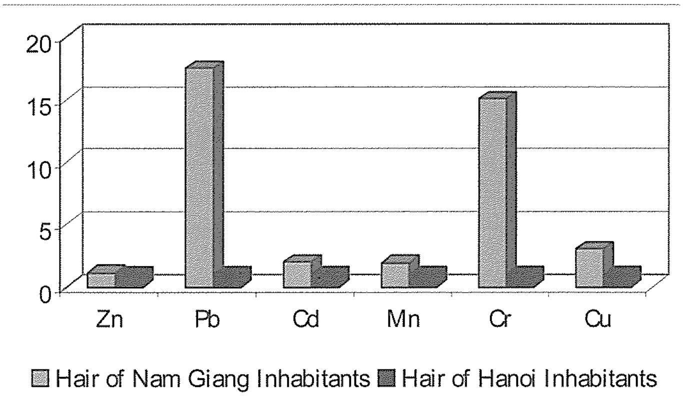

Figure 2: Heavy metal concentrations in the hairs of Van Chang inhabitants in relation to the heavy metal concentrations in the hair of Hanoi inhabitants.

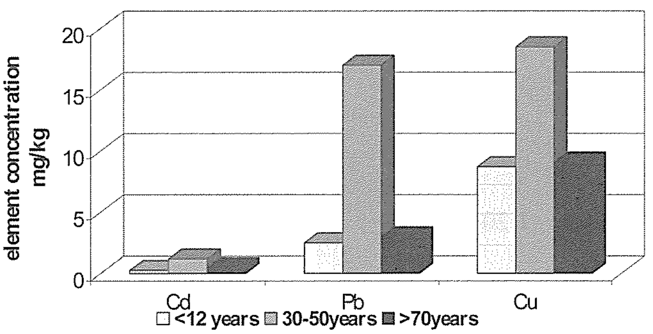

Figure 3: Heavy metal concentrations in various groups of people.

It is consider, hair is an elimination path and also storage place for many metals in our body. That means, when a metal elimination in hair is realized, than a great amount of these metals is available in the body. High concentrations of metals in hair are an indication that large amounts of these metals are in the body. This is the case of the inhabitants of Van Chang. In Fig. 2 the heavy metal concentrations in the hair of inhabitants of Van Chang is compared to the heavy metal concentrations of inhabitants of Hanoi. It is clear, that the concentrations of metal in the hair of inhabitants of Van Chang are higher than that in the hair of inhabitants of Hanoi. *Fig. 3* shows the concentrations of metal in the hair of three groups of people in this metal working settlement: (1) Children of under 12 years of age, (2) worker between 30 and 50 years of age and people of over 70 years of age. It is clearly to recognize, that the people, whose have direct contact with metal manufacturing work are the ones most affected by heavy metals.

CONCLUSION

The present data document the intensive impact of the metal manufacturing on soil and sediment in the watercourses of Van Chang and Dong Coi. High percentages values of anthropogenic input and high enrichment factors of various heavy metals in sediment and soil indicate that the study area is highly polluted by heavy metals.

The high content of various heavy metals in the hair of inhabitants and in plants indicates the toxic dimension of pollution on people and on vegetables of the study area.

It is necessary to continue the investigation of pollution especially in water, dust, plants, and in the hair of inhabitants, to determine the real toxic dimension of pollution, to recognize the most common pollutant path and also to design an in - situ system for the attenuation of pollution in this region.

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References

1. Ansari A.A., Sigh I.B., Tobschall, H.-J. (1999) Status of anthropogenically induced metal pollution in the Kanpur-Unnao industrial region of the Ganga Plain, India. *Envir Geol* 38, 25-33
2. Bailly F, Gieske M, Kleinwort S, Wolf N (1993) Kupfer, Blei, Zink und Cadmium in Auenboeden der Duete und der Hase im suedlichen Landkreis Osnabrueck. Osnabrueck *Naturwiss. Mitt* 19, 167-182
3. Eikmann T, Kloke A (1993) Eikmann-Kloke-Werte Teil 6/4.1.3. Seite 1-21. Januar 1997, http://www.uni-duesseldorf.de/AWMF/II/cadmium.htm
4. Kloke A, Koenig W, Miehlich G, Prueess A, Sauerbeck D, Wiesner J (?) Entscheidung zur Bewertung von Arsen, Blei und Cadmium in Boeden von Ballungsgebieten. Resuemee der *DECHEMA-Arbeitsgruppe "Bewertung von Gefaehrdungspotentialen im Bodenschutz"*
5. *Leitlinien der DGAUM*: Arbeiten unter Einwirkung von Cadmium.
6. Neue Holland-Lisie, In: Dennemann CAJ, Robberse JG (1993) Boden Standards im Rahmen des Niederlandischen Bodenschutzes. Dtsch. Uebersetzung in Rosenkranz, Einsele, Harress: *Handbuch Bodenschutz,* 13 Lfg. VI/93, Nr. 0480, 27S, 2 Tab, Berlin (Schmidt), Paragraph 6/4.1.1.1
7. Scheffer F. , Schachtschabel P. (1992) Lehrbuch der Bodenkunde. *Ferdinand Enke Verlag*, Stuttgart
8. Ricking M, Terytze (1999) Trace metals and organic compounds in sediments samples from the River Danube in Russe and Lake Srebarna (Bulgaria). *Envir Geol* 37, 40-46
9. Seeger R. (1988) Seeger/Neuman *Giftlexikon*
10. *ZEBS* (Zentrale Erfassungs- und Bewertungsstelle fuer Umweltchemaikalien des Bundesgesundheitsamtes) (1990) Blei und Cadmium in Pflanzen. http://www.sensut.berlin.de/UISonline/dua96html/11033.htm