



CONTAMINATED SITES AND THEIR MANAGEMENT

Case studies: Kazakhstan and Armenia



The European Union's Non-State Actors in
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CONTENT

General Introduction.....	9	5. Sampling procedures and analytical methods.....	47
1. Introduction.....	10	6. Results.....	48
2. Acknowledgements.....	12	7. Discussion.....	53
3. References.....	12	8. Evaluation of pollutant levels.....	56
4. Abbreviations.....	13	9. Health risk assessment.....	59
Pesticide monitoring in Armenia.....	15	10. Conclusions.....	62
1. Introduction.....	16	11. References.....	63
2. Methodology of sampling and sample analysis.....	16	Identification and Management of mercury, PCB and dioxin	
3. Visited localities.....	17	contaminated sites in Kazakhstan: A Collective Impact approach	
4. Annexes.....	22	to civil society engagement.....	67
Yeraskh, Armenia – site contaminated by POPs.....	31	1. Introduction.....	68
1. Introduction.....	32	2. Kazakhstan: Steps to ratification of the Minamata Convention on Mercury.....	71
2. Sampling and analytical methods.....	32	3. Site identification and Characterisation- What is a mercury contaminated site?...73	
3. Results.....	34	4. Site identification and preliminary screening: A role for NGOs.....	77
4. Conclusions.....	36	5. Risk Assessment.....	81
5. References.....	36	6. Contaminated Sites: Management and Remediation Approaches.....	83
6. Photos from the site.....	37	7. Remediation technology.....	87
Results of environmental sampling in Kazakhstan:		8. Dioxin and PCB contamination remediation.....	96
mercury, methylmercury, PCBs and OCPs contamination of the		9. Occupational and Community Safety and Health Management for	
River Nura.....	39	Contaminated Sites.....	100
1. Introduction.....	40	10. Kazakhstan contaminated sites – case studies.....	104
2. Contamination of River Nura.....	40	11. Community engagement on contaminated sites: Empowering civil Society through	
3. River Nura Clean-Up Project.....	41	information sharing and raising awareness.....	111
4. Sampling sites.....	42	12. References and bibliography.....	116

General Introduction

Arnika – Toxics and Waste Programme, Prague, 2015

Karaganda Regional Ecological Museum (EcoMuseum) and Center for Introduction of New Environmentally Sound Technologies (CINEST), Karaganda, 2015

1. INTRODUCTION

Toxic legacy of the past use of chemicals such, as polychlorinated biphenyls (PCBs) or pesticides like DDT or lindane (gamma-HCH) belonging to the family of persistent organic pollutants (POPs), is a common problem of many post-Soviet countries, including those presented in this publication: Kazakhstan and Armenia. Sites with abandoned chemical production of chlorine or acetaldehyde present another example of complex contamination by both mercury and POPs. The Czech NGO Arnika, as part of international network IPEN (International POPs Elimination Network), is trying to help NGOs and both local and national authorities to find out how serious the contamination of such sites is, as well as to find more complex solutions to contamination.

This publication provides case studies based on the results of two projects funded by the European Commission through its EU Aid programmes: “Scaling Up Experience in Improvement of Chemical Safety to Contribute to Poverty Reduction in Rural Armenia” and “Empowering the civil society in Kazakhstan in improvement of chemical safety”. Arnika, as a lead organization, cooperated with Armenian Women for

Health and Healthy Environment (AWHHE) in mapping problems in Armenia, and with two NGOs, the Karaganda Regional Ecological Museum (EcoMuseum) and the Center for Introduction of New Environmentally Safe Technologies (CINEST), on the second project in Kazakhstan. We decided to include case studies from both countries in this publication called “Contaminated sites and their management” as they represent a wide range of problems with contaminated sites in the CEE and EECCA region as defined by the UN.

Case studies from Armenia and Kazakhstan demonstrate different sites contaminated by organochlorinated pesticides (OCPs), mercury, PCBs and dioxins (PCDD/Fs) and summarize the work done during sampling of these sites in both countries (in 2010–2011 in Armenia and in 2013–2014 in Kazakhstan). We didn’t want to only raise the problems but also to develop some guidance on how it can be possible to address contaminated sites in a more systematic way. We also wanted to bring this guidance because international bodies, like for example INCs to Minamata Convention on mer-

cury, have so far failed to come up with some guidance for governments on how to deal with the problem of contaminated sites. We believe that part of this publication called “Identification and Management of mercury, PCB and dioxin contaminated sites in Kazakhstan: A Collective Impact approach to civil society engagement” can serve not only to CSOs, national and local authorities in Kazakhstan but in many developing countries and countries with economies in transition a facing toxic legacy of contaminated sites.

Results of environmental sampling in a vicinity of the river Nura presented in this publication are complemented by the results presented in a series of studies in the publication “Toxic Hot Spots in Kazakhstan”, where more information can be found about another contaminated site in Kazakhstan, an abandoned electrical power substation in

Ekibastuz, one of the sites with serious contamination by PCBs in Kazakhstan (Arnika, EcoMuseum et al. 2015). A case study on obsolete pesticides sites in Armenia has already been published by Arnika – “Toxics and Waste Programme” in 2011 (Arnika and AWHHE 2011) with exemption of the brief evaluation of sampling in Yeraskh.

We believe that the work presented in the following reports will contribute to implementing both the Stockholm Convention and Minamata Convention in Kazakhstan and will serve as a pilot study for the work in other countries as well. We thank all the donors for their financial support, the European Commission in particular and the International POPs Elimination Network (IPEN) for its support regarding expertise and continuous work on POPs and mercury.

Prague, April – 25, 2015

Jindrich Petrlik, Executive Director

Arnika – Toxics and Waste Programme

on behalf of the joint Arnika – EcoMusuem – CINEST project team

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ple helping us to put this publication together, and let us namely thank at least some of them: Martin Skalský – coordinator of the project on behalf of Arnika, Alena Pankova – coordinator of the project on behalf of CINEST and EcoMuseum, Dimitry Kalmykov, director of the EcoMuseum who provided very valuable information and scientific advises to the team, Martina Blažkova, assistant of Arnika – Toxics and Waste Programme, Ondřej Petrlík – graphic designer, and Mark Sixsmith, B.Sc. – Director of Environmental English who helped us to keep this publication in understandable English.

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4. ABBREVIATIONS

AAC – Approximately allowed concentrations (Ориентировочно-допустимая концентрация (уровень))

ADI – Acceptable Daily Intake

AMA – Advanced Mercury Analyser

APC – air pollution control

ASGM – Artisanal and Small-scale Gold Mining

BCD – Base Catalyzed Decomposition

BDS – BioDetection Systems (laboratory in Netherlands)

BEQ – bioanalytical equivalent

CALUX – Chemically Activated Luciferase Gene Expression

CAS – Chemical Abstracts Service Registry Number (a unique numerical identifier assigned to every chemical substance described in the open scientific literature)

CDI - Chronic Daily Intake

CEE – Central and Eastern Europe

CINEST – Center for Introduction of New Environmentally Safe Technologies

CSM – Conceptual Site Model

CSOs – civil society organizations

DDD – dichlorodiphenyldichloroethane (a metabolite of DDT)

DDE – dichlorodiphenyldichloroethylene (a chemical compound formed by the loss of hydrogen chloride from DDT)

DDT – dichlorodiphenyltrichloroethane (pesticide)

DE – Destruction Efficiency

DL PCBs – dioxin-like PCBs

DRE – Destruction and Removal Efficiency

DSI – Detailed Site Investigation

d.w. – dry weight

EECCA – Eastern Europe, Caucasus and Central Asia Region

ELCR – Excess Lifetime Cancer Risk

EU – European Union

GC – gas chromatography

GEF – Global Environment Facility

GoK – Government of Kazakhstan

GPC – gel permeation chromatography

GPCR – Gas Phase Chemical Reduction

GPS – Global Positioning System

HCB – hexachlorobenzene

HCHs – hexachlorocyclohexanes (pesticides and their metabolites)

HQ – a hazard quotient

HRGC-HRMS – high resolution gas chromatography – high resolution mass spectroscopy

IARC – International Agency for Research on Cancer

INC – Intergovernmental Negotiating Committee (normally set up for negotiations of new international convention)

IPEN – International POPs Elimination Network

IQ – intelligence quotient

LADD – Lifetime Average Daily Dose

LOAEL – Lowest Observed Adverse Effect Level

LOD – limit of detection

LOQ – limit of quantification

MAC – maximum acceptable (allowable) concentration

MF – Modifying Factors

MIA - Minamata Initial Assessment

ML – maximum level

MRL – maximum residue level

NA – not analyzed

NEPC – National Environmental Protection Council

NIA – National Interest Analysis

NGO – non-governmental organization (civil society organization)

NIP – National Implementation Plan

NOAEL – No Observed Adverse Effect Level

OCPs – organochlorinated pesticides

OCE – odour control enclosure

PAHs – polycyclic aromatic hydrocarbons

PCBs – polychlorinated biphenyls

PCDD/Fs – polychlorinated dibenzo-p-dioxins and furans

PCDDs – polychlorinated dibenzo-p-dioxins

PCDFs – polychlorinated furans

POPs – persistent organic pollutants

PPE – Personal Protective Equipment

PSI – Preliminary Site Investigation

QA/QC – Quality Assurance and Quality Control

RA – Risk Assessment

RAP – Remediation Action Plan

RfD – Reference Dose

RIS – Regulatory Impact Statement

RISC – Risk-Integrated Software for Cleanups

RSL – Regional Screening Levels

S/S – stabilisation and solidification

SC – Stockholm Convention on Persistent Organic Pollutants

SF – Slope Factor

SOP – standard operating procedures

SPSS – sulphur polymer stabilization/solidification

TEF – toxic equivalency factor(-s)

TEQ – toxic equivalent

UF – Uncertainty Factors

UNDP – United Nations Development Programme

UNECE – United Nations Economic Commission for Europe

UNEP – United Nations Environment Programme

UNIDO – United Nations Industrial Development Organization

UNITAR – United Nations Institute for Training and Research

US EPA – United States Environmental Protection Agency

UXOs – unexploded ordinance

WHO-TEQ – Toxic equivalent defined by WHO experts panel in 2005

w.w. – wet weight

XRF – X-Ray Fluorescence Analyser

Pesticide monitoring in Armenia

visit of the surroundings of Yerevan, Echmiadzin and Alaverdi, July 22–28, 2010. Final report

Ing. Zuzana Honzajková, Ing. Marek Šír

University of Chemistry and Technology, Prague, November 2010

1. INTRODUCTION

In cooperation with the Czech non-profit organisation Arnika, we visited Armenia in July 2010. The purpose of our visit was monitoring of pesticide contamination in selected localities. In Armenia, the mission was prepared and organised by a local non-governmental organisation Armenian Woman for Health & Healthy Environment (AWHHE).

Our team visited in total four localities where pesticides were present. These localities were, in particular, storages serving for pesticide distribution and storing in the

past. The localities included one dumping site of pesticide residues and wastes contaminated by pesticides, which is partially secured at present. Further, we visited a disposal site of wastes from a metallurgical plant processing copper ore.

The present report comprises detailed description of the visited localities and taken samples. Preliminary conclusions concerning the nature of contamination and possible risks ensuing from it are presented for each of the localities. An annex to the report states results of analyses of all the taken samples, and comparison with pollution criteria.

2. METHODOLOGY OF SAMPLING AND SAMPLE ANALYSIS

Several samples were taken in each of the localities. Mostly, mixed samples were taken, formed by several partial samples taken in various places of the given locality. We always endeavoured to take a sample representing the given whole to the maximum possible level. Systematic sampling, including depth profiles, was carried out in one of the localities. The samples were taken by means of a shovel into plastic sample containers with screw lids. Soil samples were stored at room temperature, water samples were stored in a refrigerator in the dark. The number and description of the taken samples is stated below in the parts of the text concerning the individual localities.

Sample analysis were carried out in laboratories of the University of Chemistry and Technology, Prague. For the analysis, there was used an efficient method, verified in the long term, of extraction by hexane in ultrasound, and subsequent analysis of the extract by gas chromatography.

In the laboratory, sample homogenization was carried out at first. Subsequently, a representative part of the sample was taken for analysis, specifically, 2.5 g of the sample. The sample was placed, together with 10 ml of hexane, into an extraction bottle, and extracted in ultrasound water bath for the period of 20 minutes. Subsequently, the extract was analysed by means of a gas chromatograph with ECD detector. Results of analyses of all the samples are presented in tables in an annex in the end of this report.

3. VISITED LOCALITIES

Our aim was to monitor occurrence of pesticides in four localities in the vicinity of Yerevan. The localities were places contaminated by pesticides because of the former activities (dumping site, storages, sale places). Further, heavy metals contamination was monitored in the neighbourhood of the disposal site of waste from a metallurgical plant in the vicinity of the city Alaverdi.

3.1 Nubarashen

Sampling date: July 23, 2010, July 26, 2010

The dumping site is located cca 20 km from Yerevan, the capital of Armenia, cca 1 kilometre from the closest residential houses. It served for disposal of pesticide resi-

dues and wastes contaminated by pesticides. Unfortunately, the dumping site is located on a hill, and, thus, rainwater and leachate from the dumping site flow down in the direction of the close, lower situated, residential houses. At present, the dumping site is sealed and fenced, the territory under the dumping site is accessible, covered by grass and shrubs, marks of livestock grazing are visible there.

3.1.1 Samples taken

In this locality, the territory under the dumping site was sampled systematically. The places of sampling are depicted in Figure 1. There were taken 9 samples from the surface, and three samples from each of the three profiles parallel with the lower base of

the dumping site. During taking of surface samples (samples N1–N9), soil overburden was removed at first. Subsequently, cca 250 g of soil was taken by means of a shovel, from the depth of at most 5 cm. In the places designated N1, N4 and N7 in Figure 1, in total 8 depth samples were taken from drill holes in the profile vertical to the lower base of the dumping site. The samples were taken from the depth 0.5 m, 1 m and 1.5 m. Manual drilling equipment with Edelman drill was used for the sampling. Sample of 250 g was taken from each of the depth profiles.

3.1.2 Results and risk assessment

In the surface samples, pesticide concentrations were found reaching hundreds of milligrams to units of grams per a kilogram of soil. Especially 4,4'-DDT, 2,4'-DDT, 4,4'-DDE, alpha-HCH, and beta-HCH were found. In the vicinity of the dumping site, high pesticide contamination was found also in the whole depth profile, in the order of hundreds mg of DDT per kg of soil, even in the depth of 1.5 m under the surface.

From these results, it is obvious that massive pesticide releases from the body of the dumping site were taking place in the past. Under the dumping site, a channel is visible through which water flows off the dumping site during rain periods. In this channel, the highest levels of pesticide concentrations were found (samples N1, N4, and N7).

The spreading contamination in the surroundings of the dumping site represents considerable risk for the environment and people living in the vicinity. It is also very likely that pesticides enter the food chain, because marks of livestock grazing were found in close vicinity of the dumping site where also the highest DDT concentrations were detected.

Covering and fencing the dumping site partially prevented direct exposure of people and livestock, but spreading into the environment could still continue. Thus, sealing the dumping site does not represent a solution of the problem. It will be necessary to decontaminate the whole territory of the dumping site, in order to prevent possible risks.



Figure 1: Places where surface samples were taken under the Nubarashen dumping site.

Author: Z. Honzajková

3.2 Echmiadzin

Sampling date: July 24, 2010

In this locality, 2 storages are located where fertilizers and pesticides were handled. In close vicinity of the storages, vegetable patches are found, and small ponds for trout breeding are located cca 30 metres from the storages. The storages form part of a local farm where people live permanently, and which is located also in close vicinity of the storages.

The storages had been partially cleared already, however, pesticide residues were noticeable on floors and shelves. The presence of pesticide residues was proved also by strong smell. In close vicinity of one of the storages, there was a patch where local people grew vegetables.

3.2.1 Samples taken

In total, 5 samples were taken. In each of the both storages, one mixed sample of the material swept from the floor was taken, and, further, there was taken one mixed sam-

ple of the soil from the patches in the vicinity of the storage, a sample of sediment from an empty pond for trout breeding, and a sample of water from another breeding pond.

3.2.2 Results and risk assessment

In the material swept from the floors of the storages, high HCH and DDT concentrations were found, in the order of up to hundreds mg kg⁻¹. In the surrounding soil and water, increased concentrations of HCH and DDT and its derivatives were also detected, in comparison with the background levels. Pesticide contamination was not proved in water from the pond. Lack of information of the local inhabitants on the hazardous properties of these substances represents the highest risk. They handle the material deposited in the storages without any protective equipment. The first storage had been swept recently. The pesticides may enter the surrounding environment also through this handling. There exists a risk of contamination of agricultural soil and crops, and contamination of breeding ponds, with the possibility of accumulation of these hazardous substances in fish meat. A further risk is pesticide accumulation in eggs of hens bred there.



Figure 2: First storage, closest to the vegetable patches, near Echmiadzin. *Author: M. Šir*

3.3 Masis, Berriutyun LTD Masis

Sampling date: July 26, 2010

The locality is used for handling of fertilizers. A big storage with corresponding facilities and railway siding is present here. At present, the storage is still used for storing fertilizers. Two small storages, where pesticides and fertilizers were handled, are located next to the big storage used up to now. The first of the small storages is a ruined building without roof, freely accessible. In this room, bags and barrels with pesticides and fertilizers are present. The barrels are rusted through, and the bags are torn. Thus, their content is spilled loosely on the floor. The room does not have a roof, and, thus, these wastes are exposed to rain and weather influences.

The second of the small storages is formed by two rooms, and it is generally secured. In the past, this place served for sale of pesticides and fertilizers, the rooms are partially cleared, pesticide and fertilizer residues are spilled on the floor (see Figure 4). In the both rooms, strong pesticide smell was noticeable.



Figure 3: Storage serving for storing fertilizers in the locality Masis. *Author: M. Šir*

3.3.1 Samples taken

In total, 5 samples were taken in this locality. A mixed sample from the bags, and another one from the floor, were taken in the first storage. A mixed sample of the material swept from the floor was taken in the second storage. Further, there were taken a mixed sample of plasters from the both storages, and a mixed sample of soils in close vicinity of the storages, cca 10 metres from the storages.

3.3.2 Results and risk assessment

In the samples from the storages, alpha-HCH, beta-HCH and gamma-HCH is found predominantly, in concentrations up to the order of units g kg^{-1} . Plasters from the storages are contaminated predominantly by beta-HCH and 4,4'-DDT. In the vicinity of the storages, increased concentrations of DDT and DDE were found. Thus, the analyses confirmed that pesticides were present in the both small storages in high concentrations.

The situation presents risks mainly for the employees working in the locality. In the first, freely accessible, room with the pesticides, cigarette ends were found on the floor, originating, with the highest likeliness, from the employees. They move here without any protective equipment, and this presents a huge health risk for them. Contamination of the stored fertilizers, and of landscape in the vicinity, represents another risk.

3.4 Jرات

Sampling date: July 24 and July 26, 2010

A big storage of fertilizers, serving also as a pesticide storage in the past, is found in the locality. The storage is locked, and accessible only with consent of the owner. Pesticide residues in barrels, and fertilizers in bags, are found in the storage. Further, ruins of a small storage, without a roof, are found in the locality. The small storage is filled with barrels and bags with fertilizers and pesticides. A railway siding, which served for handling of fertilizers and pesticides, is located close to the storages. Further, a pond for trout breeding is found cca 50 m from the small storage.



Figure 5: Interior of the building of the big storage in Jرات. Author: Z. Honzajková



Figure 6: Ruins of the small storage where torn bags with crude DDT were found in Jرات. Author: M. Šir



Figure 7: View of a part of the small storage, with barrels containing waste contaminated with DDT. Author: M. Šir

3.4.1 Samples taken

In total, 8 samples of solid substances were taken in this locality. There were taken 3 mixed samples of the material swept from the floor, and plaster, in the big storage, and, further, 2 samples in the small storage, samples of soils in the vicinity of the big storage and of the small one, and, finally, water from the breeding pond located nearby.

3.4.2 Results and risk assessment

Results of analyses proved that the powder in the torn bags in the ruined storage is essentially a raw pesticide DDT. The sample contained in total 647 g of pesticides per kg, majority of them was formed by 4.4-DDT (515 g kg^{-1}), and 2.4-DDT (100 g kg^{-1}). Further, the sample contained by-products and decomposition products of DDT, including predominantly DDD and DDE, the toxicity of which is similarly high as in the case of DDT. The estimated stored amount is in the order of hundreds of kilograms.

The rusted-through barrels contain wastes contaminated by DDT. The fertilizers stored in the big storage come in contact with spilled pesticide residues, and with raw pesticides in inadequate packaging. In the material swept under the barrels with pesticides, high concentrations of DDT, DDD and DDE were found, in the order of tens g kg^{-1} . Also the plasters in the storage are contaminated, predominantly by DDT.

The risk is obvious at first sight, because the building where pesticides are deposited is ruined, and without a roof. Only parts of walls remained of the building. The pesticides are deposited, practically, in open landscape. Rain and wind cause transport of pesticides into the surrounding landscape. This was confirmed also by the results of analysis of a soil sample from the vicinity of the storage. In total 280 mg of DDT, DDE and HCH per kg was found in this sample. This corresponds to values for a highly contaminated territory.

One of the further big risks is the possibility of contamination of breeding ponds in close vicinity of the storage (see Figure 9). In view of the possibility of accumulation of these persistent pollutants in animal adipose tissues, it would be recommendable to carry out an analysis of fish meat taken from several samples of fish.

3.5 Alaverdi

Sampling date: July 27, 2010

Several concrete structures are located in the locality, serving in particular for disposal of slag and fly ash from a nearby metallurgical plant processing copper ore. Some of the structures are already full, and covered by grass and shrubs. The disposal site is located in hilly area above the town Alaverdi.

3.5.1 Samples taken

3 samples of solid material were taken. A sample of metallurgical waste, and a sample of fly ash with slag, were taken in the structures. Further, a soil sample was taken in the vicinity under the disposal site.

3.5.2 Results and risk assessment

As expected, high percentage of metals, namely of copper, lead, zinc, cadmium, chromium and arsenic, was found in waste and slag from the metallurgical plant. However, high concentrations of heavy metals were found also in the soil sample taken in the distance cca 20 m from the disposal site, out of the actual disposal site area. The surrounding environment is contaminated in particular by lead, cadmium and arsenic. These hazardous substances are being washed out of the disposal site by rain precipitations, and are spreading downhill towards the town Alaverdi, the suburbs of which are located in the order of hundreds of metres from the disposal site. The neighbourhood of the disposal site is freely accessible.

4. ANNEXES

In the tables, the found out concentrations can be compared with contamination criteria for soils and underground water according to the Methodical Instruction of the Ministry of Environment of the Czech Republic. The amounts of pesticides in many localities exceed the criterion C several times.

4.1 Criterion A

For OCPs = 0.05 mg kg⁻¹ of dry matter

Criterion A levels correspond approximately to background content of the monitored substances in the environment (in connection with the usual sensitivity limit of analytical determination). When criteria A are exceeded, it is regarded as pollution of the corresponding environmental component, with the exception of areas with naturally higher content of the monitored substances. However, if criteria B are not exceeded, the pollution is not regarded as significant to the extent that it would be necessary to obtain more detailed data for its assessment, i.e., to start investigation or to monitor the pollution.

4.2 Criterion B

For OCPs = 2 mg. kg⁻¹ of dry matter

Exceeding of criteria B is regarded as pollution that may have adverse impacts on human health and the individual environmental components. It is necessary to collect further data for assessment whether the case presents a significant environmental burden, and what are the risks connected with it. Thus, criteria B are set as intervention

limits, exceeding of which means that it is necessary to deal with the pollution further. If criteria B are exceeded, it is necessary to preliminarily assess risks ensuing from the found out pollution, to determine its source and causes, and, depending on the results, to decide on further investigation or start of monitoring.

4.3 Criteria C

For OCPs: residential areas: 2.5 mg kg⁻¹ of dry matter; recreational areas: 5 mg kg⁻¹ of dry matter; industrial areas: 10 mg kg⁻¹ of dry matter for sum of DDT and its metabolites – all land use areas: 2.5 mg kg⁻¹ of dry matter

Exceeding of criteria C is regarded as pollution that may represent a significant risk of endangering human health and environmental components. Seriousness of the risk may be confirmed only by its analysis. Recommended values of target parameters for decontamination may be also higher than the stated criteria C, depending on the results of risk analysis. Documents necessary for deciding on the method of corrective measure are formed, in addition to the risk analysis, by studies evaluating technical and economic aspects of the proposed solution.

Criterion values are valid in case of OCPs for each pesticide separately.

However, not so strict criteria are valid in Armenia yet. When assessing the pollution level, the so-called Provisional Low POPs Content Level may be taken into consideration, this level being 50 mg kg⁻¹. The value 50 mg means weight of each pesticide contained in a sample separately.

TABLE 1: SUMMARIZED RESULTS OF ANALYSES AT NUBARASHEN DUMPING SITE

underground samples taken in three profiles down the hill from the dumping site. Samples were taken from the drill hole.

Locality		NUBARASHEN						Criterion C residential; recrea- tional; industrial
Sample Description	NV1	NV2	NV3	NV4	NV5	NV6	NV7	
	soil samples - first profile			soil samples - second profile		soil samples - third profile		
Depth (m)	0.5	1.0	1.5	0.5	1.0	0.5	1.0	
SUBSTANCE		CONTENT IN DRY MATTER (mg kg ⁻¹ d.m.)						
alpha-HCH	2.40	5.35	6.8	-	0.06	-	-	2.5; 5; 10
beta-HCH	1.37	1.61	0.87	0.03	0.04	-	0.01	2.5; 5; 10
gamma-HCH	0.49	0.06	0.01	-	-	-	-	2.5; 5; 10
HCB	1.23	0.50	0.30	-	-	-	-	2.5; 5; 10
heptachlor	0.06	0.01	-	-	-	-	-	2.5; 5; 10
heptachlor exo-epoxide	-	-	-	-	-	-	-	2.5; 5; 10
alpha-endosulfan	0.07	0.03	-	-	-	-	-	2.5; 5; 10
beta-endosulfan	-	-	-	-	-	-	-	2.5; 5; 10
dieldrin	-	-	-	-	-	-	-	2.5; 5; 10
endrin	-	0.02	0.07	-	-	-	-	2.5; 5; 10
2,4'-DDE	0.24	0.19	0.61	-	0.01	-	0.01	2.5; 5; 10
4,4'-DDE	1.37	1.30	2.40	0.03	0.09	0.02	0.08	2.5; 5; 10
2,4'-DDD	1.32	0.41	1.88	-	-	-	0.01	2.5; 5; 10
4,4'-DDD	4.15	1.52	13.36	0.04	0.02	0.01	0.02	2.5; 5; 10
2,4'-DDT	17.8	7.33	24.54	0.11	0.05	0.01	0.06	2.5; 5; 10
4,4'-DDT	148.31	64.18	214.12	0.79	0.35	0.08	0.59	2.5; 5; 10
DDT	173.19	74.93	256.91	0.97	0.52	0.12	0.77	2.5
TOTAL	178.10	82.51	264.23	1.1	0.62	0.13	0.79	

TABLE 2: SUMMARIZED RESULTS OF ANALYSES AT NUBARASHEN DUMPING SITE –
surface layer samples taken in several profiles down the hill from the dumping site.

Locality	NUBARASHEN										Criterion C residential; recreational; industrial
Sample Description	N1	N2	N3	N4	N5	N6	N7	N8	N9	NS	
	soil samples - surface										
SUBSTANCE	CONTENT IN DRY MATTER (mg kg ⁻¹ d.m.)										
alpha-HCH	248.36	0.12	0.72	10.90	0.07	0.77	0.21	0.12	0.11	-	2.5; 5; 10
beta-HCH	45.50	-	2.11	14.75	0.03	2.3	0.12	0.42	0.05	0.01	2.5; 5; 10
gamma- HCH	67.94	0.01	-	2.19	0.00	-	0.02	0.02	0.02	-	2.5; 5; 10
HCB	9.80	-	0.30	3.92	-	0.34	0.17	-	-	-	2.5; 5; 10
heptachlor	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
heptachlor exo-epoxide	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
alpha-endosulfan	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
beta-endosulfan	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
dieldrin	-	-	-	-	-	-	-	-	-	-	2.5; 5; 10
endrin	2.17	-	-	-	-	-	-	-	-	-	2.5; 5; 10
2,4'-DDE	30.81	5.95	1.4	7.58	-	0.48	0.68	-	0.38	-	2.5; 5; 10
4,4'-DDE	30.49	30.69	5.57	27.51	0.03	2.33	4.97	0.14	5.80	-	2.5; 5; 10
2,4'-DDD	36.57	0.39	1.13	11.85	-	1.8	0.28	0.07	0.07	-	2.5; 5; 10
4,4'-DDD	152.93	0.18	4.24	51.47	-	4.3	0.78	0.28	0.06	0.01	2.5; 5; 10
2,4'-DDT	664.89	3.63	15.69	177.19	0.01	16.57	4.60	0.89	1.00	-	2.5; 5; 10
4,4'-DDT	4,045.22	6.45	115.31	1,250.78	0.04	100.25	18.5	5.13	1.87	-	2.5; 5; 10
DDT	4,960.91	47.29	143.34	1,526.38	0.08	125.73	29.81	6.51	9.18	0.01	2.5
TOTAL	5,334.68	47.30	146.11	1,558.15	0.19	127.89	29.87	7.05	9.35	0.02	

TABLE 3: RESULTS OF ANALYSES FOR SAMPLES TAKEN IN OBSOLETE PESTICIDES STORAGE NEAR ECHMIADZIN AND ITS VICINITY.

Locality	ECHMIADZIN				Criterion C residential; recreational; industrial	ECHMIADZIN
Sample Description	E1 storage 1 - sweepings	E2 storage 2 - sweepings	E3 patch near the storage - soil	E4 trout pond - sediment		EV trout pond - water
SUBSTANCE	CONTENT IN DRY MATTER (mg kg ⁻¹ d.m.)					µg kg ⁻¹
alpha-HCH	2.27	7.36	0.06	0.06	2.5; 5; 10	0.29
beta-HCH	34.95	7.17	0.05	0.05	2.5; 5; 10	-
gamma-HCH	31.73	-	-	-	2.5; 5; 10	-
HCB	1.1	41.92	-	-	2.5; 5; 10	0.02
heptachlor	-	4.13	-	-	2.5; 5; 10	-
heptachlor exo-epoxide					2.5; 5; 10	
alpha-endosulfan	15.31	329.25	-	-	2.5; 5; 10	-
beta-endosulfan	-	106.81	-	-	2.5; 5; 10	-
dieldrin	-	3.28	-	-	2.5; 5; 10	-
endrin	-	83.93	-	-	2.5; 5; 10	-
2,4'-DDE	0.52	361.72	-	0.01	2.5; 5; 10	-
4,4'-DDE	0.73	499.81	0.03	0.01	2.5; 5; 10	-
2,4'-DDD	-	30.90	0.04	-	2.5; 5; 10	-
4,4'-DDD	0.35	279.45	-	-	2.5; 5; 10	-
2,4'-DDT	2.30	610.22	0.01	-	2.5; 5; 10	-
4,4'-DDT	8.55	-	0.02	-	2.5; 5; 10	0.01
DDT	12.45	1,782.10	0.10	0.02	2.5	0.01
TOTAL	97.72	2,358.57	0.20	0.13		0.31

TABLE 4: RESULTS OF ANALYSES FOR SAMPLES TAKEN IN OBSOLETE PESTICIDES STORAGE IN MASIS AND ITS VICINITY.

Locality	MASIS					Criterion C residential; recreational; industrial
Sample Description	M1 storage 1 - sweepings	M2 storage 1 - pink material	M3 storage 2 - sweepings	M4 storage 1 and 2 - plaster	M5 vicinity of the storages - soil	
SUBSTANCE	CONTENT IN DRY MATTER (mg kg ⁻¹ d.m.)					
alpha-HCH	6.65	4,145.98	1.44	4.19	0.06	2.5; 5; 10
beta-HCH	10.35	4,795.80	4.1	30.12	0.20	2.5; 5; 10
gamma-HCH	1.51	3,587.43	7.84	0.26	0.01	2.5; 5; 10
HCB	0.03	25.98	0.15	-	-	2.5; 5; 10
heptachlor	-	26.29	-	-	-	2.5; 5; 10
heptachlor exo-epoxide	-	3.83	-	-	0.01	2.5; 5; 10
alpha-endosulfan	-	24.22	-	-	0.02	2.5; 5; 10
beta-endosulfan	8.2	5.1	1.13	0.20	0.19	2.5; 5; 10
dieldrin	1.1	1.85	-	-	0.07	2.5; 5; 10
endrin	-	-	-	-	-	2.5; 5; 10
2,4'-DDE	45.11	10.42	4.65	0.40	0.07	2.5; 5; 10
4,4'-DDE	55.70	8.88	6.34	0.73	0.58	2.5; 5; 10
2,4'-DDD	5.60	9.92	5.18	0.59	0.19	2.5; 5; 10
4,4'-DDD	1.67	12.31	0.99	0.94	0.02	2.5; 5; 10
2,4'-DDT	70.59	31.57	4.76	3.97	0.14	2.5; 5; 10
4,4'-DDT	18.72	14.74	11.17	16.52	0.38	2.5; 5; 10
DDT	197.39	87.84	33.09	23.15	1.38	2.5
TOTAL	224.96	12,704.23	47.67	57.91	1.94	

TABLE 5: RESULTS OF ANALYSES FOR SAMPLES TAKEN IN OBSOLETE PESTICIDES STORAGE IN JRARAT AND ITS VICINITY.

Locality	JRARAT								Criterion C residential; recreational; industrial
Sample Description	J1 big storage – sweepings from the floor	J2 big storage - sweepings under barels	J3 big storage - powder from the cover of the barrels	J4 big storage - plaster	J5 vicinity of the big storage - soil	J6 small storage without a roof - mixed sample from the bags	J7 small storage without a roof - mixed sample from the barrels	J8 vicinity of the small storage without a roof - soil	
SUBSTANCE	CONTENT IN DRY MATTER (mg kg ⁻¹ d.m.)								
alpha-HCH	0.67	14.41	0.26	-	0.06	210.99	0.75	7.55	2.5; 5; 10
beta-HCH	0.25	19.25	0.74	-	0.08	19.25	3.14	13.42	2.5; 5; 10
gamma-HCH	-	377.46	0.27	-	-	1,609.47	0.47	1.30	2.5; 5; 10
HCB	-	-	0.05	-	-	-	0.36	-	2.5; 5; 10
heptachlor	-	-	-	-	-	-	28.40	-	2.5; 5; 10
heptachlor exo-epoxide	0.03	-	-	-	-	-	-	-	2.5; 5; 10
alpha-endosulfan	-	-	-	-	-	-	-	-	2.5; 5; 10
beta-endosulfan	0.02	16.68	-	-	0.02	16.68	12.00	-	2.5; 5; 10
dieldrin	-	0.24	-	-	-	0.24	-	-	2.5; 5; 10
endrin	-	-	-	-	-	-	-	-	2.5; 5; 10
2,4'-DDE	0.07	78.03	-	-	0.10	204.56	153.10	9.6	2.5; 5; 10
4,4'-DDE	0.19	430.01	0.94	0.18	0.26	1,925.96	474.67	40.94	2.5; 5; 10
2,4'-DDD	0.05	1,704.72	-	0.23	0.04	5,286.43	31.54	4.21	2.5; 5; 10
4,4'-DDD	0.32	6,256.25	-	-	0.01	23,087.13	18.4	10.10	2.5; 5; 10
2,4'-DDT	0.30	5,855.78	15.16	1.68	0.06	99,479.88	332.87	30.3	2.5; 5; 10
4,4'-DDT	0.49	12,485.27	70.32	9.14	0.12	515,918.01	297.49	163.46	2.5; 5; 10
DDT	1.42	26,810.06	86.42	11.23	0.59	645,901.97	1,308.07	258.61	2.5
TOTAL	2.40	27,238.09	87.76	11.22	0.75	647,758.6	1,352.83	280.06	

TABLE 6: RESULTS OF ANALYSES FOR SAMPLES TAKEN ON METALLURGICAL WASTE DISPOSAL SITE IN ALAVERDI AND ITS VICINITY.

Locality									
ALAVERDI									
Sample Description	A1	A2	A3	Criterion	A	B	C	C	C
	solid waste from metallurgical plant	fly ash, slag	soil, vicinity of the disposal site	Land use specification	-	-	residential	recreational	industrial
SUBSTANCE	CONTENT IN DRY MATTER (mg.kg ⁻¹)			LIMIT VALUES	CONTENT IN DRY MATTER (mg.kg ⁻¹)				
Pb	12,060	19,820	1,374	Pb	80	250	300	500	800
Zn	155	2,644	133	Zn	150	1,500	2,500	3,000	5,000
Cu	48,120	61,170	1,022	Cu	70	500	600	1,000	1,500
As	1,765	7,514	453	As	30	65	70	100	140
Cr	112	92	59	Cr	130	450	500	800	1,000
Fe	21,000	174,800	99,700	Fe	-	-	-	-	-
Cd	12	94	1.3	Cd	0.5	10	20	25	30

Yeraskh, Armenia – site contaminated by POPs

Report about results of monitoring of the site in 2011

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Arnika – Toxics and Waste Programme, Prague

April, 2015

1. INTRODUCTION

A team of people from both Czech NGO Arnika and Armenian NGO AWHHE working on joint project “Scaling Up Experience in Improvement of Chemical Safety to Contribute to Poverty Reduction in Rural Armenia“ has visited an abandoned obsolete pesticides stockpile in Yeraskh close to Nakhchivan Autonomous Republic which was destroyed by fire during the war between Armenia and Azerbaijan in 1992. We visited

the site in June 2011 and took 4 samples in the area of potentially contaminated site in order to obtain some data about potential contamination by POPs. This is the first publication of the results since that time. We believe that results are interesting and can play an important role in the further investigation and remediation of the site.

2. SAMPLING AND ANALYTICAL METHODS

Only 4 samples were taken in the locality of the former pesticides storage/obsolete pesticides stockpile in Yeraskh. Three mixed samples and one point sample were taken. Mixed samples were formed by several partial samples taken in a larger area of the given locality. The samples were taken by means of a shovel into plastic sample containers with screw lids. Soil samples were stored at room temperature. The number and description of the taken samples is stated below in Table 1.

Sample analysis was carried out in the laboratories of the Institute of Chemical Technology in Prague. For the analysis, there was used an efficient method, verified in the long term, of extraction by hexane in ultrasound, and subsequent analysis of the extract by gas chromatography.

In the laboratory, sample homogenization was carried out at first. Subsequently, a representative part of the sample was taken for analysis, specifically, 2.5 g of the

TABLE 1: DESCRIPTION OF SAMPLES TAKEN IN YERASKH IN 2011.						
Sample Code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Soil						
Yeraskh 1	3/6/2011	+39° 44' 14.54" +44° 49' 51.18"	Yeraskh, abandoned pesticides storage (obsolete pesticides skockpile site)	Soil/partly sediment at the bottom of lower part of area. Mixed and homogenized.	Soil, mixed sample out of 5 partial samples. 5×5 m square, 5×5 cm squares sampled, sampling depth 2–10 cm.	Sampled by stainless shovel.
Yeraskh 2	3/6/2011	+39° 44' 14.52" +44° 49' 51.62"	Yeraskh, abandoned pesticides storage (obsolete pesticides skockpile site)	Soil mixed with residues after fire. Mixed and homogenized.	Soil, mixed sample out of 5 partial samples. 5×5 m square, 5×5 cm squares sampled, sampling depth 2–10 cm.	Sampled by stainless shovel. Smell of fire.
Yeraskh 4	3/6/2011	+39° 44' 10.79" +44° 49' 54.03"	Yeraskh, abandoned pesticides storage (obsolete pesticides skockpile site)	Soil very light brown with visible contamination by pesticides. Mixed and homogenized.	Soil, mixed sample out of 3 partial samples. 1×1.5 m square, 5×5 cm squares sampled, sampling depth 2–10 cm.	Sampled by stainless shovel. Typical smell of OCPs.
Other solid materials						
Yeraskh 3	3/6/2011	+39° 44' 11.54" +44° 49' 53.69"	Yeraskh, abandoned pesticides storage (obsolete pesticides skockpile site)	Yellow brownish material from old packaging of some pesticide.	Point sample of the material partly already mixed with soil.	Sampled by stainless shovel.

sample. The sample was placed, together with 10 ml of hexane, into an extraction bottle, and extracted in ultrasound water bath for the period of 20 minutes. Subsequently, the extract was analysed by means of a gas chromatograph with ECD detector.

One sample was also determined for the analysis of PCDD/Fs and dioxin-like PCBs using the DR CALUX method were sent to a Dutch ISO 17025 certified laboratory (Bio-Detection Systems B.V., Amsterdam). The procedure for the BDS DR CALUX® bioassay has previously been described in detail (Besselink H 2004).

3. RESULTS

Results of analyses of all the samples are presented in Table 2. Only 4 samples taken in total cannot represent the full picture of the level of contamination at the investigated site, but the results give an indication of how seriously it was polluted. For the evaluation of the results the same method and criteria was used as for the other localities in Armenia by Honzajková and Šír (2011)¹. A very high level of pollution by OCPs (almost 3 g per kg d.m.) was found in one sample from Yeraskh. An elevated level which ex-

¹ Their report is reprinted in this publication (Contaminated sites and their management) as well. The criteria used for evaluation of the contamination level are explained in their report.

ceeded Czech criteria for remediation for 2 DDT metabolites and total sum of DDT was also found in another nearby sample from Yeraskh. The level of sum of DDT was high in sample Yeraskh 2 as well. The levels of PCDD/Fs and DL PCBs was comparable with pollution of soils in areas with higher burden in Central Europe (Holoubek and Adamec 2003, Holoubek, Dusek et al. 2009). Levels of OCPs and DDT observed in Yeraskh were comparable with levels found at Nubarashen and Echmiadzin contaminated sites in a previous report (Honzajková and Šír 2011). This level of contamination is dangerous when the area is accessible by cattle as we witnessed during sampling in 2011.

TABLE 2: SUMMARIZED RESULTS OF ANALYSES FOR OCPs, PCDD/Fs AND DL PCBs FOR SAMPLES FROM YERASKH, ARMENIA, TAKEN IN 2011.

Locality	Yeraskh				Criterion C
Sample	Yeraskh 1	Yeraskh 2	Yeraskh 3	Yeraskh 4	residential; recreational; industrial
Substance (in mg kg ⁻¹ d.m.)					
alpha-HCH	<LOD	<LOD	<LOD	<LOD	2.5; 5; 10
beta-HCH	<LOD	<LOD	<LOD	<LOD	2.5; 5; 10
gamma-HCH	<LOD	<LOD	<LOD	1.3982	2.5; 5; 10
HCB	<LOD	<LOD	<LOD	<LOD	2.5; 5; 10
Heptachlor	<LOD	<LOD	0.6156	9.8853	2.5; 5; 10
Metoxychlor	<LOD	<LOD	<LOD	25.3095	2.5; 5; 10
alpha-endosulfan	<LOD	<LOD	<LOD	<LOD	2.5; 5; 10
beta-endosulfan	<LOD	0.1502	0.3914	<LOD	2.5; 5; 10

Locality	Yeraskh				Criterion C
Sample	Yeraskh 1	Yeraskh 2	Yeraskh 3	Yeraskh 4	residential; recreational; industrial
Substance (in mg kg ⁻¹ d.m.)					
2,4'-DDE	0.0248	2.2258	6.3473	<LOD	2.5; 5; 10
4,4'-DDE	0.0518	1.4779	19.2143	1,253.3392	2.5; 5; 10
2,4'-DDD	<LOD	<LOD	1.0891	75.5067	2.5; 5; 10
4,4'-DDD	<LOD	<LOD	<LOD	<LOD	2.5; 5; 10
2,4'-DDT	0.0159	<LOD	11.0679	925.4032	2.5; 5; 10
4,4'-DDT	0.0341	0.2240	1.2781	380.6873	2.5; 5; 10
Σ DDT	0.1266	3.9277	39.1967	2,634.9364	2.5
Total OCPs	0.1266	4.0779	41.5524	2,765.4483	-
PCDD/Fs and DL PCBs (pg BEQ g ⁻¹ d.m.)	10	NA	NA	NA	0.5; 10; 30 (pg I-TEQ g ⁻¹ d.m.)

4. CONCLUSIONS

Limited investigation and analyses of 4 samples from Yeraskh have shown that this site should be added to the list of sites with serious contamination by OCPs such as those evaluated by Honzajková and Šír (2011) in previous years. This site requires more detailed research followed by remediation of contaminated soil. Restricted access for

cattle and unauthorized persons should be secured until the remediation of the site. Also measures for reduction of spread of contamination should be taken (e.g. to cover area in order to prevent spread of contaminated dust).

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6. PHOTOS FROM THE SITE



**Results of environmental sampling in Kazakhstan:
mercury, methylmercury, PCBs and OCPs
contamination of the River Nura**
(Final report)

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University of Chemistry and Technology Prague, 2015

1. INTRODUCTION

This study is focused on the presentation and discussion of data related to contamination of the River Nura and its surroundings by mercury, methylmercury, polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs). A series of different kinds of samples were taken for analysis, which included both abiotic (sediments, soils) and biotic (fish, eggs) samples. A part of the study is also aimed at measurement of heavy metals in sediments and soils in this area. Samples were obtained during two field visits conducted in Kazakhstan in August 2013 and in July 2014.

Sampling campaigns represent an important part of the project “Empowering the civil society in Kazakhstan in improvement of chemical safety”, a joint project of the Czech not-for profit organization Arnika Association and two Kazakh partners, the Karaganda Regional Ecological Museum (EcoMuseum) and the Center for Introduction of New Environmentally Safe Technologies (CINEST).

2. CONTAMINATION OF RIVER NURA

The River Nura is the main river of central Kazakhstan. The river rises in the Kyzyltas Mountains in the west and passes through the heavily industrialized area of Temirtau, and then flows another 260 km to the capital Astana and the internationally important national park Korgalzhyn. The total length of the river is 978 km. The river is a typical steppe river: 80 % of the flow is caused by the spring thaw. Water is widely used for household water supply, irrigation, industrial use and also for recreation and commercial fishing (Heaven et al. 2000). Estimated annual naturalised flow is 5.9 and 19.6 m³ s⁻¹ in the cities of Karaganda and Astana, respectively. The size of the spring flood, however, is extremely variable and peak annual flow can range from 40 to 980 m³ s⁻¹.

The Nura has received high inputs of mercury since the 1950s, the source being the Karbid chemical factory in the city of Temirtau near Karaganda. This chemical factory produced acetaldehyde by direct hydration of acetylene in the presence of a catalyst -

mercuric sulphate. Development of the project was carried out by the Hiprokauchuk Company. Wastewater from the acetaldehyde factory with a high content of mercury was discharged into the river without treatment for a period of approximately 25 years. During that time, total mercury concentrations in the effluent are suspected to have reached up to 50 mg l⁻¹ and the average annual input of mercury to the river between 1950 and 1976 has been estimated as 22–24 tons. Until 1969 sludge containing mercury was discharged into Zhaur swamp. From the mid-1970s, wastewater received partial treatment by sulphide precipitation, and the amount of mercury entering the river was considerably reduced. The overall level of acetaldehyde production was also reduced. Precipitated sludge from the settling tanks was also deposited in ash landfills from the thermal power station KarGRES-1, located on the banks of the River Nura. During this storage period there was uncontrolled discharge of ash and sludge containing mercury into the

River Nura. During the 1980s and most of the 1990s, approximately 1 ton annually was discharged into the river, most likely in dissolved and elemental form. Production of acetaldehyde was stopped in 1997, and a major source of mercury pollution disappeared (Ullrich et al., 2007, Hsiao et al., 2010).

Preliminary investigations of the extent of pollution on the Nura carried out in the 1980s revealed extremely high levels of contamination. This non-statistical based study of mercury in the silt of 33 river profiles showed that the sediments are highly polluted, with average total mercury concentrations in excess of 200 mg kg^{-1} in the first 9 km downstream of the source. On the basis of the detected concentrations, it was estimated

that the total amount of mercury in the bed of the river could be in the order of 140 tons. During the period when the mercury was discharged, up to 5 million tonnes of fly ash was also discharged into the river by a local power station. At the same time the Karbid factory discharged water high in calcium hydroxide, which precipitated to form thousands of tonnes of calcium carbonate in the sediments. In 1992 it was discovered that most of the mercury in the river had become associated with this alkali ash, forming a new type of chemical deposit. During the spring floods, large amounts of these highly contaminated sediments were transported down the river and dispersed over the floodplain and caused widespread pollution (Ilyushchenko et al., 2002, Ilyushchenko et al., 2005).

3. RIVER NURA CLEAN-UP PROJECT

Since the 1980s there have been a number of surveys and studies to determine the extent of contamination and appropriate measures to eliminate contamination. These studies led to a project proposing measures to clean up the River Nura and Zhaur Swamp, and in parallel to carry out an independent project to clean up the Karbid factory and ash disposal site. Construction of landfill for hazardous waste was also intended. The aim of the project was to improve the living conditions of the population in the surroundings of the River Nura by removing serious mercury pollution. A clean-up criterion was intended to establish the level to monitor and determine the results of the project. Material with a mercury concentration exceeding the maximum allowable value was intended to be removed. Because of the importance of this criterion, extensive studies were conducted in the area of mercury contamination in 2004.

Contaminated areas were cleaned in the River Nura Clean-up project, funded by The World Bank and the Republic of Kazakhstan, in the years 2007–2011. Criteria

set out in the “River Nura Clean Up Project” were based on Kazakhstani hygienic normatives for soil - soil pollution standards (established on November 29, 1997) and international levels of pollution. A criterion of 2.1 mg kg^{-1} was applied for agricultural areas and inhabited localities (e.g. gardens used for growing vegetables and fruits). A clean-up criterion of 10 mg kg^{-1} was adopted for river bed sediments, river banks, Zhaur swamp, and floodplains, and for more remote areas it was 50 mg kg^{-1} . These criteria were confirmed by the Ministry of Health of Kazakhstan.

A document of the World Bank “Implementation Completion and Results Report” (Abdullah et al., 2013) describing the Nura Clean Up project was published on June 27, 2013. The main conclusions are that previous mercury levels in soil and sediments range from $50\text{--}1,500 \text{ mg kg}^{-1}$ (based on detailed pollution sampling and mapping) and after clean-up they confirmed accepted criteria for safe levels (Abdullah et al., 2013).

4. SAMPLING SITES

A detailed spatial and interactive depiction of sampling sites and spots is given in a special CD annex of the report “Toxic Hot Spots in Kazakhstan” (Arnika, EcoMuseum and

CINEST, 2015) and information about samples taken is in the following Table 1.

TABLE 1: DESCRIPTION OF SAMPLES TAKEN FROM THE RIVER NURA AND ITS SURROUNDINGS.

Sample Code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Temirtau						
NUR - 24/4	24/8/2013 13:35	+50° 06' 00.0" +72° 54' 16.5"	River Nura – alluvial soil on the right bank	Loamy sediment	Sediment, point sample	Surroundings littered with rubbish
NUR - 24/5	24/8/2013 13:35	+50° 06' 00.0" +72° 54' 16.5"	River Nura – right bank near the bridge	Black sandy sediment with putrid smell	Sediment, mixed sample out of 5 point samples	
NUR - 24/8	24/8/2013 17:30	+50° 06' 56.0" +72° 56' 57.7"	Samarkand Reservoir, the Japanese bay	Clayey and gritty sediment	Sediment, point sample	
NUR - 24/6	24/8/2013 14:30	+50° 04' 40.5" +72° 55' 32.5"	Samarkand Reservoir, southwest bank near the old factory drain	Clayey and sandy sediment, homogenization	Sediment, mixed sample out of 5 point samples	Non-homogenic samples (sand and clay apart)
NUR - 24/7	24/8/2013	+50° 04' 27.3" +72° 58' 22.5"	Samarkand Reservoir, bank behind the old factory	Black sediment with growing roots, homogenization	Sediment, mixed sample out of 5 point samples, top layer of the sediment (2 cm)	Surroundings littered with rubbish, foam on the water
NUR - 24/9	24/8/2013 18:45	+50° 04' 41.4" +72° 53' 04.4"	River Nura, wetland near Karbid factory – forbidden zone	Black clayey sediment, homogenization	Sediment, mixed sample out of 4 point samples	
TEM - CHL 1	18/8/2013 11:15	+50° 04' 16.3", +72° 51' 27.4"	Chemical tailings pond of Karbid factory, middle of tailings pond, near dam	Dark grey ash, homogenization	Ash, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	
TEM - CHL 2	18/8/2013 11:30	+50° 04' 19.7", +72° 51' 28.3"	Near chemical tailings pond of Karbid factory, the wetland pond at the foot of tailings pond	Dark brown and grey sediment, homogenization	Sediment, mixed sample out of 5 partial samples taken in 20 m line along the shore	

Sample Code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Temirtau						
TEM - CHL 3	18/8/2013 12:05	+50° 04' 20.6", +72° 51' 05.7"	Chemical tailings pond of Kardbid factory, northern end of the pond	Black and grey clayey sediment, homogenization	Sediment, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	Occasionally waterlogging
TEM - CHL 4	18/8/2013 12:13	+50° 04' 20.6", +72° 51' 05.7"	Chemical tailings pond of Kardbid factory, northern end of the pond	Black and grey clayey sediment with white blob	Sediment, point sample, depth 70 cm	Occasionally waterlogging
TEM - CHL 5	18/8/2013 12:28	+50° 04' 19.6", +72° 51' 09.8"	Chemical tailings pond of Kardbid factory, northern end of the pond	Black and grey clayey sediment	Sediment, point sample, depth 5 cm	Most humid place
TEM - CHL 6	18/8/2013 12:45	+50° 04' 14.1", +72° 51' 30.5"	Chemical tailings pond of Kardbid factory, southern end of the pond	Dark grey clayey ash, homogenization	Ash, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	Completely dry, slight chemical smell
TEM - CHL 8	18/8/2013 16:00	+50° 04' 11.6", +72° 50' 58.2"	Chemical tailings pond of Kardbid factory, western edge of the pond	Light brown clayey surface crust	Sediment, point sample, depth 5 cm	Light area at the edge of the reeds
TEM - CHL 9	18/8/2013 16:10	+50° 04' 10.7", +72° 50' 59.5"	Chemical tailings pond of Kardbid factory, western edge of the pond	Grey and black, dense, wet, homogenization	Sediment, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	
TEM - CHL 10	18/8/2013 17:00	+50° 04' 00.6", +72° 50' 44.2"	Near chemical tailings pond of Kardbid factory, west of the pond, along the field road	Light brown, slightly moist soil, slightly yellowish- white clay, homogenization	Soil, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	
TEM - CHL 11	18/8/2013 17:25	+50° 04' 32.4", +72° 51' 01.6"	Near chemical tailings pond of Kardbid factory, wetland near the drainage to the river near the road to Temirtau	Grey and black sediment, muddy, clayey, partly sand, homogenization	Sediment, mixed sample out of 5 partial samples taken along the shore of the wetland from 0.5 to 1.5 m from the shore, depth 10 cm	
TEM - CHL 12	18/8/2013 17:25	+50° 04' 15.9", +72° 51' 31.1"	Chemical tailings pond of Kardbid factory, middle of tailings pond, near eastern dam	Grey dust, mixing	Dust, mixed sample out of 8 partial samples swept from the surface of the pond	

Sample Code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Chkalovo						
NUR GR 24/1	24/8/2013 13:25	+50° 04' 41.4" +72° 53' 04.4"	River Nura, edge of the village	Brown, loamy soil, homogenization	Soil, mixed sample out of 5 point samples	
NUR SED 6	19/8/2013 16:00	+50° 05' 79.20" +72° 53' 00.15"	Confluence of two wastewater drains – right drain	Fine black sediment, distinctly stratified, homogenization, quartation	Sediment, mixed sample out of 5 point samples, 0-10 cm deep	
NUR SED 7	19/8/2013 16:30	+50° 02' 53.3" +72° 41' 45.8"	Confluence of two wastewater drains – left drain	Sandy sediment, homogenization	Sediment, mixed sample out of 5 point samples	Drain probably from Karbid
NUR SED 6. – HIST	19/8/2013 15:50	+50° 05' 79.20" +72° 53' 00.15"	Confluence of two wastewater drains – right drain	Black sediment	Sediment, mixed sample out of 3 point samples, 16-25 cm deep	
NUR WAT 1	19/8/2013 16:45	+50° 05' 83.86" +72° 52' 97.37"	Confluence of two wastewater drains – left drain	Water	Point sample	Strongly polluted, emulsion with oil, probably from Karbid
NUR – EGG 24/2	24/8/2013 13:25	+50° 05' 56.1" +72° 52' 40.4"	Dacha near the drain	Eggs	Sample of 6 eggs	
NUR-14/1	5/8/2014 19:00	+50° 06' 15.13" +72° 52' 14.04"	River Nura, near transformer close to waterpump station	Loamy, sandy/earthy soil, homogenization, quartation	Soil, mixed sample out of 4 point samples, 1-6 cm deep	Smelly of oily compounds
NUR-SED-14/4	5/8/2014	+50° 06' 08.19" +72° 52' 54.02"	Left side bank of River Nura, North from Chalovo village - small island in the middle of the river	Dark greyish black sediment, loamy (sandy/earthy), homogenization, quartation	Sediment, mixed sample out of 5 point samples	Organic sediment smell
NUR-SED-14/5	5/8/2014	+49° 51' 25.62" +72° 22' 38.68"	Chkalovo, left bank of River Nura by the road leading into river	Greyish brown loamy (sandy/earthy), homogenization, quartation	Sediment, mixed sample out of 2 point samples	
NUR-EGG-14/2	5/8/2014	+50° 05' 17.1" +72° 52' 05.3"	Chkalovo	Eggs, boiling	Sample of 6 eggs, from various free range hens fed with wheat, eggshells, pumpkins, water-melons	
Krasniye Gorki						
NUR GR 3	19/8/2013 15:00	+50° 06' 96.99" +72° 51' 64.78"	River Nura under road bridge	Sandy soil, homogenization	Soil, mixed sample out of 10 point samples	Dug out of river bed
NUR SED 5	19/8/2013 14:50	+50° 06' 96.57" +72° 51' 75.16"	River Nura – open landscape around the surroundings	Sandy sediment, homogenization, quartation	Sediment, mixed sample out of 5 point samples removing of the upper layer	

Sample Code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Samarkand						
NUR GR 1	19/8/2013 12:50	+50° 07' 64.38" +72° 49' 07.47"	River Nura, river surroundings behind the village	Sandy soil and grey dust, homogenization	Soil, mixed sample out of 10 point samples	
NUR SED 1	19/8/ 2013 12:40	+50° 07' 74.74" E 72° 48' 89.81"	River Nura	Sandy sediment, homogeniza- tion, 2x quartation	Sediment, mixed sample out of 5 point samples, depth 10 cm, removing of 5 cm tall sand plug in one sample	
NUR EGG 1	19/8/2013 12:15	+50° 06' 82.95" +72° 48' 50.47"	Private house in Samarkand	Eggs, boiling	Sample of 6 eggs, from various free range hens fed with garden grass and food scraps (bread etc.)	
Gagarinskoe						
NUR GR 2	19/8/2013 13:40	+50° 08' 33.41" +72° 47' 31.82"	River Nura, the river's overflow	Dry, loamy soil, homogenization	Soil, mixed sample out of 10 point samples	
NUR SED 2	19/8/2013 13:10	+50° 08' 09.24" +72° 48' 31.17"	River Nura – the river surroundings	Sandy sediment, homogenization, quartation	Sediment, mixed sample out of 5 point samples, 5 cm of bottom layer removed	
NUR SED 3	19/8/2013 13:35	+50° 08' 36.48" +72° 47' 32.33"	River Nura – the river surroundings	Sandy sediment, homogenization, quartation	Sediment, mixed sample out of 5 point samples	
NUR SED 4		+50° 08' 36.48" +72° 47' 32.33"	River Nura – dry spring near the river	Sediment with a rusty layer on the surface	Sediment, point sample	
Tegiszhol						
NUR – 24/3	24/8/2013 12:30	+50° 05' 47.9" +72° 45' 24.4"	River Nura – left bank near the bridge	Brown-black sandy sediment, homogenization	Sediment, point sample	Visibly polluted with rubbish
Rostovka						
NUR – 24/1	24/8/2013 11:25	+50° 02' 53.3" +72° 41' 45.8"	River Nura cove	Brown, loamy sediment, homogenization	Sediment, mixed sample out of 5 point samples	
NUR – 24/2	24/8/2013 11:40	+50° 02' 53.3" +72° 41' 45.8"	River Nura cove – alluvial soil on the right bank	Brown-black clay sediment	Sediment, point sample	
NUR – EGG 24/1	24/8/2013 11:45	+50° 02' 54.5" +72° 41' 38.0"	Dacha next to River Nura	Eggs, boiling	Sample of 6 eggs	
NUR-EGG-14/1	5/8/2014	+50° 02' 00.2" +72° 40' 10.3"	Rostovka	Eggs, boiling	Sample of 6 eggs, from various free range hens fed with grass, vegetables	

Sample Code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Kyzylzhar						
NUR-SED-14/3	5/ 8/2014 14:00	+49° 58' 35.94" +72° 36' 48.91"	Right shore of River Nura next to Kyzylzhar village	Dark greyish black sediment, homogenization, quartation	Sediment, mixed sample out of 5 point samples	Organic sediment smell
Intumak Reservoir						
NUR-SED-14/1	5/8/2014 11:45	+49° 52' 22.47" +72° 23' 35.46"	Beginning of the Intumak Reservoir right after conflu- ence of River Nura, on the right side of the shore.	Dark greyish black sediment, homogenization, quartation	Sediment, mixed sample out of 5 point samples	Organic sediment smell
NUR-SED-14/2	5/8/2014 12:45	+49° 51' 36.83" +72° 22' 40.83"	Intumak Reservoir, lagoon on the right side of the shore at beginning of the water reservoir	Black, sandy sediment, homogenization, quartation	Sediment, mixed sample out of 5 point samples representing the square 5×5 m	
NUR-F-14-1/1	5/8/2014 12:15	+49° 51' 25.62" +72° 22' 38.68"	Intumak Reservoir, near Aktobe	1 whole individual fish	Crucian carp (Carassius caras- sius), 4+ years old*	
NUR-F-14-1/2	5/8/2014 12:15	+49° 51' 25.62" +72° 22' 38.68"	Intumak Reservoir, near Aktobe	1 whole individual fish	Perch (Perca fluviatilis), 3+ years old*	
NUR-F-14-1/3	5/8/2014 12:15	+49° 51' 25.62" +72° 22' 38.68"	Intumak Reservoir, near Aktobe	1 whole individual fish	Perch (Perca fluviatilis), 2+ years old*	
NUR-F-14-2/1	5/8/2014 12:45	+49° 51' 27.72" +72° 22' 17.30"	Intumak Reservoir	1 whole individual fish	Roach (Rutilus rutilus), 5+ years old*	
NUR-F-14-2/2	5/8/2014 12:45	+49° 51' 27.72" +72° 22' 17.30"	Intumak Reservoir	1 whole individual fish	Roach (Rutilus rutilus), 4+ years old*	

5. SAMPLING PROCEDURES AND ANALYTICAL METHODS

Samples of soils and sediments were usually taken as mixed samples formed by several partial samples taken in various places of the given locality. Soil samples were taken by means of a shovel into polyethylene containers ($V = 500$ ml) with screw lids or into polyethylene bags. Samples of sediments were taken by a core sampler into polyethylene containers ($V = 500$ ml). Mixed samples were homogenized in a steel bowl, some of them quartered after homogenization. During soil sampling, the sampling shovel and core sampler were washed with tap water or with available river or lake water. Samples were stored in a cold and dark environment before analysis. Fish samples were obtained from local fishermen and kept in a freezer wrapped in two polyethylene bags. Egg samples were obtained from local homes, stored in egg boxes wrapped in polyethylene bag and later cooked. Eggs were stored in a fridge at $4-8^{\circ}\text{C}$ (ČSN, 1997).

Analytical procedures for samples of soils and sediments were as follows: after transport to the laboratory, samples were homogenised and a representative part (50 g) was used for the determination of dry matter by a gravimetric method. Another representative part was taken for analysis of heavy metals (cadmium, copper, chromium, lead, zinc and arsenic) by mineralization procedure. The analytical procedure of mineralization was as follows: 5 g of sample was placed into a beaker together with 30 ml of distilled water and 10 ml of concentrated nitric acid. The sample was boiled for a period of 2 hours. Then it was filtered through a fluted filter paper. Metals and arsenic were determined in the mineralization procedure

by atomic absorption and emission spectrometer SensAA. Mercury was measured directly in solid samples by Advanced Mercury Analyser (AMA 254, Altec). PCBs and OCPs content were measured as follows: a representative part of the sample was taken for analysis, specifically, 2.5 g of the sample. The sample was placed, together with 10 ml of hexane, into an extraction bottle, and extracted in an ultrasound water bath for a period of 20 minutes. Subsequently, the extract was analysed by means of a gas chromatograph GC HP 5,890 with ECD detector and capillary column HP – 5MS (length: 60 m, stationary phase: 5 % diphenyl and 95 % dimethylsiloxan). Analyses were conducted using standard operating procedures (SOP) established at the University of Chemistry and Technology, Prague.

Methylmercury content in samples was analysed with atomic absorption spectrometry by Advanced Mercury Analyser (AMA 254, Altec) using standard operating procedure SOP AAS-CZL 2/13(S) at the State Veterinary Institute, Prague.

Content of PCBs and OCPs in fish and egg samples was analysed with GPC (Gel Permeation Chromatography) at the University of Chemistry and Technology, Prague. Samples were extracted with a mixture of organic solvents (hexane:dichloromethane, 1:1), purified with GPC. The identification and quantification of the analyte was conducted by gas chromatography coupled with tandem mass spectrometry detection in electron ionization mode. Dioxine-Like PCBs were measured by standard operating procedure with HRGC/HRMS.

6. RESULTS

Results of the analytical measurement of mercury, methylmercury, other heavy metals and PCBs are presented in the following tables.

TABLE 2: CONTENT OF HEAVY METALS IN SEDIMENTS AND SOILS FROM THE RIVER NURA AND ITS SURROUNDINGS.
THE CONTENT OF ELEMENTS IS GIVEN IN mg kg⁻¹ OF DRY MATTER.

<LOD: analyte concentration was below limit of detection. NA: not analysed.

Sample Code	Mercury (mg kg ⁻¹)	Lead (mg kg ⁻¹)	Cadmium (mg kg ⁻¹)	Copper (mg kg ⁻¹)	Chromium (mg kg ⁻¹)	Zinc (mg kg ⁻¹)	Arsenic (mg kg ⁻¹)
Temirtau							
NUR – 24/4	0.69	35.5	0.50	27.9	26.9	121	NA
NUR – 24/5	0.49	21.9	<LOD	21.6	16.8	64.9	NA
NUR – 24/8	0.04	6.90	<LOD	7.90	7.70	22.2	NA
NUR – 24/6	0.08	15.7	<LOD	17.4	13.4	41.0	NA
NUR – 24/7	0.05	19.9	<LOD	12.0	9.20	34.2	NA
NUR – 24/9	0.05	14.6	<LOD	10.2	15.9	33.7	NA
TEM – CHL 1	0.04	2.60	0.20	9.30	<LOD	20.2	NA
TEM – CHL 2	0.20	8.20	<LOD	3.50	2.90	9.20	NA
TEM – CHL 3	0.11	7.20	0.60	22.1	2.50	111	NA
TEM – CHL 4	<LOD	0.50	0.40	14.2	7.30	23.2	NA
TEM – CHL 5	0.05	2.90	0.30	12.4	<LOD	64.2	NA
TEM – CHL 6	0.03	<LOD	<LOD	7.90	<LOD	94.6	NA
TEM – CHL 8	0.01	<LOD	<LOD	4.10	NA	6.70	NA
TEM – CHL 9	0.04	3.00	0.30	10.80	3.30	46.0	NA
TEM – CHL 10	<LOD	8.50	<LOD	13.10	28.40	51.2	NA
TEM – CHL 11	0.38	10.10	<LOD	10.60	14.90	38.3	NA
TEM – CHL 12	<LOD	3.30	<LOD	9.00	NA	64.5	NA

Sample Code	Mercury (mg kg ⁻¹)	Lead (mg kg ⁻¹)	Cadmium (mg kg ⁻¹)	Copper (mg kg ⁻¹)	Chromium (mg kg ⁻¹)	Zinc (mg kg ⁻¹)	Arsenic (mg kg ⁻¹)
Chkalovo							
NUR GR 24/1	1.6	232	<LOD	38.9	30.2	146	NA
NUR SED 6	11.8	14.0	<LOD	23.5	24.4	62.0	NA
NUR SED 7	10.1	7.80	<LOD	7.80	11.7	43.8	NA
NUR SED 6. – HIST	17.0	15.7	0.60	21.4	15.3	66.2	NA
NUR WAT 1	NA	NA	NA	NA	NA	NA	NA
NUR-14/1	1.24	38.6	<LOD	406	35.2	156	<LOD
NUR-SED-14/4	1.23	2.60	<LOD	20.9	24.6	60.1	<LOD
NUR-SED-14/5	0.71	8.59	<LOD	7.95	<LOD	30.5	<LOD
Krasniye Gorki							
NUR GR 3	<LOD	5.70	<LOD	10.8	12.6	23.9	NA
NUR SED 5	178	20.7	<LOD	20.2	14.7	64.8	NA
Samarkand							
NUR GR 1	<LOD	5.40	<LOD	16.7	11.4	49.9	NA
NUR SED 1	10.8	12.0	<LOD	14.9	21.2	42.2	NA
Gagarinskoe							
NUR GR 2	<LOD	10.0	<LOD	23.4	23.0	70.7	NA
NUR SED 2	70.8	18.0	<LOD	18.0	20.7	73.9	NA
NUR SED 3	4.03	9.10	<LOD	11.1	11.4	35.3	NA
NUR SED 4	80.0	11.6	0.80	29.0	40.3	122	NA
Tegiszhol							
NUR – 24/3	2.19	14.7	<LOD	17.2	23.6	52.8	NA
Rostovka							
NUR – 24/1	2.17	10.7	<LOD	15.6	17.1	42.6	NA
NUR – 24/2	5.26	14.2	<LOD	20.5	19.9	56.9	NA

Sample Code	Mercury (mg kg ⁻¹)	Lead (mg kg ⁻¹)	Cadmium (mg kg ⁻¹)	Copper (mg kg ⁻¹)	Chromium (mg kg ⁻¹)	Zinc (mg kg ⁻¹)	Arsenic (mg kg ⁻¹)
Kyzylhar							
NUR-SED-14/3	0.15	5.86	<LOD	11.3	<LOD	26.7	<LOD
Intumak Reservoir							
NUR-SED-14/1	1.99	38.6	<LOD	406	35.2	156	<LOD
NUR-SED-14/2	0.34	<LOD	<LOD	11.4	17.7	27.1	<LOD

TABLE 3: CONTENT OF METHYLMERCURY IN SELECTED SEDIMENTS FROM THE RIVER NURA. THE CONTENT OF METHYLMERCURY IS GIVEN IN mg kg⁻¹ OF DRY MATTER.

Standard deviation (SD) of the measurement is 10 %.

Sample Code	Methylmercury (mg kg ⁻¹)
NUR SED 1	0.015
NUR SED 2	<0.007
NUR SED 3	0.048
NUR SED 5	0.093
NUR SED 6	0.015
NUR SED 7	0.026
NUR SED 6 – HIST.	0.025

TABLE 4: CONTENT OF MERCURY AND OF METHYLMERCURY IN FISH FROM INTUMAK RESERVOIR. THE CONTENT IS GIVEN IN mg kg⁻¹ OF FISH MEAT.

Standard deviation (SD) of the measurement is 12 %.

Sample Code	Mercury (mg kg ⁻¹)	Methylmercury (mg kg ⁻¹)
NUR-F-14/1/1	0.442	0.343
NUR-F-14/1/2-3	1.38	1.36
NUR-F-14/2	0.634	0.543

TABLE 5: CONTENT OF PCBS IN SEDIMENTS AND SOILS. CONTENT IS GIVEN IN µg kg⁻¹ OF DRY MATTER.

<LOD: analyte concentration was below limit of detection.

Sample Code	PCB 28 (µg kg ⁻¹)	PCB 52 (µg kg ⁻¹)	PCB 101 (µg kg ⁻¹)	PCB 118 (µg kg ⁻¹)	PCB 138 (µg kg ⁻¹)	PCB 153 (µg kg ⁻¹)	PCB 180 (µg kg ⁻¹)	Sum of PCB 28, 52, 101, 138, 153, 180 (µg kg ⁻¹)
NUR-24/1	0.19	14.0	0.30	<LOD	<LOD	<LOD	<LOD	14.49
NUR-24/2	2,860	1,237	435	<LOD	58	333	63.6	4,986.6
NUR-24/3	0.27	7.32	<LOD	<LOD	<LOD	<LOD	<LOD	7.59
NUR-24/5	1.07	4.70	0.08	<LOD	<LOD	<LOD	<LOD	5.85

Sample Code	PCB 28 ($\mu\text{g kg}^{-1}$)	PCB 52 ($\mu\text{g kg}^{-1}$)	PCB 101 ($\mu\text{g kg}^{-1}$)	PCB 118 ($\mu\text{g kg}^{-1}$)	PCB 138 ($\mu\text{g kg}^{-1}$)	PCB 153 ($\mu\text{g kg}^{-1}$)	PCB 180 ($\mu\text{g kg}^{-1}$)	Sum of PCB 28, 52, 101, 138, 153, 180 ($\mu\text{g kg}^{-1}$)
NUR-24/6	0.17	8.21	5.16	<LOD	2.57	2.70	2.94	21.75
NUR-24/7	0.18	4.37	0.63	<LOD	<LOD	<LOD	<LOD	5.18
NUR-24/8	29,090	4,550	759	<LOD	50.4	415	56	34,920.4
NUR SED 5	27,600	4,880	1,100	<LOD	94.1	699	128	29,621.1
NUR SED 6	0.30	3.07	3.59	<LOD	1.51	2.36	1.62	12.45
NUR SED 7	1.04	6.60	1.96	<LOD	<LOD	<LOD	<LOD	9.6
TEM-CHL 2	0.05	2.29	0.36	<LOD	<LOD	<LOD	<LOD	2.7
TEM-CHL 11	0.09	0.53	0.19	<LOD	<LOD	<LOD	<LOD	0.81

TABLE 6: CONTENT OF PCBS IN FISH AND EGGS (PER KG OF FRESH WEIGHT).

Sample Code	Fat (%)	PCB 28 ($\mu\text{g kg}^{-1}$)	PCB 52 ($\mu\text{g kg}^{-1}$)	PCB 101 ($\mu\text{g kg}^{-1}$)	PCB 118 ($\mu\text{g kg}^{-1}$)	PCB 138 ($\mu\text{g kg}^{-1}$)	PCB 153 ($\mu\text{g kg}^{-1}$)	PCB 180 ($\mu\text{g kg}^{-1}$)	Sum of PCB 28, 52, 101, 138, 153, 180 ($\mu\text{g kg}^{-1}$)
NUR-F-14/1/1	3.3	0.20	0.34	0.53	0.68	0.89	0.89	0.20	3.05
NUR-F-14/1/2+3	1.4	0.07	0.14	0.24	0.27	0.38	0.38	0.09	1.30
NUR-F-14/2	2.2	0.08	0.13	0.22	0.20	0.30	0.30	0.08	1.11
NUR-EGG-14/1	15	0.25	< 0.01	0.27	6.59	14.2	14.2	12.4	41.32
NUR-EGG-14/2	13.7	0.12	< 0.01	0.16	4.76	14.7	14.7	19.7	49.38

TABLE 7: CONTENT OF PCBS IN SELECTED SEDIMENTS AND FISH (DIOXINE-LIKE CONGENERS).

Standard deviation (SD) of the measurement is 30 %. Levels in sediments are in dry matter. Levels in fish are given per gram of fresh weight.

Sample Code	PCB 81 (pg g ⁻¹)	PCB 77 (pg g ⁻¹)	PCB 123 (pg g ⁻¹)	PCB 118 (pg g ⁻¹)	PCB 114 (pg g ⁻¹)	PCB 105 (pg g ⁻¹)	PCB 126 (pg g ⁻¹)	PCB 167 (pg g ⁻¹)	PCB 156 (pg g ⁻¹)	PCB 157 (pg g ⁻¹)	PCB 169 (pg g ⁻¹)	PCB 189 (pg g ⁻¹)	Sum of PCBs (pg g ⁻¹)
NUR SED 5	4.69	60.2	51	3,680	137	1,430	7.97	135	374	94.3	<0.143	13.6	5,987.76
NUR SED 6	8.76	114	49.7	1,760	73.3	810	5.78	70.3	205	49.1	<0.238	11.7	3,157.64
NUR-F-14/1/2-3	5.46	3.2	222	6.57	78.4	1.22	17.8	30.2	5.38	<0.143	1.6	1.6	373.43

TABLE 8: CONTENT OF OCPS IN SEDIMENTS AND SOILS. CONTENT IS GIVEN IN $\mu\text{g kg}^{-1}$ OF DRY MATTER.

<LOD: analyte concentration was below limit of detection.

Sample Code	2,4'DDD ($\mu\text{g kg}^{-1}$)	4,4'DDD ($\mu\text{g kg}^{-1}$)	2,4'DDE ($\mu\text{g kg}^{-1}$)	4,4'DDE ($\mu\text{g kg}^{-1}$)	2,4'DDT ($\mu\text{g kg}^{-1}$)	4,4'DDT ($\mu\text{g kg}^{-1}$)	alpha- HCH ($\mu\text{g kg}^{-1}$)	beta- HCH ($\mu\text{g kg}^{-1}$)	gamma- HCH ($\mu\text{g kg}^{-1}$)	delta- HCH ($\mu\text{g kg}^{-1}$)	delta- HCH ($\mu\text{g kg}^{-1}$)	hepta chlor ($\mu\text{g kg}^{-1}$)	methoxy chlor ($\mu\text{g kg}^{-1}$)
NUR-24/1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NUR-24/2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NUR-24/4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	6.5	<LOD	<LOD	<LOD	<LOD	<LOD
NUR-24/5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NUR-24/8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NUR-24/9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NUR GR 24/1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	6.3	<LOD	<LOD	<LOD	<LOD	<LOD
NUR SED 1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4.9	<LOD	<LOD	<LOD	<LOD	<LOD
NUR SED 2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
NUR SED 3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4.8	<LOD	<LOD	<LOD	<LOD	<LOD
NUR SED 4	<LOD	20.1	<LOD	<LOD	<LOD	<LOD	3.4	7.8	<LOD	<LOD	<LOD	11.0	<LOD
NUR SED 5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.8	<LOD	<LOD	<LOD	<LOD	<LOD
NUR SED 6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.4	<LOD	<LOD	<LOD
NUR SED 7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
TEM-CHL 2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	5.3	18.7	3.9	46.3	4.5	<LOD	<LOD
TEM-CHL 3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	18.6	<LOD	<LOD	<LOD	<LOD	<LOD
TEM-CHL 4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	5.9	<LOD	<LOD	<LOD	<LOD	<LOD
TEM-CHL 5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
TEM-CHL 6	4.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	19.4	<LOD	<LOD	<LOD	<LOD	<LOD
TEM-CHL 11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	177.5	<LOD	<LOD	<LOD

TABLE 9: CONTENT OF OCPs IN FISH AND EGGS.

Sample Code	Fat (%)	2,4'DDD (µg kg ⁻¹)	4,4'DDD (µg kg ⁻¹)	2,4'DDE (µg kg ⁻¹)	4,4'DDE (µg kg ⁻¹)	2,4'DDT (µg kg ⁻¹)	4,4'DDT (µg kg ⁻¹)	alpha-HCH (µg kg ⁻¹)	beta-HCH (µg kg ⁻¹)	gamma-HCH (µg kg ⁻¹)	HCB (µg kg ⁻¹)
NUR-F-14/1/1	3.3 %	0.12	3.56	0.31	0.05	2.50	0.24	0.34	0.64	0.16	0.22
NUR-F-14/1/2+3	1.4 %	0.02	1.54	0.16	< 0.03	0.72	0.09	0.11	0.23	0.04	0.12
NUR-F-14/2	2.2 %	0.02	1.65	0.16	0.05	0.68	< 0.03	0.15	0.39	0.08	0.13
NUR-EGG-14/1	15.0 %	< 0.01	12.90	< 0.03	0.14	0.54	6.88	0.48	6.03	0.34	0.35
NUR-EGG-14/2	13.7 %	< 0.01	8.21	< 0.03	0.21	0.53	6.29	0.14	1.80	0.16	0.69

7. DISCUSSION

Various legal standards and auxiliary evaluation criteria are presented in this chapter. The heavy metals and PCB concentrations determined in samples from the investigated locations are then compared to respective legal standards. Finally, target samples with high content of metals and PCBs were chosen for calculation of health risks associated with them.

7.1 Legal standards

The pollutant concentrations determined in the samples from the investigated sites were compared to maximum or allowed concentrations of these pollutants as defined in national and international decrees, norms and laws.

Concentrations of mercury in soils and sediments were compared with criteria set out in the “River Nura Clean Up Project”. These criteria were confirmed by the Ministry of Health of Kazakhstan and were defined as follows: the clean-up criterion of 2.1 mg kg⁻¹ was applied for agricultural areas and inhabited localities (e.g. house gardens used

for growing vegetables and fruits); a clean-up criterion of 10 mg kg⁻¹ was adopted for river bed sediments, river banks, Zhaur swamp, and floodplains; and for more remote areas it was 50 mg kg⁻¹.

Concentrations of pollutants were compared with values given in the legal normative Act no. 168 on hygienic requirements for air quality in urban and rural settlements and the quality of soil and its safety, which was established by the Government Resolution of the Republic of Kazakhstan in January 2012 (GORK, 2012). Maximum allowable concentrations of certain chemicals in soil are given in the Annex of the Act. Limits for chemicals, which are not given by the Act no. 168, can be found in the regulation on norms of maximum allowable concentrations of harmful substances, harmful micro-organisms and other biological contaminants in the soil, established by the Ministry of Health and Ministry of Environment of Kazakhstan in 2004 (MH and MoE, 2004).

Concentrations of pollutants in samples were also compared with RSL (Regional Screening Levels). These levels were derived using exposure parameters and factors representing the maximum justifiable chronic exposure. This exposure is based on direct contact with target compounds. Regional screening levels were derived by the US EPA (United States Environmental Protection Agency) for some compounds that have a CAS registration number (MZP, 2014, US EPA, 2015a). RSL are concentrations of chemical compounds in the environment (soils, sediments, water and air). If RSL are exceeded,

further exploration or removal of contamination should be carried out. Some specifics should be taken into account when RSL are used - such as the content of some substances as a result of geological conditions.

Whereas the sediments from the River Nura can be floated on surrounding land, we can compare concentration of pollutants with limits in Decree no. 257/2009 for use of sediments on agricultural soils (MZe, 2009). This decree defines the maximum possible concentrations of hazardous metals in sediments which are intended for use on agricultural land.

TABLE 10: LEGAL STANDARDS FOR HEAVY METALS IN SOILS. THE CONTENT OF ELEMENTS IS GIVEN IN mg kg⁻¹ OF DRY MATTER.

	Mercury	Lead	Cadmium	Copper	Chromium (total)	Zinc	Arsenic
Clean-up criterion for agricultural areas and inhabited localities	2.1	-	-	-	-	-	-
Clean-up criterion for river bed sediments, river banks, Zhaur swamp, and floodplains	10	-	-	-	-	-	-
Clean-up criterion for more remote areas	50	-	-	-	-	-	-
Kazakhstan – hygienic normatives for soil	2.1	32	0.5	3.0	6.0	-	2.0
Levels of pollution limits – industrial areas (based on US EPA)	43	800	800	41,000	-	310,000	2.4
Levels of pollution limits – other areas (based on US EPA)	10	400	70	3,100	-	23,000	0.61
Cz Decree – use of sediments on agricultural soils	0.8	100	1	100	200	300	30

TABLE 11: LEGAL STANDARDS FOR PCBS AND OCPS IN SOILS. THE CONTENT OF ELEMENTS IS GIVEN IN mg kg⁻¹ OF DRY MATTER.

	PCB (individual congeners)	PCB (a mixture of congeners)	DDD	DDE	DDT	alpha-HCH	beta-HCH	gamma-HCH	HCB	hepta chlor	me-thoxy chlor
Kazakhstan – hygienic normatives for soil	-	-	-	-	0.1	0.1	0.1	0.1	0.08	0.05	-
Levels of pollution limits – industrial areas (based on US EPA)	0.38	0.74	7.2	5.1	7.0	0.27	0.96	2.1	1.1	0.38	3,100
Levels of pollution limits – other areas (based on US EPA)	0.11	0.22	2.0	1.4	1.7	0.077	0.27	0.52	0.3	0.11	310
Cz Decree – use of sediments on agricultural soils	-	0.2	-	-	0.1	-	-	-	-	-	-

Ed.1: US EPA screening levels were derived for individual congeners PCB 105, 114, 118, 123, 156, 157, 167 and 189. According to Czech law, the sum of congeners PCB 28, 52, 101, 138, 153 and 180 can be used instead of congeners defined by the US EPA.

Ed.2: According to Cz Decree - use of sediments on agricultural soils - limit for PCBs is given by the sum of PCB 28, 52, 101, 118, 138, 153 and 180, limit for DDT also includes the sum of the concentrations of all types of its metabolites.

Concentration of contaminants in fish and eggs were compared with limits defined in Commission Regulation (EC) no. 1881/2006, dated 19 December 2006, setting maximum levels for certain contaminants in foodstuffs. In the case of polychlorinated biphenyls (PCBs) the sum of 6 congeners (PCB 28, 52, 101, 138, 153 and 180) is used. The sum of dioxine-like polychlorinated biphenyls (PCBs) is expressed in toxicity equivalency factor (TEF) of the World Health Organization (WHO) using WHO-TEF. WHO-TEF for assessing human health risks based on the conclusions of the WHO meeting in Stockholm, Sweden, 15 to 18 June 1997. In the interests of effective protection of public health, products containing contaminants in excess of the maximum levels should not be placed on the market.

According to EPA-823-R-01-001, a Reference Dose (RfD) for methylmercury (based on noncancerous human health effects) is 0.0001 mg methylmercury/kg body weight-day. It is intended to serve as a level of exposure without expectation of adverse effects when that exposure is encountered on a daily basis for a lifetime.

TABLE 12: MAXIMUM LEVELS FOR MERCURY IN FOODSTUFFS (COMMISSION REGULATION (EC) NO. 1881/2006).

Foodstuffs	Maximum level for mercury (mg kg ⁻¹ of fresh weight)
Fishery products and muscle meat of fish (excluding species listed below)	0.5
Selected fishery products and muscle meat of fish: <i>Lophius</i> spp., <i>Anarhichas lupus</i> , <i>Sarda sarda</i> , <i>Anguilla</i> spp., <i>Hoplostethus</i> spp., <i>Coryphaenoides rupestris</i> , <i>Hippoglossus hippoglossus</i> , <i>Genypterus capensis</i> , <i>Makaira</i> spp., <i>Lepidorhombus</i> spp., <i>Mullus</i> spp., <i>Genypterus blacodes</i> , <i>Esox lucius</i> , <i>Orcynopsis unicolor</i> , <i>Trisopterus minutus</i> , <i>Centroscymnus coelolepis</i> , <i>Raja</i> spp., <i>Sebastes marinus</i> , <i>S. mentella</i> , <i>S. viviparus</i> , <i>Istiophorus platypterus</i> , <i>Lepidopus caudatus</i> , <i>Aphanopus carbo</i> , <i>Pagellus</i> spp., <i>Carcharodon</i> spp., <i>Lepidocybium flavobrunneum</i> , <i>Ruvettus pretiosus</i> , <i>Gempylus serpens</i> , <i>Acipenser</i> spp., <i>Xiphias gladius</i> , <i>Thunnus</i> , <i>Euthynnus</i> , <i>Katsuwonus pelamis</i> .	1.0

Concentration of pesticide residues (any specified substances in food, agricultural commodities, or animal feed resulting from the use of a pesticide; the term includes any derivatives of a pesticide, such as conversion products, metabolites, reaction products, and impurities considered to be of toxicological significance) were compared to Maximum Residue Limit (MRL), which is the maximum concentration of a pesticide residue (expressed as mg kg⁻¹) legally permitted in food or food commodities and animal feeds. MRLs are based on Good Agricultural Practice in the Use of Pesticides (GAP) data and foods derived from commodities that comply with the respective MRLs are intended to be toxicologically acceptable. MRLs values are defined in Commission Regulation (EC) no. 396/2005 and in Codex Maximum Residue Limits for Pesticides adopted by the Codex Alimentarius Commission up to and including its 36th Session (July 2013). The foods listed shall not contain more than the MRL of the pesticide residue (defined in each individual case in the definition of residue) at (a) the point of entry into a country or (b) at the point of entry into trade channels within a country. This maximum limit shall not be exceeded at any time thereafter.

TABLE 13: MAXIMUM LEVELS FOR PCBs IN FOODSTUFFS (COMMISSION REGULATION (EC) NO. 1881/2006).

Foodstuffs	Maximum level	
	The sum of dioxine-like PCBs (WHO-PCDD/F-PCB- TEQ)	The sum of PCB28, PCB52, PCB101, PCB138, PCB153 a PCB180 (ICES – 6)
Muscle meat and fishery products of wild-caught freshwater fish, with the exception of diadromic species caught in freshwater	6.5 pg g ⁻¹ of fresh weight	125 ng g ⁻¹ of fresh weight
Muscle meat and fishery products without: - wild-caught European eel - muscle meat and fishery products of wild-caught freshwater fish, with the exception of diadromic species caught in freshwater - fish liver and products derived there from - fat of marine animals	6.5 pg g ⁻¹ of fresh weight	75 ng g ⁻¹ of fresh weight
Chicken eggs and egg products	5.0 pg g ⁻¹ of fat	40 ng g ⁻¹ of fat

Ed. Detailed specifications of contaminants in foodstuffs are given in Commission Regulation (EC) no. 1881/2006.

TABLE 14: MAXIMUM RESIDUE LIMIT (MRL) FOR PESTICIDES IN COMMODITIES (COMMISSION REGULATION (EC) NO. 396/2005).

Commodity	Maximum Residue Limit (MRL)			
	DDT (sum of 2,4-DDT, 4,4-DDT, 4-4-DDE and 4,4- DDD expressed as DDT)	alpha - HCH	beta - HCH	gamma - HCH
Eggs	0.05 mg kg ⁻¹	0.02 mg kg ⁻¹	0.01 mg kg ⁻¹	0.01 mg kg ⁻¹
Meat (from mammals other than marine mammals)	5.0 mg kg ⁻¹	0.1 mg kg ⁻¹		

8. EVALUATION OF POLLUTANT LEVELS

The main objective of the research was to determine the concentration of mercury in the profile of the river between Samarkand Reservoir and Intumak Reservoir. Other objectives of the study were to determine the content of methylmercury, polychlorinated biphenyls – PCBs, organochlorinated pesticides – OCPs and heavy metals in selected samples of sediments and soils and determination of pollutants in fish and egg samples.

The following are descriptions of the sites that are listed by distance from Samarkand Reservoir near Temirtau.

Three samples of sediments were taken from Samarkand Reservoir (two samples on the bank beneath the Karbid factory grounds, near the sewage drain into the reservoir, and one sample in the northern part of the reservoir at the Japanese bay, opposite the

factory building) and two samples of sediments from the River Nura under a road bridge between two parts of Temirtau. Content of mercury was below clean-up criterion in all samples from the area. In one sample from Samarkand Reservoir (Japanese bay), high concentrations of PCBs were determined (34.9 mg kg⁻¹ for the sum of PCB 28, 52, 101, 138, 153, 180) which exceed levels of pollution limits for soils for non-industrial areas by more than 100 times. Nine samples of sediments, soils and ash were taken from the chemical tailings pond of the Karbid factory and three samples of sediments and soils from its vicinity. Conducted analysis did not show significant contamination of the area.

Five samples of sediments, two samples of soil, one sample of water and two mixed samples of eggs were taken from local homes and dachas in Chkalovo, which is the first

village downstream from Temirtau. The River Nura spills wider here, forming distributaries with small islands and sand spits. There are two sewage drains close to Chkalovo, probably from the Karbid factory, that flow into the River Nura. Concentration of mercury in three samples of sediments from both sewage drains (11.8 mg kg⁻¹, 17.8 mg kg⁻¹ and 10.1 mg kg⁻¹) exceed clean-up criterion. Increased concentration of mercury were detected in soils (1.60 mg kg⁻¹ and 1.24 mg kg⁻¹) taken at the edge of the village. Maximum levels for PCBs in foodstuffs (Commission Regulation (EC) no. 1881/2006) were exceeded in eggs obtained from local homes.

The highest concentration of mercury was determined in a sample taken near Krasniye Gorki, which is a rocky site on the edge of Temirtau, next to a road. The sediment sample comes from an open landscape near the road bridge. One soil sample was taken under the bridge from an excavated alluvial soil pile. The content of mercury in the sediment was 178 mg kg⁻¹. This value exceeds clean-up criterion by almost 18-times. In this sample very high concentrations of PCBs were also determined (29.6 mg kg⁻¹ for the sum of PCB 28, 52, 101, 138, 153, 180) which exceed levels of pollution limits for soils for non-industrial areas by more than 100 times.

One sample of sediment, one sample of soil and one mixed egg sample were taken in Samarkand. The clean-up criterion was exceeded in the sediment sample (10.8 mg kg⁻¹) which was taken near sandy beaches and spits.

Serious remaining mercury contamination was detected in sediments sampled near Gagarinskoe. Concentrations of 70.8 mg kg⁻¹, respectively 80.0 mg kg⁻¹ of mercury was determined in two of three samples of sediments taken there. Content of mercury in one soil sample was below the detection limit.

Another sediment sample taken near the bridge next to Tegiszhul showed the content of mercury of 2.19 mg kg⁻¹; clean-up criterion was not exceeded there.

Increased concentrations of mercury were detected in two samples of sediments taken on the edge of the village of Rostovka (max. 5.26 mg kg⁻¹). In one sample, high concentrations of PCBs were also determined (4.99 mg kg⁻¹ for the sum of PCB 28, 52, 101, 138, 153, 180) which exceed levels of pollution limits for soils for non-industrial areas by 22 times. Maximum levels for PCBs in foodstuffs (Commission Regulation (EC) no. 1881/2006) were exceeded in eggs from a household on the southern end of the village, next to the road to Kyzylzhar and close to the river.

One sample of sediment with relatively low concentrations of mercury (0.15 mg kg⁻¹) was taken next to Kyzylzhar, which is a village in the River Nura bed, located close to Intumak Reservoir.

Two samples of sediments were taken at the beginning of the Intumak Reservoir, after the River Nura confluence. Increased levels of mercury were detected there (max. 1.99 mg kg⁻¹). Five fish samples were collected from local fishermen at the beginning of the reservoir. The sampled fish species were crucian carp (*Carassus carassus*), perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*). Roach and crucian carp are omnivores, feeding on plant material and invertebrates, while perch is a carnivore feeding on smaller fish. Maximum levels for mercury in foodstuffs (Commission Regulation (EC) no. 1881/2006) were exceeded in roach and exceeded by almost three times in perch. The daily reference dose for methylmercury (according to US EPA, 2001) was significantly exceeded for an average consumption of all collected fish.

Concentration of OCPs in soils and sediments were below international levels of pollution limits (US EPA, 2015a) and also below Kazakhstani hygienic normatives for soil. OCPs were detected in samples of fish and eggs with concentrations below the international maximum pesticide residue limits (Commission Regulation (EC) no. 396/2005).

Concentrations of other measured heavy metals (lead, cadmium, copper, chromium, zinc and arsenic) did not exceed international levels of pollution limits. Increased concentration of lead (slightly exceeding Kazakhstani hygienic normatives for soils) was measured in one soil sample near Chkalovo.

8.1 Auxiliary criteria

Content of metals can be compared with other auxiliary criteria - soil, ground water and soil air pollution criteria according to the methodological guidelines of the Czech Ministry of Environment of 31 July 1996 (MZP, 1996). These criteria are not legally binding, however, and often applied in the Czech Republic on a voluntary basis. Criteria A approximately correspond to the natural concentration level of the chemical substance in the environment; therefore it may serve to estimate the approximate background levels.

TABLE 15: AUXILIARY CRITERIA FOR SOILS. THE CONTENT OF ELEMENTS IS GIVEN IN mg kg⁻¹ OF DRY MATTER (IF NOT SPECIFIED).

Criterion	Mercury	Lead	Cadmium	Copper	Chromium (total)	Zinc	Arsenic	PCBs - the sum of PCB 28, 52, 101, 118, 138, 153 and 180 -in ng I-TEQ Te CDD g ⁻¹	Organochlorinated pesticides (individual)
A	0.4	80	0.5	70	130	150	30	0.02	0.05
B	2.5	250	10	500	450	1,500	65	2.5	2
C – residential area	10	300	20	600	500	2,500	70	5	2.5
C – recreation area	15	500	25	1,000	800	3,000	100	10	5
C – industrial area	20	800	30	1,500	1,000	5,000	140	30	10

Criteria A approximately correspond to the natural concentration level of the chemical substance in the environment. The exceedance of criteria A is considered as a contamination of the particular environmental compartment except in areas with a naturally higher abundance of the chemical substance. If criteria B are not exceeded, the contamination is not considered sufficiently significant to justify the need for more detailed information on the contamination, e.g. to start an investigation or monitoring of the contamination.

Criteria B are considered a contamination level that may have negative impacts on human health and individual environmental compartments. It is necessary to gather additional information to find out whether the site represents a significant environmental burden and what risks it poses. Criteria B are therefore designed as intervention levels which, when exceeded, justify the demand for further investigation on the contamination. The exceedance of criteria B requires a preliminary assessment of risks posed by the contamination, the identification of its source and reasons and - according to the investigation results - a decision on further investigation and start of a monitoring campaign.

The exceedance of criteria C represents a contamination which may pose a significant risk to human health and environmental compartments. The risk level can be determined only by a risk analysis. The recommended levels of remediation target parameters resulting from the risk analysis can be higher than criteria C. In addition to the risk analysis, assessments of technical and economic aspects of the problem solution are necessary documents for the decision on the type of remedial measures.

9. HEALTH RISK ASSESSMENT

Health risk assessment is based on the assumption that, under certain specified conditions, there is a risk of damage to human health, while the risk rate from zero to maximum is determined by the type of activity, state of the location and conditions of the environment. Zero health risk is not really possible; however, the risk of damage must be minimized to an acceptable level in terms of health and environmental risks. To determine the risk, it is necessary to clarify the most important transport routes and then specify exposure scenarios for potentially threatened recipients. There are two approaches to evaluate the dose effects – for substances with threshold (non-carcinogenic) and non-threshold (carcinogenic) effect.

For substances with non-carcinogenic effects it is anticipated that the body repair processes are able to successfully cope with exposure to a toxic substance, but only to a certain dose, when the negative effect on human health is already apparent. At threshold value, known as the NOAEL (No Observed Adverse Effect Level), the exposure level is one at which no adverse effects is observed. Alternatively, values such as LOAEL (Lowest Observed Adverse Effect Level) can be used. They correspond to the lowest dose levels at which the negative health effects are observed. ADI (Acceptable Daily Intake) or RfD (Reference Dose) are derived using NOAEL or LOAEL values and relevant UF (Uncertainty Factors) or MF (Modifying Factors). These factors have to compensate for all the uncertainty and variability in determining the NOAEL and LOAEL values. The results of calculations (ADI or RfD) are usually much lower than NOAEL or LOAEL and represent the estimation of a daily exposure to the human population (including sensitive population groups), which is very likely to pose no risk of adverse effects to human health, even if it lasts throughout a lifetime (US EPA, 2015b). In the case of carcinogenic substances, it is assumed that there is no such

dose that would not cause modifications at the molecular level and subsequently lead to the formation of malignant disease. Evaluation of the dose-effect relation uses parameter SF (Slope Factor) which indicates the possible top edge of the probability of malignant disease per unit of average daily dose received throughout a lifetime (IARC, 2015).

For the calculation of risk exposure to substances with non-carcinogenic effects, a received and absorbed dose with acceptable toxicological intake of the substance is compared (i.e. RfD – Reference Dose). The risk level then represents Hazard Quotient HQ. The calculation is performed according to the equation:

$$HQ = \frac{E}{RfD}$$

E – parameter Average Daily Dose (ADD) or Lifetime Average Daily Dose (LADD), respectively Chronic Daily Intake (CDI) (mg kg⁻¹ day);

RfD – Reference Dose (mg kg⁻¹ day).

The calculation method for substances with carcinogenic effects uses the parameter ELCR - Excess Lifetime Cancer Risk (dimensionless indicator) corresponding to the probability of developing cancer with a lifetime of exposure, which can be described by the following equation:

$$ELCDR = CDI \times SF$$

$$ELCDR = LADD \times SF$$

CDI – parameter Chronic Daily Intake, respectively Lifetime Average Daily Dose (LADD) relative to lifetime exposure of 70 years (mg kg⁻¹ day);

SF – Slope Factor (mg kg⁻¹ day).

TABLE 16: AGENTS CLASSIFIED BY THE IARC MONOGRAPHS.

Group 1	Carcinogenic to humans
Group 2A	Probably carcinogenic to humans
Group 2B	Possibly carcinogenic to humans
Group 3	Not classifiable as to its carcinogenicity to humans
Group 4	Probably not carcinogenic to humans

Samples in which levels of pollution limits for other areas (US EPA, 2015b) were exceeded were used to perform human health risk assessment. In these samples high levels of arsenic and lead were detected and the corresponding risks for these heavy metals were calculated.

The International Agency for Research on Cancer (IARC) recognizes: mercury and inorganic mercury compounds as Group 3 – Not classifiable as to its carcinogenicity to humans; methylmercury compounds as Group 2B – Possibly carcinogenic to humans;

and Polychlorinated biphenyls, dioxin-like, with a Toxicity Equivalency Factor (TEF) according to WHO (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) as Group 1 – Carcinogenic to humans (IARC, 2015).

On the basis of the toxicological data, a risk assessment using RISC software was performed.

RISC model

Risk-Integrated Software for Cleanups (RISC) is software developed to assess human health risks in contaminated areas. It can integrate up to fourteen possible exposure pathways, and calculates the risks associated with them, both carcinogenic and non-carcinogenic.

If the carcinogenic risk is $<10^{-6}$, it is considered that there are not significant adverse health effects. If it is between 10^{-6} and 10^{-4} , adverse effects may occur in the future, thus factors need to be taken into consideration. Finally, if it is $>10^{-4}$, the risk is unacceptable and serious measures must be immediately taken. A hazard quotient (HQ) <1 is considered when there are not significant adverse health effects, whereas a HQ >1 implies that potential adverse health effects exist. More research must be done in order to determine any toxic threats.

TABLE 17: RESULTS OF THE CALCULATION OF HUMAN HEALTH RISKS ASSOCIATED WITH MERCURY IN SELECTED SAMPLES – HAZARD QUOTIENTS (HQ).

Contaminant	Locality	Sample	Concentration in soil (mg kg ⁻¹)	Exposition pathway			
				Ingestion of soil	Dermal contact of soil	Ingestion of vegetable	
Mercury	Chkalovo	NUR SED 6	11.8	8.4E-02	1.7E-02	3.5E+00	3.6E+00
		NUR SED 7	10.1	7.2E-02	1.4E-02	3.0E+00	3.1E+00
		NUR SED 6. - HIST	17.0	1.2E-01	2.4E-02	5.1E+00	5.2E+00
	Krasniye Gorki	NUR SED 5	178	1.3E+00	2.5E-01	5.3E+01	5.5E+01
	Samarkand	NUR SED 1	10.8	7.7E-02	1.5E-02	3.2E+00	3.3E+00

Contaminant	Locality	Sample	Concentration in soil (mg kg ⁻¹)	Exposition pathway			
Mercury				Ingestion of soil	Dermal contact of soil	Ingestion of vegetable	
	Gagarinskoe	NUR SED 2	70.8	5.0E-01	9.9E-02	2.1E+01	2.2E+01
		NUR SED 3	4.03	2.9E-02	5.6E-03	1.2E+00	1.2E+00
		NUR SED 4	80.0	5.7E-01	1.1E-01	2.4E+01	2.5E+01
	Tegiszhol	NUR 24/3	2.19	1.6E-02	3.1E-03	6.6E-01	6.8E-01
	Rostovka	NUR 24/1	2.17	1.5E-02	3.0E-03	6.5E-01	6.7E-01
		NUR 24/2	5.26	3.7E-02	7.4E-03	1.6E+00	1.6E+00

TABLE 18: RESULTS OF THE CALCULATION OF HUMAN HEALTH RISKS ASSOCIATED WITH DIOXIN-LIKE PCBS WITH A TOXICITY EQUIVALENCY FACTOR (TEF) ACCORDING TO WHO IN SELECTED SAMPLES - CARCINOGENIC RISK.

Contaminant	Locality	Sample	Concentration in soil (mg kg ⁻¹)	Exposition pathway			
Dioxine-Like PCBs				Ingestion of soil	Derma contact of soil	Ingestion of vegetable	Total
	Chkalovo	NUR SED 6	5,987.76	2.2E-06	6.0E-07	1.2E-06	4.0E-06
	Krasniye Gorki	NUR SED 5	3,157.64	1.2E-06	3.2E-07	6.6E-07	2.1E-06

TABLE 19: RESULTS OF THE CALCULATION OF HUMAN HEALTH RISKS ASSOCIATED WITH PCBS IN SELECTED SAMPLES – HAZARD QUOTIENTS (HQ).

Contaminant	Locality	Sample	Concentration in soil (mg kg ⁻¹)	Exposition pathway			
Sum of PCBs				Ingestion of soil	Derma contact of soil	Ingestion of vegetable	Total
	Temirtau	NUR-24/8	34,920.4	3.7E+00	1.0E+00	2.1E+00	6.9E+00
	Chkalovo	NUR SED 6	6,000.21	6.4E-01	1.8E-01	3.6E-01	1.2E+00
	Krasniye Gorki	NUR SED 5	32,778.74	3.5E+00	9.6E-01	2.0E+00	6.5E+00
	Rostovka	NUR-24/2	4,986.6	5.3E-01	1.5E-01	3.0E-01	9.8E-01

Results are based on standard calculation coefficients defined in Risk-Integrated Software for Cleanups (RISC). Results are related to the average population. Risks result both from direct contact with soil or sediment and from ingestion of vegetables grown in contaminated localities. Contaminated sediments can be floated to agricultural land during the spring floods. Health risks arising from growing vegetables on such contaminated soil are shown on the hazard quotient (HQ). In the case of the most contaminated sample from Gagarinskoe - hazard quotients (HQ) resulting from ingestion of grown vegetable was exceeded more than 50 times. Hazard quotients (HQ) were also exceeded in the case of PCB content in some sediments from Temirtau, Chkalovo and Krasniye Gorki.

10. CONCLUSIONS

This study is focused on the monitoring and evaluation of contamination of the River Nura and its surroundings by mercury, methylmercury, polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs). A series of different kinds of samples were taken for analysis, which included both abiotic (sediments, soils) and biotic (fish, eggs) samples.

In general, mercury contamination still remains in some places where the concentration of mercury exceeds the defined limits. The most contaminated sediment samples were taken in an open landscape near Krasniye Gorki (178 mg kg^{-1}) and near Gagarinskoe (80 mg kg^{-1} and 70.8 mg kg^{-1}). These concentrations of mercury significantly exceed both international levels of pollution limits for non-industrial areas (10 mg kg^{-1}) and local criteria set out in the River Nura Clean-Up Project, defined as follows: 2.1 mg kg^{-1} for agricultural areas and inhabited localities; 10 mg kg^{-1} for river bed sediments, river banks, Zhaur swamp, and floodplains. High concentrations of mercury in sediments and soils represent unacceptable health risks for local inhabitants that result partly from direct contact with soil or sediment, but the main risk results from the ingestion of agricultural crops grown in contaminated localities. Contaminated sediments can be floated to agricultural land during the spring floods. Moreover, it was shown that mercury in sediments is transformed into a more toxic form of methylmercury. Long-term adverse health effects can be exacerbated by the consumption of local fish in which mercury and methylmercury have accumulated. Maximum levels for mercury in foodstuffs was exceeded almost three times in one sample of fish from Intumak Reservoir, and

the daily reference dose for methylmercury was significantly exceeded for an average consumption of fish from Intumak Reservoir.

There has been a significant reduction in the average mercury concentrations and the highest measured concentrations of mercury in the area due to the River Nura clean-up project. However, with such an extensive project it is necessary to pay high attention to further exploration and extended post-remediation monitoring that can reveal areas (remaining or undiscovered) with an increased concentration of mercury and provide for additional remedial measures.

Another worrying finding is that high concentrations of PCBs were determined in samples of sediments and eggs taken at several locations. Levels of pollution limits for soils for non-industrial areas were exceeded more than 100 times in the case of most contaminated samples. It was shown that PCBs enter the food chain - they were detected in fish from Intumak Reservoir, and concentration of PCBs in eggs from Chkalovo and Rostovka exceeded maximum levels for PCBs in foodstuffs. Concentration of OCPs in soils and sediments were below levels of pollution limits, OCPs were detected in samples of fish and eggs with concentrations that were below the international maximum pesticide residue limits.

Finally, continued research should be carried out, mainly in order to measure levels and spread of remaining mercury contamination resulting in additional remediation measures.

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Identification and Management of mercury, PCB and dioxin contaminated sites in Kazakhstan:

A Collective Impact approach to civil society engagement.

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Contract in support of Project:

“Empowering the civil society in Kazakhstan in improvement of chemical safety”
and Dioxin, PCBs and Waste WG of IPEN, April 2015

1. INTRODUCTION

This report is part of a broader project conducted by the Arnika – Toxics and Waste Programme (Czech Republic) in cooperation with EcoMuseum Karaganda and Center for Introduction of New Environmentally Safe Technologies (both Kazakhstan) entitled “Empowering the civil society in Kazakhstan through improvement of chemical safety”. This report provides guidance about identification and management of sites contaminated by toxic chemicals, in particular those polluted by mercury in Kazakhstan. In addition this document can also serve as a basis for further discussion between Civil Society Organizations (CSOs) and Government Agencies in Kazakhstan about additional steps needed in management of sites contaminated by mercury and persistent organic pollutants (POPs).

Contaminated sites result from a range of anthropogenic practises including industrial activity, mining and waste disposal. The primary concern in addressing contaminated sites is the potential threat to human health and the environment. Contaminated sites may be impacted by a single substance or a highly complex mixture of chemicals and metals depending on the source of the contamination.

The focus of this report is on sites contaminated by mercury but there is also discussion of dioxins¹ and furans (PCDD/PCDF), and dioxin like PCBs² (DL PCB) which are present at some contaminated sites in Kazakhstan.

1 The term Dioxin is commonly used to refer to a family of toxic chemicals that all share a similar chemical structure and a common mechanism of toxic action. This family includes seven of the polychlorinated dibenzo dioxins (PCDDs), ten of the polychlorinated dibenzo furans (PCDFs) and twelve of the polychlorinated biphenyls (PCBs). US EPA <http://www.epa.gov/pbt/pubs/dioxins.htm>. Dioxins are also regulated under the Stockholm Convention on Persistent Organic Pollutants due to their classification as a POP and extreme toxicity.

2 Polychlorinated Biphenyl (PCB) are Persistent Organic Pollutant (POP) banned from manufacture and use by the Stockholm Convention on Persistent Organic Pollutants. PCBs are no longer manufactured but are persistent in the environment from historical uses and dumps and have been demonstrated to cause cancer, as well as a variety of other adverse health effects on the immune system, reproductive system, nervous system, and endocrine system.

1.1 Basic information about mercury and contaminated sites

The toxic properties of elemental mercury have long been known and in recent decades the significance of mercury pollution at a global scale has become apparent. Contamination of the atmosphere, oceans, lakes and rivers with mercury has led to food chain impacts and widespread contamination of fisheries – a key protein source for much of the world’s population. In aquatic environments inorganic metallic mercury is converted to the highly toxic organic methylmercury by bacterial organisms. The methylmercury bioaccumulates and biomagnifies in aquatic organisms, reaching high concentrations in peak predators such as sharks, tuna and swordfish. In turn, human consumption of fish can lead to toxic levels of mercury accumulating in body tissues.

Mercury exposure at high levels can harm the brain, heart, kidneys, lungs, and immune system of people of all ages. High levels of methylmercury in the bloodstream of unborn babies and young children may harm the developing nervous system (US EPA 2014), making the child less able to think and learn and potentially reducing their IQ.

Mercury contaminated sites are a significant source of anthropogenic mercury contamination due to the physical properties of mercury that allow it to enter a vapor phase at room temperature (with a vapor pressure at room temperature of 0.002 mm Hg) and escape to atmosphere where it may deposit to aquatic environments far from the source (Rom 1992). Mercury from contaminated sites may also impact the local environment as rain washes it into waterways and drives infiltration into groundwater systems eventually carrying it to aquatic environments where methylation occurs. Contaminated sites can represent a serious health hazard to local communities from direct inhalation of vapor and contaminated dust, dermal exposure and contamination of food sources.

Global recognition of the severity of mercury pollution has led to the recent adoption of the Minamata Convention on Mercury³ which was opened for signing in October 2013. This Convention is an international legal instrument or Treaty designed to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds. The Convention currently has been signed by 128 countries and ratified by 12. The Minamata Convention will enter into legal force 90 days after it has been ratified by 50 nations. Kazakhstan has not yet signed or ratified the Minamata Convention on Mercury which would enable it to access international resources to better identify and manage mercury contamination. Further dialogue should be held between Civil Society Organisations (CSOs) and national decision-makers to explore the barriers to signing the treaty and the advantages of moving toward ratification.

The Minamata Convention requires the phase out of many products containing mercury, implements restrictions on trade and supply of mercury and establishes a framework to reduce or eliminate emissions and releases of mercury from industrial processes and mining. The Treaty addresses various elements of mercury contaminated sites under Article 11 (Waste) and Article 12 (Contaminated Sites).

A related international treaty, The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (The Basel Convention)⁴ also provides guidance on the management of mercury contaminated sites and wastes. The Basel Convention entered into force in 1992 with the overarching objective to protect human health and the environment against the adverse effects of hazardous wastes. The Basel Convention provides additional technical guidance on the management of mercury waste and mercury contamination in a consolidated document that is currently under review (Basel Convention 2012). Revision 5 of the Basel technical guidelines on mercury waste will be considered by the Conference of Parties in 2015. If accepted by the COP, the latest revision will contain more detailed guidance on mercury waste and contaminated sites that are relevant to the Articles of the Minamata Convention on Mercury. Updates and revisions of the guidance are accessible on the Basel Convention website.⁵

3 For more details on the adoption of the convention see the UNEP website <http://www.mercuryconvention.org/>

4 <http://www.basel.int/TheConvention/Overview/tabid/1271/Default.aspx>

5 <http://www.basel.int/Implementation/TechnicalMatters/DevelopmentofTechnicalGuidelines/MercuryWaste/tabid/2380/Default.aspx>

While these treaties serve to raise awareness of mercury contaminated sites and their impacts they do not contain legally binding requirements to remediate (clean up) mercury contaminated sites or suggest who is responsible for this activity. The stakeholder for site identification, assessment and remediation is generally national governments in the context of local legislation and regulation. However, there are critical roles for other stakeholders in this process, particularly for NGOs, CSOs and local communities affected by contaminated sites. These groups can play an active role in the identification and mapping of sites, sampling and analysis (under supervision from qualified authorities and with appropriate protection) and development of remediation options and post-remediation land use considerations. At a broader level CSOs and NGOs can raise awareness in the community about the sources and impacts of mercury pollution and ways to reduce it.

This document also provides guidance on principles to address contaminated sites that can be adopted irrespective of the national context. It includes a range of suggestions as to how contaminated sites policy, legislation and management may be developed taking into account local contexts including limited resources and cultural diversity. While taking into consideration legal, regulatory and financial issues relevant to mercury impacted sites this guidance prioritises the protection of human health and ecological integrity from the impacts of anthropogenic mercury pollution arising from contaminated sites.

1.2 The Minamata Convention and contaminated sites

The Minamata Convention on Mercury outlines activities parties can undertake to address contaminated sites and generate information for the public to raise awareness about their implications for human health and the environment. Kazakhstan is not yet a signatory to the convention and will need to take further steps at a national level to prepare for the necessary requirements. In the meantime guidance such as this document can assist to build capacity within the community, among NGOs and policy makers to address mercury and POPs contaminated sites within Kazakhstan.

Article 12 of the Minamata Convention on Mercury states that *‘each Party will endeavour to identify and assess sites contaminated by mercury and mercury compounds and that actions to reduce the risks posed by these sites will be performed in*

an environmentally sound manner (ESM). While Kazakhstan is not yet a signatory to the Convention, national environmental authorities could benefit from adopting the suggested approaches of the Convention for assessing mercury contaminated sites.

At this point the parties to the Convention have not yet developed specific guidance for contaminated sites but this does not prohibit national governments from developing their own management frameworks, policies and legislation to assess, identify, characterize and remediate contaminated sites. As Kazakhstan makes progress toward ratification of the Minamata Convention on Mercury it is important to be aware of the specific statements made in the treaty about mercury contaminated sites and the need for public engagement.

While the Convention is yet to develop specific, detailed guidance on the management of mercury contaminated sites it is suggested that the activities that should be undertaken include:

- » Site identification and characterization;
- » Engaging the public;
- » Human health and environmental risk assessments;
- » Options for managing the risks posed by contaminated sites;
- » Evaluation of benefits and costs; and
- » Validation of outcomes.

In addition, Parties are encouraged to develop strategies and implementing activities for *“identifying, assessing, prioritizing, managing and, as appropriate, remediating contaminated sites.”*

The Minamata Convention is specifically focused on sites contaminated with mercury and mercury compounds but the processes identified above can be applied to sites with any form of chemical contamination.

Other articles of the Convention that may have relevance to contaminated sites include:

Article 11 – Mercury wastes;

Article 13 – Financial resources and mechanism;

Article 14 – Capacity-building, technical assistance and technology transfer;

Article 16 – Health aspects;

Article 17 – Information exchange;

Article 18 – Public information, awareness and education;

Article 19 – Research, development and monitoring.

Under Article 12 “Contaminated sites”, the Conference of Parties are required to prepare guidance on managing contaminated sites that include methods and approaches for “Engaging the Public” (UNEP 2013).

In addition, under Article 18 “Public information, awareness and education”, each Party is required to provide to the public information on mercury pollution as well as the “results of its research, development and monitoring activities under Article 19”. Parties are also required to provide education, training and public awareness related to mercury health effects in collaboration with relevant intergovernmental and NGOs and vulnerable populations.

Public engagement and the empowerment of civil society through cross-sector collaboration and cooperation requires an integrated two way approach between a national and regional level engagement of civil society and a local site specific process of stakeholder engagement. Each process should have the capacity to inform and adapt the other. However, public engagement needs also to take into consideration the specific cultural, social and political context to be most effective.

Kazakhstan should give further consideration to the steps necessary to ratify the Convention to improve potential access to technical assistance and technology transfer (Article 14) and financial resources (Article 13) that would support the development of mercury (and mercury waste) inventories, contaminated sites databases and other critical information needed to address domestic mercury contamination.

2. KAZAKHSTAN: STEPS TO RATIFICATION OF THE MINAMATA CONVENTION ON MERCURY

In order for Kazakhstan to ratify the Minamata Convention on Mercury it is required to accede to the Convention. Usually a party first signs the Convention and ratifies the Convention at a later date. Signing does not incur any legal obligations beyond formally confirming their intention to take steps to be bound by the treaty at a later date. Signing does create an obligation, in the period between signing and ratification or consent to be bound, to refrain from acts that would defeat the object and purpose of the treaty. No prior signing is required if a country accedes to the Convention. Accession is the most likely process for Kazakhstan as signing of the Convention was officially closed on 9th October 2014. Accession has the same effect as ratification.

Heads of State, Heads of Government or Ministers for Foreign Affairs are empowered to sign or ratify a treaty on behalf of a State without having to produce full powers to that effect.

Under the Convention States may express their consent to be bound in several ways:

- » Ratification (for States)
- » Accession (for States and regional integration organizations)
- » Formal confirmation (for regional integration organizations)

2.1 International ratification

The Convention provides for States to express their consent to be bound by signature, subject to ratification. Upon ratification at the international level, the State becomes legally bound by the treaty (The Minamata Convention enters into legal force 90 days after ratification by 50 countries).

2.2 Ratification at the national level

Ratification at the international level should not be confused with ratification at the national level. At the national level, the State might have to ratify the treaty in accordance with its own constitutional or legal provisions before it expresses consent to be bound internationally. For example, the constitution might require parliament to consider the terms of the Convention and decide on ratification prior to any action at the international level that would indicate that the State consents to be bound by the treaty. However, ratification at the national level alone is not sufficient to establish a State's intention to be legally bound at the international level. That is why ratification at the international level is still necessary, regardless of national procedures.

2.3 Accession

A State or regional integration organization may also express its consent to be bound by the Convention or the Optional Protocol by depositing an instrument of accession with the Secretary-General of the United Nations. Accession has the same legal effect as ratification; however, unlike ratification, which must be preceded by signing to create binding legal obligations under international law, accession requires only one step, namely, depositing the instrument of accession United Nations (2015).

2.4. The role of Parliaments in ratification

The role of parliaments in the ratification process varies from country to country. In some countries Parliament reviews Government actions to ratify a treaty. When the Treaty is tabled in parliament a National Interest Analysis (NIA) and Regulatory Impact Statement (RIS) is conducted, which explains why the Government considers it appropriate to ratify and what foreseeable impacts (positive or otherwise) may arise if government regulators align national regulations with the Treaty requirements. The NIA includes information relating to:

- » The economic, environmental, social and cultural effects of the proposed treaty;
- » The obligations imposed by the treaty;
- » How the treaty will be implemented domestically;
- » The financial costs associated with implementing and complying with the terms of the treaty; and
- » Consultations that have been held with states, industry, community groups and other interested parties.

A Treaties Committee reviews the NIA, RIS and any other relevant material, and then publishes its reviews in the national press and on its website, inviting comments from anyone with an interest in the proposed treaty action. The parliament of Kazakhstan will have its own internal processes for considering ratification and the implications for their nation which may differ from those described but will be likely to consider the range of issues listed above.

The Convention was opened for signature by States and regional economic integration organizations at Kumamoto, Japan, on 10 and 11 October 2013, and, thereafter, at the United Nations Headquarters in New York until 9 October 2014. Whilst the Convention is no longer open for signing, joining the convention by accession is still permitted through deposition of the instrument of accession with the Office of Legal Affairs at United Nations Headquarters in New York.

A specific action that Kazakhstan should undertake prior to ratification is a Minamata Initial Assessment (MIA). A key input into this activity is obtaining reliable information about mercury releases into air, water and wastes at national level. An analysis of this data will provide important information for the MIA.

2.5. Minamata Convention Initial Assessments (MIA)

In seeking to ratify the treaty Kazakhstan will need to conduct an MIA. An MIA will be the basis for each country to collect information that will assist its decision to ratify the convention. It will also provide a basis for the country to:

- » notify the convention if it has more than insignificant levels of artisanal and small-scale gold mining (a requirement of Article 7),
- » develop a National Implementation Plan required in accordance with Article 20
- » develop a National Action Plan to reduce emissions of mercury in accordance with Article 8

The Minamata Convention Initial Assessments include the following activities:

- » assess institutional capacity and help to establish coordination mechanisms;
- » identify gaps in legislative and policy frameworks;
- » create a national initial inventory of mercury stocks, supplies and emissions sources, prioritize emissions and sources for intervention;
- » raise awareness among relevant stakeholder groups; and
- » share knowledge and lessons learned (UNITAR 2014)

The identification and characterisation of mercury contaminated sites, creating an inventory of their location, raising public awareness of their impacts and assessing any relevant regulations and legislation would be a significant contribution to the development of the Kazakhstan MIA.

3. SITE IDENTIFICATION AND CHARACTERISATION – WHAT IS A MERCURY-CONTAMINATED SITE?

In developing a robust definition of a mercury contaminated site it is necessary to address key issues including the definition of a 'site' as well as what concentration or form of mercury present constitutes 'contamination' as opposed to naturally occurring levels.

In general terms a site that has soil, air, water or sediment (or a combination) impacted by elemental mercury, mercury compounds or mercury waste should at least be considered a suspected mercury contaminated site. Concentrations of just 0.13 ppm mercury in soil have been identified as the tolerable limit for soil health in terms of plants and micro-organisms.

Levels of mercury in soil that 'trigger' further investigation are also called screening levels. These vary between countries but are generally in the same order of magnitude. As an example the Australian national guidelines (NEPC 1999) listed 10 ppm methyl mercury and 15 ppm elemental mercury as a screening level for residential property. Dutch Intervention Levels (Netherlands Ministry of Housing, Spatial Planning and the Environment 2010) use 10 ppm elemental mercury as intervention levels for further assessment of sites suspected of contamination. These screening levels are used in the identification of mercury contaminated sites which may render it necessary to manage the site and subject it to further investigation and possibly remediation. For the

purposes of NGO identification of contaminated sites, sampling that reports a level of 5–10 ppm of total mercury content should be considered a suspected contaminated site requiring further investigation.

These can be complex issues. Some sites may have naturally occurring levels of mercury or mercury compounds present that exceed levels at which negative impacts to human and ecological health may occur. This is often the case at sites where primary mining of mercury has taken place or continues to operate due to naturally occurring high concentrations of mercury in the soil.

In many countries risk based approaches are used to define and manage contaminated sites which take into account the nature of the site (e.g. terrestrial, aquatic), its context (e.g. urban, agricultural or wilderness) and the threat it poses to different 'receptors' such as people, wildlife and ecological processes. This approach can act as a useful tool to prioritise the order in which sites may need to be remediated using limited resources. Generally those sites that present most risk to human health and the environment are remediated sooner and those with least risk later. However the remediation of large, complex, high risk sites may still be delayed for years or decades due to financial, legal, political and social complications including conflict, despite having a high priority for remediation.

3.1. Defining a ‘site’

A site may not necessarily be limited to a terrestrial form such as a field, forest or a hill. It can include aquatic environments such as streams, rivers, lakes, swamps, damp-lands, estuaries and bays. In other cases sites may include modified landforms that have both terrestrial and aquatic features such as rice paddies, irrigated fields and fish raising ponds. In addressing mercury contamination at different sites the identification, characterisation, management and remediation (clean-up) may vary considerably when taking into account the form of the site, its current use and the intended use following remediation.

It is also important to consider the geophysical and hydrogeological structure of a given site for the purpose of characterising the extent of contamination into the soil profile and the groundwater. This can also assist in estimating or predicting off-site movement and impacts of contamination through groundwater systems now and in the future as well as estimating the extent and type of remediation that may be necessary.

Terrestrial mercury contaminated sites can also be subject to periodic natural events that may result in the spread of contamination beyond property boundaries such as regular or occasional flooding, earthquake and landslides and extreme weather such as storms, cyclones or hurricanes which can blow contaminated dust from a site. These events should be considered and their impacts managed in an effort to reduce the spread of pollutants from known and/or suspected contaminated sites. These natural activities can create diffuse mercury contaminated sites such as that found in the River Nura and its floodplain in Central Kazakhstan. At this site mercury-rich wastewater from an acetaldehyde plant was historically discharged (largely without treatment) and then mixed in the river with fly ash from power stations. This action created a mercury laden silt that was spread by floodwaters contaminating large areas downstream of the initial discharge site (Heaven et al 2000).

3.2. Site Identification

The identification of contaminated sites provides a key opportunity for community engagement and interaction between CSOs and other stakeholders including environment and health officials. The process of investigating a suspected contaminated site often necessitates the involvement of local residents and officials, workers and former workers and local environmental NGOs who may have detailed knowledge of the history

of a site, waste dumped at the site or transported to other locations that also may have become contaminated.

Suspected contaminated sites may be identified without specialised technical equipment by the following means (Basel Convention 2012):

- » Visual observation of the site conditions or attendant contaminant sources;
- » Visual observation of manufacturing or other operations known to have used or emitted a particularly hazardous contaminant;
- » Observed adverse effects in humans, flora, or fauna presumably caused by the proximity to the site;
- » Physical (e.g. pH) or analytical results showing contaminant levels; and
- » Reports from the community to the authorities of suspected releases.

Mercury contamination on sites in Kazakhstan is most likely to arise from industrial activities, waste disposal and mining (particularly refining of ores and tailings disposal). Observation of sites that were historically or currently are engaged in these practices should be considered for assessment.

Artisanal and Small-scale Gold Mining (ASGM) is a large source of global mercury contamination but has not been reported in Kazakhstan. ASGM refers to informal mining activities carried out using low technology or with minimal machinery. Mercury is one of few metals that amalgamates with gold and is used to separate the gold from unrefined or concentrated ore. The mercury is then burned off leaving behind a small amount of gold. This practice causes widespread mercury contamination to air, water and soil as well as direct mercury exposure to those engaged in ASGM, their families and some gold traders who supply mercury or partially process the mercury amalgam in their shops (IPEN 2014). However, the scale of ASGM activity in Kazakhstan is likely to be insignificant and published literature indicates that most mercury contaminated sites (as well as dioxin and DL PCBs contamination) are the result of industrial activity (Heaven et al 2012, Ullrich 2004 and Petrlik 2014)

Mercury contaminated sites are generally caused by industrial activities, primarily mining, coal ash from power stations, chlorine production⁶, and the manufacture of

6 Chlorine production from chlor-alkali plants involves the use of large quantities of elemental mercury which have a tendency to contaminate the facility from emissions and releases to soil, water and air. Many of these mercury based chlor-alkali plants have been replaced by non-mercury based chlorine production technology such as the membrane method. However, the sites of the older plants may remain contaminated after the facility has been closed or demolished.

mercury-added products. Disposal of mercury-added products to landfill or incineration can also lead to mercury contaminated sites. Wastes from the incineration of mercury-added products such as fly ash can also create contaminated sites if the hazardous ash is dumped at sites not authorised for disposal.

Identification of mercury contamination can be linked closely to these types of industrial activity and waste disposal. Regulatory authorities in many countries often scrutinise the history of a specific site as part of a preliminary site investigation. In this phase of investigation the information of community members close to the site can provide critical insights based on observations across long time periods and specific knowledge of the local environment, livestock and biota across seasonal variations.

For instance, a local farmer near the site boundary or drainage routes may detect an unusual cluster of animal sickness, death or birth deformities that may be caused by contamination or a local resident may notice tankers regularly leaving an industrial site at night and dumping waste. These observations may go unnoticed by authorities who only have intermittent or brief attendance at an industrial site. These local observations can be very important in terms of assessing community health impacts from contamination where local residents may have specific knowledge of unusually high rates of illness in their locality and can communicate this to authorities.

Once a suspected contaminated site is identified the following activities should be conducted:

- » Preliminary site investigation (and emergency response if required)
- » Detailed site investigation
- » Site management
- » Remediation, validation and ongoing management.
- » Waste transport and treatment (on-site or off-site).

3.3. Preliminary Site Investigation

A Preliminary Site Investigation (PSI) generally consists of a review of site history (desktop study), a site inspection and interviews with stakeholders, and the preparation of a report. The results of the PSI help explain how the site became contaminated and the potential exposure pathways between the contamination sources and receptors such as people, crops, wildlife or livestock.

3.3.1 Desktop study

When investigating an industrial site a desktop study should always seek to include interviews with current or former workers, management and waste haulage drivers to broaden the information base about hot spots of contamination on and off-site.

In addition to stakeholder interviews investigators can draw upon:

- » current and historical aerial photographs
- » historical certificates of title (land ownership documents)
- » local government documentation (industrial development approvals or landfill wauthorisations)

3.3.2. Site Inspection

A site inspection should then take place with a person with historical knowledge of the site. The inspection is to collect visual, oral and anecdotal information relating to:

- » topography
- » surface water bodies and flow direction
- » type and condition of hardstand material
- » site infrastructure (current and historical)
- » current site activities (and historical where possible)
- » surrounding land uses
- » any evidence of soil contamination (staining, odour, stressed vegetation etc.)
- » chemical or fuel storage areas
- » waste management.

3.4. PSI and Emergency Response

After completion of the PSI, further information about the nature and extent of site contamination is assessed through a Detailed Site Investigation (DSI). However, the PSI may reveal gross contamination by mercury, dioxins, PCBs or other highly hazardous materials. If the contamination is severe and nearby populations are at risk of exposure that is an immediate threat to their health then an emergency response may be required prior to performing the DSI.

The first priority is to isolate the contamination from the receptors as far as possible in order to minimize further exposure. In this way, sites contaminated with mercury are similar to a site with another potentially mobile, toxic contaminant (Basel Convention 2012). If the site cannot be controlled and the risk is high, temporary evacuation of residents and workers may be required until the site can be controlled and the contamination isolated. The volatility of mercury in vapor form at room temperature can make isolation a difficult task in highly impacted sites. Barrier technologies as a means of reducing mercury vapor from contaminated sites are discussed further in this document under remediation technologies (section 7.).

Further information on emergency response for small-scale mercury contamination from spills can be found in the US EPA Mercury Response Guidebook for Emergency Responders (US EPA 2004). For larger site contamination issues involving mercury some guidance is provided in Protocols for Environmental and Health Assessment of Mercury Released by Artisanal and Small –Scale Gold Miners (Veiga and Baker 2004) that may also be applicable to contamination from industrial and waste related sites in terms of health assessments and sampling methods.

3.5. Detailed Site investigation and Characterisation

The DSI involves the taking of samples in the field from air, soil, groundwater or other water sources to confirm the presence or absence of contamination identified or suspected in the PSI. The DSI sampling should be comprehensive enough to identify the nature of the contamination and describe its lateral and vertical extent to a sufficient level that human health and environmental risk assessment can be undertaken and to provide the basis for the development of an appropriate remediation or management strategy.

Risk assessment for contaminated sites relies on the development of a Conceptual Site Model (CSM) which provides a representation of site contamination data (often in the form of a graphic or map) and potential pathways of exposure between the suspected or confirmed contamination and potential receptors. This aspect of the investigation can also be described as ‘characterisation’ of the site.

Data obtained from sampling during the DSI can then be included in the CSM to assist in building a more complete representation of the contamination at the site and how it may impact on the environment and human health. Any sampling data obtained

from the site should be subject to Quality Assurance and Quality Control (QA/QC) procedures to ensure that the data obtained is representative of the contamination at the site (see also Veiga and Baker 2004 p.123 for specific QA/QC for mercury impacted sites). This includes details on the storage and handling of samples, taking blind duplicate samples⁷ and holding times of samples. The integrity of the sample and reliability of results will depend not only on the length of time the sample has been stored, but also conditions of the sample handling, preservation and storage. All tests should be carried out as soon as practicable after sampling, and it is recommended that at least half the holding time remains when received by the laboratory.

Quality assurance (QA) refers to the overall management system which includes the organization, planning, data collection, quality control, documentation, evaluation, and reporting activities of your DSI while QC refers to the routine technical activities whose purpose is, essentially, error control. All US EPA methods for mercury analysis require that samples be refrigerated as soon as possible and analysed within 28 days of collection (Veiga and Baker 2004).

This can be particularly relevant for sampling of dioxins and PCBs, which are hazardous at extremely low levels and where technical accuracy is paramount.

Following the PSI and DSI stages and the construction of a Conceptual Site Model, risk assessment can be conducted for human health and ecological receptors. In many cases the outcome of the risk assessment determines whether and how the site is remediated (contamination removed to a specific level) or managed (contamination remains on-site with a range of management activities). Despite its utility as a management tool for contaminated sites, risk assessment should not be the sole method by which the future of a contaminated site is determined. Once the contamination on a site has been adequately characterised public discussions about its future use should be held including how and whether the site should be remediated. Obtaining agreement from civil society about the clean up and future of these sites can avoid protracted anxiety, conflict and expense while creating opportunities for social renewal around sites that may have been unproductive for many years.

⁷ To check reproducibility of laboratory and field procedures and to indicate non-homogeneity. Assign two separate (unique) sample numbers (i.e. one number to the primary sample and one to the duplicate) and submit blind to the lab.

4. SITE IDENTIFICATION AND PRELIMINARY SCREENING: A ROLE FOR NGOs

In most developed countries the process of site identification, characterisation, risk assessment and remediation is carried out by private consulting companies regulated by or in cooperation with government agencies. The process often occurs within a legal and regulatory framework that requires specific standards and accreditation to perform this work and to report any suspected or identified sites to an agency that inventories the sites and monitors their management or remediation.

As part of this process guidelines are established by which concentrations of a substance (e.g. chemical or metal) in soil, sediment, air and water are defined as a ‘trigger’ level (or threshold concentrations) for further or formal investigations (PSI and DSI). Not all countries develop their own trigger levels and choose to adopt them from other countries. Commonly used guides include the US EPA Regional Screening Levels⁸, the Dutch Intervention Values⁹ and Canada-Wide Standards¹⁰ and Australian Health Investigation Levels (HILs)¹¹.

8 See United States Environmental Protection Agency <http://www.epa.gov/region9/superfund/prg/>

9 http://www.rivm.nl/en/Documents_and_publications/Scientific/Reports/2013/januari/Proposal_for_Intervention_Values_soil_and_groundwater_for_the_2nd_3rd_and_4th_series_of_compounds

10 <https://www.ec.gc.ca/mercure-mercury/default.asp?lang=En&n=C6953AC5-1>

11 <http://www.scew.gov.au/nepms/assessment-site-contamination>

Comprehensive PSI and DSI can be an expensive process if the contaminated sites are large and complex, involve multiple contaminants or ongoing industrial activities. Full site characterisation often involves grid sampling for multiple samples repeated seasonally. The cost of drilling test bores for groundwater sampling and specialised laboratory analysis for multiple samples can also be very expensive and beyond the capacity of NGOs and CSOs. However, the key role that can be played by these organisations is raising awareness of potentially contaminated sites by locating suspected contaminated sites, documenting the activities that may have caused contamination and even conducting some basic screening sampling. NGOs can also document an inventory of known and suspected contaminated sites to assist regulatory authorities to conduct further investigations that require a significant level of resources.

NGOs raising public awareness of an inventory or ‘list’ of contaminated sites can encourage national decision makers to address the issue by developing national frameworks for investigation and remediation and can lead to the development of legal frameworks to determine liability for cleaning up the sites and compensation arrangements. A notable example of this arrangement is the US Superfund (US EPA Region 9 2015) which provided funds for hazardous site remediation and created a database of known contaminated sites requiring remediation.

Once sites have been confirmed as contaminated with mercury, dioxin or PCBs (or any other pollutant) NGOs can raise awareness in the community and with local authorities about the hazards posed by these sites and precautionary measures that may be taken to minimise exposure to the contamination. This is particularly relevant to sites contaminated with mercury where nearby fisheries (particularly downstream of contamination) are a food source and may contain elevated levels of methylmercury (MeHg). Similarly, other forms of indirect sampling can reveal localised contamination sources such as chicken eggs, cow milk etc. Sampling of eggs can be useful in alerting authorities to elevated levels of dioxins and DL PCBs. Humans' primary mode of exposure to dioxins and DL PCBs is through food supplies¹² which makes eggs a relevant sampling target.

In the case of dioxin and DL PCBs laboratory analysis for individual soil and sediment samples or biological samples can be very expensive. More recently analytical techniques such as DR CALUX (Chemically Activated Luciferase Gene Expression)¹³ have been developed that can report dioxin levels based on the calibrated response of micro-organisms in contact with toxic substances. This method is significantly less expensive and is being adopted as a screening tool at some contaminated sites to indicate if there is a need for additional sampling.

4.1. Site Screening (sampling)

Direct (on-site) screening sampling (soil, water and air) at suspected contaminated sites or indirect sampling nearby of food sources such as eggs, milk, fish or human biological samples can provide strong indicators of the presence of contaminated sites and the migration path of pollutants leaving the site.

Biological samples can also be taken if people living or working in close proximity to a contaminated site volunteer to provide them. This process has to be approached with sensitivity as there are privacy and ethical considerations to take into account including how individuals may need to be supported and counselled if the sampling shows high

levels of exposure. The most common samples that people can provide which report mercury exposure, include hair, urine and blood. Hair sampling is often used initially because it is less invasive than other methods and relatively inexpensive to analyse. Hair sampling methodology is described further below.

4.2. Indirect sampling

Dioxins (PCDD/PCDF) and DL PCBs are lipophilic meaning they bind strongly to fats in humans and animals. Screening sampling of biological materials such as eggs and milk with significant lipids content can provide strong indicators of localised dioxin contamination. The data reported can be compared to control samples from uncontaminated areas or national or international reference doses that establish acceptable maximum limits for contaminants in food. In the EU the maximum permissible level for PCDD/Fs in eggs is 2.5 pg WHO-TEQ g⁻¹ fat and for the combined sum of PCDD/Fs and DL PCBs is 5 pg WHO-TEQ g⁻¹ fat. The maximum permissible level for PCDD/Fs in milk is 2.5 pg WHO-TEQ g⁻¹ fat and for the combined sum of PCDD/Fs and DL PCBs is 5.5 pg WHO-TEQ g⁻¹ fat, (European Commission 2011). Suitably accredited laboratories should be contacted to conduct the analysis and they may also assist with instructions on how to take samples, handle and store them and holding times. If the results of sampling show dioxin and DL PCB levels above 5 pg WHO-PCDD/F-TEQ g⁻¹ fat, further investigation of hot spots can be undertaken.

For sites that are suspected of mercury contamination soil and air can be screened effectively at a relatively low cost. For indirect screening fish sampling is useful as it can be compared to control fish population known to be uncontaminated from other areas as well as to known reference doses that state the allowable level of methylated mercury in fish that can be consumed per month. A monthly consumption guideline of 0.2 ppm of methylmercury has been established by the US EPA (US EPA 2001).

The European Commission and the World Health Organization recommend that fish with a level exceeding 1 ppm of mercury should not be commercially traded. As in the case of dioxin sampling of eggs, milk and fish, accredited laboratories should be contacted to conduct the analysis and they may also assist with instructions on how to take samples, handle and store them and allowable holding times. If results show fish samples exceed the reference dose for methylmercury more investigation is required to identify the source of the contamination.

¹² More than 90% of human exposure is through food, mainly meat and dairy products, fish and shellfish. Many national authorities have programmes in place to monitor the food supply. World Health Organisation <http://www.who.int/>

¹³ European Union Reference Laboratory for Dioxins and PCBs in Feed and Food
– Dioxins and PCBs <http://www.crl-freiburg.eu/dioxin/bioanalytical.html>

Extensive information on field sampling of fish for methyl mercury is provided in Global Mercury Project Protocols for Environmental and Health Assessment of Mercury Released by Artisanal and Small-Scale Gold Miners. (GEF/UNDP/UNIDO, 2004 p86)

4.3. Hair sampling for mercury exposure

Taking hair samples for mercury analysis can provide an indicator of localised ongoing mercury contamination. The US EPA reference dose (RfD) level of 1.0 ppm of mercury in hair establishes a threshold against which hair samples from local workers or community members can be compared to test for elevated mercury levels.

People can be exposed to mercury from numerous industrial and mining sources including coal-fired power plants and pulp and paper mills, and mixed industrial sites that contain mixtures of chlor-alkali production, oil refining, waste incineration, cement manufacturing, and other potential mercury sources. This has to be taken into account when analysing whether elevated mercury levels in hair are from a local contaminated site or more diffuse sources. Hair sampling of children can be used to assess whether mercury is present at levels of concern that may impact on their neurological development and allow for early intervention by authorities to reduce their exposure (Grandjean 1999).

The National Institute of Minamata Disease, Japan recommends the following process for taking hair samples (other methods may also be valid).

4.4. Collection of Hair Samples:

- » Cut hairs with scissors close to hair root. A minimum requirement is twenty strands of hair each with about 10 cm in length. The shorter the length is, the more strands are required. If longer hair strand is available, a proximal portion of hair strand (a hair root side) with about 10 cm in a length may be kept by removal of excessive distal hair strand (a hair tip side) after cutting out of the entire hair strands. *Note:* A proximal portion of hair (a hair root side) is suitable rather than a distal part (a hair tip side) for the analysis in the aim of estimation for methylmercury exposure. The reason is that the contents of methylmercury might decrease during growth of hair under certain conditions including treatment with artificial hair waving.
- » Put the collected hair sample into envelope on which the identification (ID) number of the participant is indicated. Use one envelope for one participant.

4.5. Sending the Collected Hair Samples

- » Collect and store hair samples until the number of participants exceeds 50 individuals, and thereafter send the samples with list of participants. The number of participants is not more than 100 for each sampling site.
- » The list of participants should include identification (ID) number, sex, age, date of sampling, and sampling site. *Note:* Personal information, including name and address, that can be used for identification of individual participant should be protected from free access. It should be under a strict control by specific administrator. The personal information might be necessary in certain cases, for example, a feedback of the analysis results to local community.

4.6. Direct sampling (on-site)

Soil, sediment and water samples can be taken directly from a known or suspected contaminated site by NGOs with some preliminary supervision. However it is also important to be aware of the exposure hazards present at such sites and the need for an appropriate level of Personal Protective Equipment (PPE) to reduce exposure risks. It is also preferable to take rather more representative pooled samples of soil or sediments from larger area than just samples from one point as hotspots may be missed and the site characterisation may be inadequate. A sampling protocol which includes a detailed description of the sampling process is crucial. This should include a description of the sampling equipment and methods, locations of samples (preferable latitude and longitude coordinates) and the rationale behind the sampling. If grid patterns for sampling are employed then the grid intervals should be documented.

One technique to detect mercury contamination at a suspected contaminated site with minimal disturbance of potentially contaminated material thereby minimising exposure is the use of mercury 'sniffers'.

The 'sniffers' are portable electronic devices that can detect elevated levels of mercury on-site in the field. Some are calibrated for mercury in soil or other solid objects and others for mercury vapor. Some devices can be adapted with additional kits to test soil, water and air for mercury.



Figure 1: Example of a contaminated site investigator using a portable mercury vapor analyser.

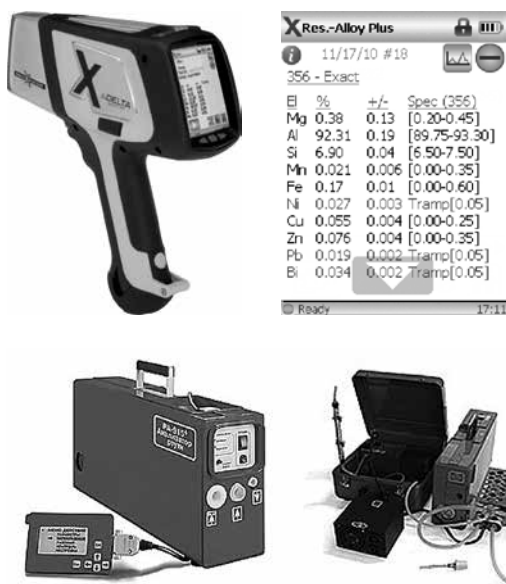


Figure 2: The Olympus Delta portable X-Ray Fluorescence Analyser with screen shot example of digital screen readout for metals in polymer. Source: www.innovx.com

- » Lumex's RA-915+ Portable Mercury Analyser, Atomic Absorption Spectrometer, Thermal Decomposition Attachment RP 91C
- » MTI, Inc.'s PDV 5000 Hand Held Instrument, Anodic Stripping Voltammeter
- » Olympus Delta portable X-Ray Fluorescence Analyser

These portable devices are particularly useful for taking rapid readings at multiple points on a given site which can assist in the location of hot spots.

The X-Ray Fluorescence Analyser depicted above (see Figure 2) is an example of a solid sample analyser (soil, objects) that can be programmed with different software packages to analyse consumer goods and environmental media such as soil. The device is held close to the target and activated. The analysis in ppm then appears on the screen. This type of device specialises in heavy metals but can also detect other chemicals if calibrated correctly.

For detecting mercury vapor on a contaminated site a device such as the 'Lumex' analyser (see Figure 3) can be effective. These devices can be expensive to purchase but in many countries can be hired for varying periods of time.

The role of NGOs in conducting initial screening level site sampling has proven highly effective in many countries in raising awareness of contaminated sites and stimulating authorities to address pollution from these sites. Whether it is simple hair testing or more complex use of sniffer devices there are many options that NGOs consider for identifying contaminated sites impacted by mercury and other metals as well as dioxin and DL PCBs.

4.7. Soil and water sampling for laboratory analysis

For those intending to take samples of soil or water from a suspected contaminated site to a laboratory for analysis it is advisable to consult with an accredited laboratory using internationally recognised methods of analysis before taking the samples. They will advise you on the correct procedure for taking samples and the correct type of storage container. These details are important as some sampling and storage materials (plastics and metals) can contaminate the samples giving false readings. In some cases laboratories will provide sampling containers that have been pre-prepared to ensure there is no inadvertent cross-contamination of samples. They will also advise of sample holding times and any need for refrigeration or freezing (in the case of fish) of samples.

Figure 3: Ohio Lumex RA915+ Portable Mercury Vapor Analyser which can also be adapted to sample soil and water.

Portable 'sniffer' devices include but are not limited to:

- » Metorex's X-MET 2000 Metal Master Analyser, X-Ray Fluorescence Analyser
- » Milestone Inc.'s Direct Mercury Analyser (DMA-80), Thermal Decomposition Instrument
- » NITON's XL-700 Series Multi-Element Analyser, X-Ray Fluorescence Analyser (XRF device)

5. RISK ASSESSMENT

Risk assessment (RA) of contaminated sites is an important component in determining exposure of human and environmental receptors and for making the decision whether to manage or remediate a site.

Risk assessment can also provide a useful tool for prioritising the remediation of numerous contaminated sites based on those that provide the greatest risk. This section provides a brief overview of the basic principles of risk assessment and directs the reader towards comprehensive guidance for those applying risk assessment to sites contaminated with mercury or dioxin and DL PCBs.

Risk assessment models can have significant limitations and many of values assigned as inputs to the models involve a degree of value judgement on the part of the RA practitioner. Models may also be limited by toxicological data that traditionally has been based on the analysis of single chemical compounds and their dose-response characteristics¹⁴. A contaminated site may be impacted by a single chemical or metal but more commonly they are impacted by a suite of metals and contaminants especially if the site has been used for dumping of mixed wastes.

¹⁴ A dose-response relationship describes how the likelihood and severity of adverse health effects (the responses) are related to the amount and condition of exposure to an agent (the dose provided).

In some cases when chemicals are present on a site as a mixture they may develop synergistic toxicity effects whereby the total toxicity of the mixture is far greater than the sum of its parts. The potentiation of the toxicity of some chemicals by others is often poorly represented in traditional risk assessment models though work is being conducted to address this issue. However, with over 100,000 chemicals currently in production (Winder et al 2004) comprehensive analysis of all potential interactions within a traditional RA framework will remain a long-term project.

As an alternative to risk assessment of mixtures bioassays are increasingly being investigated as a determinant of the toxicological impact of contamination sources. Bioassays are a test used to evaluate the relative toxic potency of a chemical by assessing its effect on a living organism. In terms of environmental testing, bioassays provide a comprehensive assessment of total toxicity of an effluent or a sample of water, sediment, or soil from a contaminated site. A range of guidance is available for those considering the use of bioassay procedures to compliment RA or improve assessment and characterisation of contaminated water (enHealth 2012) soil (Hooper 2008) and sediment (Barcelo and Petrovic 2006).

Risk assessment of mercury contaminated sites is possible using existing models but they are subject to some important limitations that may significantly underestimate

the potential exposure of receptors. The main issue is the lack of site specific speciation and substance specific bioavailability estimation in current models. Bioavailability can vary between different forms of mercury and related compounds and can be defined as ‘the fraction of a compound in a matrix that, when released from the matrix, can be absorbed by an organism. This absorbed compound is then available to cause a biologi-

cal effect’ (Stein et al 1996). A typical example is where high levels of mercury in fish are found while there are not high levels in sediments at the site where the fish was caught.

Traditional RA models have a less defined approach as they use total concentration input data and assume fixed coefficients for real impact on the receptor to develop a risk profile of a site at a specific point in time and assume a steady state situation (US EPA 1996).

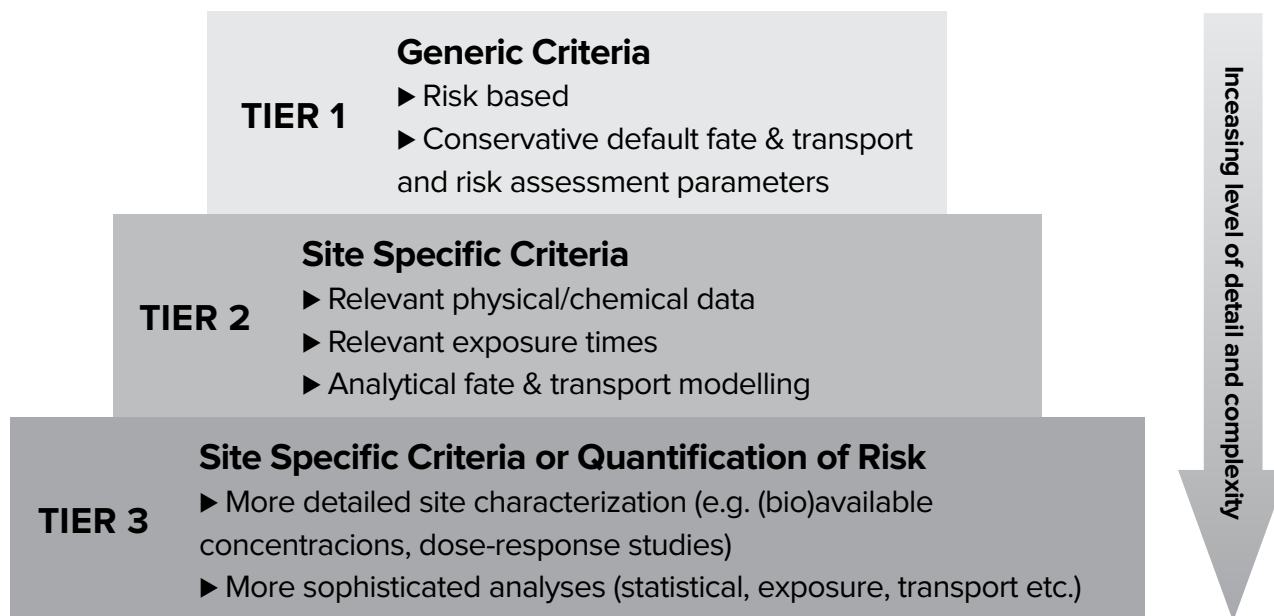


Figure 4: The three Tiers in contaminated land risk assessment. The steps may be somewhat different in different countries and risk assessment frameworks. Source: (Ohlsson et al 2014)

6. CONTAMINATED SITES: MANAGEMENT AND REMEDIATION APPROACHES

This section addresses different approaches to the management and remediation of sites contaminated with mercury and where specified, POPs such as dioxin and DL PCBs. There is a focus on industrial contaminated sites of the sort that would be expected from former and current industrial activity in Europe and that is relevant to the emerging issues of mercury and POPs contaminated sites in Kazakhstan. Specific commentary on the management and remediation of mercury contaminated ASGM sites is not within the scope of this report and ASGM is unlikely to occur at significant levels in Kazakhstan in any event.

Production of chlorine at chlor-alkali plants using the mercury cathode process has been a major source of mercury contamination in Europe and former Soviet Union countries due to the large quantities of mercury involved in the production process, loss of fugitive emissions in the vapour phase and spills, leaks and waste disposal.

An example of this type of legacy can be found in the town of Pavlodar in northern Kazakhstan where the soil, sediment, and water is severely contaminated with mercury and mercury compounds. Numerous ongoing efforts to decontaminate impacted areas around Pavlodar and investigate the impacts on human health and the environment are ongoing.

While chlor-alkali plants are a notable source of industrial contamination, other activities, such as wood preservation (HgCl_2), battery manufacturing & recycling, and other manufacturing activities such as production of thermometers and electrical switches have potential to cause mercury contamination. Industrial processes using mercury based catalysts can cause on-site contamination and impact other sites through waste disposal. Oil and natural gas production is also a source of mercury as elemental mercury is stripped from production and refinery plants to protect equipment from corrosion.

Waste disposal (solid wastes, sludges and effluent releases) from industrial operations are the cause of many mercury contaminated sites. The River Nura and its floodplain in Central Kazakhstan was contaminated with mercury when contaminated effluent from an acetaldehyde plant was discharged into the river. This has led to downstream impacts with contamination of fish from the River Nura with methylmercury. In turn this has led to elevated mercury in residents of Temirtau who catch and eat fish from the River Nura (Nekvapilová 2015). In addition to the acetaldehyde effluent a synthetic rubber factory in Temirtau discharged 2000-3000 tonnes of mercury into the River Nura and surrounding areas further contributing to the widespread mercury pollution in the Nura valley with the potential to affect the health of tens of thousands of people who utilise the river water, wells and other uses of the Nura for agricultural irrigation, watering livestock, swimming and fishing (Šír 2015 a; in this publication). Further information on this site is detailed in section 10.1.2.

In some cases a decision may be made following risk assessment and/or other deliberations that a contaminated site should be managed and not remediated. This may entail the containment on-site of the highest concentration contamination, fencing and signage to warn people of the hazard and regular monitoring of the site using visual observation and technical instruments (such as mercury vapor 'sniffers') to ensure exposure levels have not increased. In most cases where groundwater is threatened then monitoring bores (wells) should be established to sample and characterise the potential spread of contaminants. All of this data should be reviewed annually to ensure that the contamination is contained.

Whether the option chosen is to manage or remediate, additional contamination to a known contaminated site should be prevented. In addition, the management or remediation of a known contaminated site should not cause the creation or proliferation of additional contaminated sites (e.g. through waste dumping off-site, disposal of contaminated bore cuttings, wastewater etc).

Management of sites is usually chosen for economic reasons where insufficient resources are available for full scale remediation. However in some cases disturbing the contamination through a remediation process may cause more environmental damage than leaving it in situ. In some cases there have been reports that dredging of mercury contaminated sediments has led to re-suspension of mercury bearing sediments and pollution impacts in aquatic environments causing elevated levels of mercury in down-

stream biota (Anchor Environmental 2003). Management of contamination on residential sites should not be a preferred option if remediation is available.

6.1. Management

Contaminated site management strategies should reflect the need to protect all segments of the environment, both biological and physical.

During both assessment and remediation of sites action must be taken to control emissions to air, land and water.

Mercury can present particular difficulties due to its tendency to be released in vapor phase at ambient temperatures. This includes risk from vapor release during disturbance of mercury laden sediments, demolition of mercury contaminated buildings and excavation of test pits.

Drilling of bore holes for groundwater monitoring can also create pathways for release of mercury vapour from sub-soil contamination. Careful monitoring with mercury vapor detectors at any disturbed sites should be conducted regularly to ensure the safety of workers and adjacent residents.

Clean-up should not proceed if the process is likely to create a greater adverse effect than leaving the site undisturbed. This decision would need to be revised in the light of new technologies or clean-up strategies becoming available or if the risk is noted to increase due to mobilisation of the contaminants beyond the site or confinement structures.

6.1.1. Monitoring

If it is determined that a site is contaminated but circumstances, or risk based assessment lead to a decision to manage a site rather than remediate it then a monitoring plan must be developed and implemented.

The detailed site investigation should have already characterised the geology, hydrogeology and hydrology of the site to contribute to risk assessment, management and/or remedial options.

For mercury contaminated sites (and those impacted by Volatile Organic Compounds or VOCs) monitoring must include vapor monitoring targeted to relevant areas of the site identified by a soil gas survey which should have been conducted during the detailed site investigation. This applies to elemental mercury only as vapor monitor-

ing does not detect mercuric or mercurous salts which potentially represent a risk to groundwater due to their solubility.

Groundwater monitoring is also critical to monitor contaminant plume movement or growth including that precipitated by 'draw down effects' of off-site bores and wells used for water production which can influence movement of contaminated plumes outside of natural flow directions.

In general terms monitoring wells or bores should be constructed 'upstream' (in groundwater terms) and 'downstream' of the contamination during the DSI to assist with hydrogeological characterisation and delineation of groundwater contamination. Once the plume of contamination has been characterised by sampling and modelling further monitoring bores should be placed 'downstream' ahead of the advancing plume to detect its spread and calibrate its movement against earlier modelling. Assumptions about the further movement of the plume can then be adjusted and assessed for risk implications. International methods exist for mercury groundwater monitoring such as Water Quality ISO 17852 – 2006.

6.2. Remediation: Principles and Approaches

The fundamental goal of remediation should be to render a site acceptable and safe for long-term continuation of its existing use and maximise to the extent practicable its potential future uses

A preferred hierarchy of options for contaminated site remediation and management

- I) On-site treatment of the soil, so that the contaminant is either destroyed or the associated hazard is reduced to an acceptable level without adverse effects on the environment, workers, the community adjacent to the site or the broader public.
- II) Off-site treatment of excavated soil, so that the contaminant is either destroyed or the associated hazard is reduced to an acceptable level, after which it is returned to the site without adverse effects on the environment, workers, the community adjacent to the site or the broader public.

If it is not possible for either of the two above options to be implemented, then other options for consideration should include:

- I) Removal of contaminated soil to an approved site or facility, followed by replacement with clean fill
- II) Isolation of the contamination on-site in an appropriately designed and managed containment facility with regular monitoring and review of remedial strategies over time
- III) Leaving contaminated material in-situ providing there is no immediate danger to the environment or community and the site has appropriate management controls in place. This requires re-evaluation of remedial measures over time to take account of development of new technologies and remedial practices that could be implemented.

Complex remediation should be supported by the development and implementation of a Remediation Action Plan (RAP). The key components of a RAP are:

- » Identification of the key stakeholders and responsibilities.
- » Development of remediation goals and clean-up acceptance criteria.
- » Assessment of the remediation options and determination of the preferred remediation option.
- » Documentation of the remediation methodology including any regulatory permit/licensing requirements.
- » Development of an Environmental Management Plan.
- » Defining the validation program to demonstrate the successful completion of the remediation, including monitoring (EPA Tasmania 2005).

6.1.1. Monitoring

If site contamination is confirmed and represents a risk, or a potential risk to human health and the environment, remediation should be conducted. The term remediation generally refers to removal and/or treatment of the contamination to reduce human exposure and risk to health or to the environment. In some countries a 'fit for use' approach is taken whereby the site is cleaned up to a certain level depending on the proposed future use of the site.

Regulatory systems for contaminated sites often categorise site uses in the following categories:

- » Residential
- » Parks and recreation
- » Commercial
- » Industrial

This system is based on potential for exposure to human receptors – particularly duration of exposure. The exposure scenarios then determine the allowable levels of contamination for a given site use category. In general terms ‘residential’ land use has the lowest permissible levels of soil contamination of all categories due to the potential for long exposure times of residents (up to 24 hours a day) and the potential for young children to occupy the site and engage in ‘pica’ behaviour (Edward et al 1997) which literally means eating small quantities of dirt through hand to mouth activity and this is particularly relevant for Balkhash and Temirtau (Watson 2015).

Exposure calculations sometimes include a scenario for eating home grown produce which is particularly important for people consuming domestically produced eggs and dairy products where dioxin and DL PCBs may be present due to the lipophilic nature of the contaminants and their potential to accumulate in the produce.

The permissible levels of contaminants then rise to higher levels for ‘Parks and Recreation’, more so for ‘Commercial’ and the highest permissible levels are generally for sites that are currently ‘Industrial’ or planned to be used for industrial activity in the future. Commercial and industrial sites are permitted higher soil contamination on the assumption that workers will only be exposed for a limited number of hours per day, may incidentally wear Personal Protective Equipment (PPE) for occupational reasons and because the site surfaces may be sealed with bitumen or concrete further limiting exposures.

This approach is not solely determined by a risk assessment approach but also by a cost/benefit approach whereby industrial sites may not receive the same standard of remediation (which is a significant cost saving to the site owners or other responsible parties) that a residential site requires. The problem with this approach is that it leaves contamination behind to be dealt with at a later date, even by future generations. It is neither precautionary nor sustainable or best practice but it is economically beneficial to those responsible for remediating the site.

This approach can also lead to further environmental problems. For example, regulators may decide a residential site may have to be remediated to the point where there is 2 ppm or less of elemental mercury present in the soil whereas an industrial site may be permitted to remediate a badly contaminated site and leave up to 200 ppm of elemental mercury in the soil.

The residential site is unlikely to contribute significant mercury vapor or runoff to the ambient air or local environment, whereas the industrial site will continue to contribute fugitive emissions for many years and potentially cause migration of mercury to groundwater. In a worst case scenario many decades will pass and records of the contamination on the site are lost or forgotten and the site is redeveloped into residential housing repeating the contamination exposure cycle.

There is also the additional issue of future costs to fully clean sites that have only been partially remediated. It is likely that future costs will be higher and that contamination may spread over time increasing the scope, expense and extent of future site remediation especially if the land use is changed to a more sensitive scenario such as residential use.

The alternative approach is to fully remediate a site when the opportunity first arises so as to avoid the cost, inconvenience and risk implications of repeated remediation at a site in future years. In terms of ecological sustainability (intergenerational equity, polluter pays and the precautionary principle) this approach is closer to best practice.

Once remediation of a contaminated site has been deemed complete further steps are required to ensure the efficacy of the operation.

6.3. Validation

Following the remediation it must be demonstrated that the remediation goals have been met in terms soil, water and air contaminant concentrations and containment integrity. The site must no longer represent a risk to human health or the environment. Validation sampling of soil, groundwater, sediment, biota and vapor should be conducted to ensure the goals have been met. Groundwater sampling will need to be continued over a period of time to take into account seasonal variations and other influences.

Ongoing monitoring plans should also include a contingency plan to address any shortcomings in the remediation and unexpected reports of contamination in monitoring data that may have arisen from poorly characterised or unknown hotspots or off-site influences.

7. REMEDIATION TECHNOLOGY

Remediation technology for sites contaminated with mercury need to deal with some unique challenges associated with the complex behaviour and characteristics of elemental mercury and mercury compounds. In particular, mercury's ability to enter vapor phase at ambient temperatures as well as the ability of some species to move downward through the soil profile.

When implementing mercury contaminated site remediation it is critical to assess and manage sub-surface mobilisation of mercury and prevent emissions and releases to air, water and soil.

When considering technology selection and the development of a remediation strategy for a site, three key issues must be addressed;

1. The development of a comprehensive conceptual site model (CSM), which includes a detailed site investigation that describes potential releases of mercury from the site as a result of using remediation technology as well as any transformations (such as solid to vapor phase) that technology may produce. This relies on accurate identification of the mercury species potentially involved in air soil and water and their potential risk to human health and the environment.
2. Elemental mercury cannot be destroyed so any remediation strategy must take into account management of residual mercury waste, including its stabilisation, transport and final disposal.
3. Remediation technologies carry the risk of remobilising mercury during remedial works. Remediation Health and Safety plans for workers and the public must take this into account. For more information see section 9.

As noted previously in this document, risk based approaches to remediation may produce outcomes that are quite different to sustainable remediation objectives which infer the integration of sustainability principles in the proposed remediation goals.

A sustainable remediation approach incorporates social, environmental and economic consideration in the clean-up of the site including the polluter pays principle and intergenerational equity. A strictly risk based approach such as that proposed by Eurochlor (2009) is determined with a focus on economic considerations. For Kazakhstan it is important that socio-economic considerations are integrated into the remedial strategies for mercury and dioxin contaminated sites. As such there is a necessity for the development of a sustainable remediation approach which promotes social goals. These may be related to and integrated with social goals for health improvement, education outcomes and agricultural and fisheries sector development that feed into broader social goals of poverty reduction. For further analysis of these issues in Kazakhstan see section 10 of this document.

7.1. Point source and diffuse contamination

In terms of the mercury contamination issues in Kazakhstan the application of mercury remediation strategies and technology should also be guided by the form in which the contamination takes place. Contamination may be in the form of a point source (such as the former chlor-alkali plant at Pavlodar) or take the characteristics of diffuse contamination such as the mercury contamination of the River Nura and its floodplains.

Hinton et al (2001) suggested two responses dependent on whether mercury contamination was of a point source or diffuse nature. For diffuse contamination Hinton was of the view that remedial measures were typically not feasible.

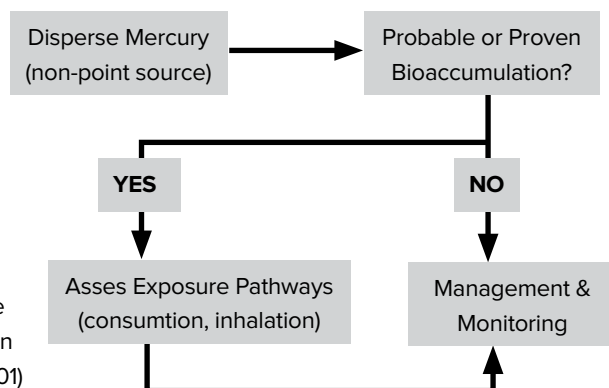


Figure 5: Response to diffuse source mercury contamination proposed by Hinton et al (2001)

For point sources the response by Hinton was consideration of the possibility of ‘dig and dump/treat’ and where not possible assessment of in-situ containment and cover techniques. In both cases Hinton views mercury bioavailability as the driver of remedial strategies.

In the absence of a remedial approach to diffuse mercury contamination risk-based behaviour modification may be implemented. This can involve providing public information to reduce exposure to mercury bearing soil and sediments, reduction or avoidance of consumption of contaminated biota (especially fish) changing land use (e.g. agriculture) to avoid areas of elevated contamination. Responses may also involve monitoring of population health with health intervention for compromised individuals.

More recently, emerging technologies are being developed which may have potential to address diffuse contamination such as phytoremediation. This is a process by which plants are applied to contaminated areas to accumulate mercury in the roots or on the shoots and leaves and then harvested. Phytoremediation is sometimes referred to as phytostabilisation, phytoextraction or phyto-volatilisation as plants may also volatilise mercury into the environment (Wang et al 2012). A key issue with this technology is how to address the residual material (harvested plant material contaminated with mercury) to ensure the mercury is not remobilised.

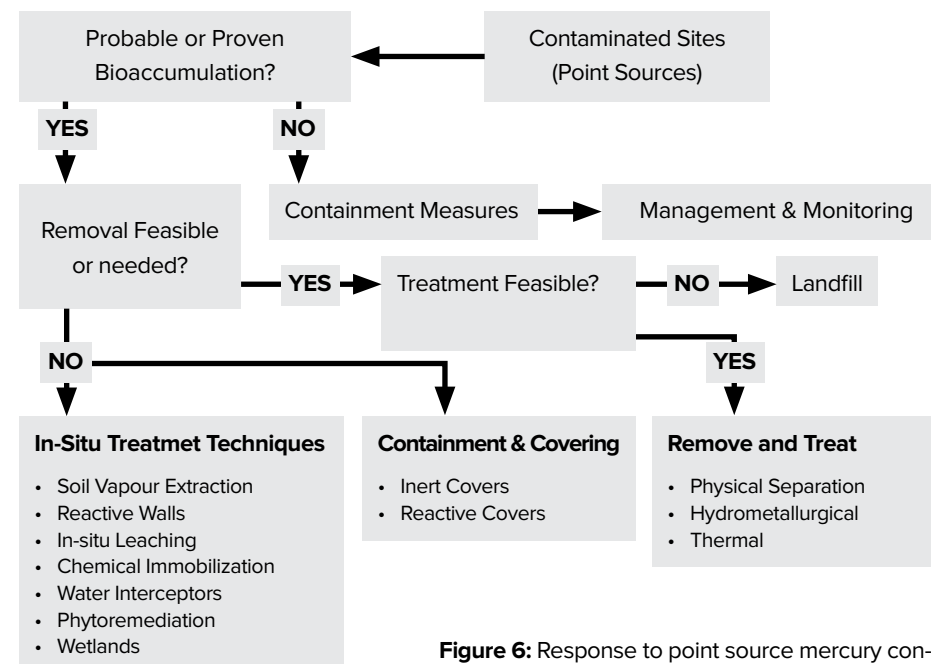


Figure 6: Response to point source mercury contamination proposed by Hinton et al (2001)

There are numerous technologies that are applied for point source contamination by mercury. These may be used individually or in treatment trains. A number of technologies are proven and are regularly implemented for soil and water contamination while others are considered to be emerging technologies with varying degrees of potential for both environmental media.

7.2. Proven mercury contaminated soil remedial technologies

7.2.1. Excavation and on site treatment (recovery)

This approach removes the highest concentrations of soil contamination by excavation and treatment followed by isolation procedures such as on-site containment and capping (to prevent vapor release) for the high concentration mass. The high concentration material may also be disposed off-site at an engineered hazardous waste landfill.



Figure 7: Remediation with Odour Control Enclosure and treatment train.
Source: Australian Federal Government (2013)



Figure 8: Interior of Odour Control Enclosure during excavation.
Source: Australian Federal Government (2013)

This approach is preferred for hot spots on a contaminated site as widespread excavation raises significant safety, cost and geotechnical issues. The most significant problem associated with this approach is the remobilisation of mercury contaminated dust and mercury vapor (rainfall can also wash mercury contaminated soils from the site during excavation or cause soil infiltration of soluble mercuric wastes). The hazards of this approach need to be considered for workers and the public near the site.

It should not be assumed that contaminated sites are vacant spaces as structures from industrial and other uses may still be present. The demolition of these buildings can cause large releases of mercury vapor in the same manner as excavation. At the Pavlodar contaminated site in Kazakhstan the removal of the roof of building 31 released a massive amount of mercury vapor resulting in the declaration of a state of emergency (Randall et al 2007). This account also confirms the need for accurate detailed site investigations and conceptual site models before major works begin.

One method to reduce the risk of mercury releases and emissions during excavation is to conduct the activity within a temporary sealed structure under negative air

pressure and create a barrier to external receptors. The image below (Figure 7) depicts a negative air pressure enclosure (circled in black) in use in New South Wales, Australia during the remediation of a former gasworks site with volatile contaminants (Australian Federal Government 2013). The 3,800 square metre, steel and fabric, odour control enclosure (OCE) has been erected at the northern end of the Platypus Site.

The contaminated material treatment works are taking place within the OCE. All air from within the OCE is being filtered through the emission control system before being released to the environment through a stack (vapor treatment train and stack is circled in white). A similar approach was chosen for remediation of a site in Spolana Neratovice, Czech Republic contaminated by dioxin and other POPs (Bozek et al 2010).

7.2.2. Treatment following excavation (soil washing and separation)

Soil washing and pre-treatment: Most forms of mercury have a high affinity for fine soils and sediment with higher adsorption rates for clay and humic (organic) material. Physical separation of fine grained soils contaminated with mercury from coarse sands and gravels minimises the final amount of material for containment. Physical separation is a 3 to 5 stage process involving physical (including mechanical) separation through sieving and screening and soil washing using either water or washing solutions such as acids, polymers and surfactants (Merly and Hube 2014).

Once soil washing or separation has been completed a third treatment step can be undertaken using thermal processes.

7.2.3. Thermal treatment processes

Thermal treatment processes to remove mercury from soil rely on the application of heat and reduced pressure to liberate the mercury through volatilisation due to its low vapor pressure of 0.002 mm Hg at 25 °C (ATSDR 1999). These techniques can also be applied to other contaminants with a relatively low vapour pressure such as DL PCBs.

Most thermal treatment methods require careful consideration before implementation due to their conversion of mercury to the vapor form. Emissions from these technologies can be a significant hazard and costly air pollution controls (APC) are required.

Once the contamination is removed from its original position (ex situ) it can be treated on-site or off-site by thermal means. The most commonly used technologies are

- » Ex situ thermal desorption or ESTD (an in-situ method is described later under emerging technologies);
- » Incineration
- » batch retorting

Thermal desorption can be conducted in two ways a) indirect thermal desorption and b) direct thermal desorption.

Indirect thermal desorption – Indirect thermal desorption should be considered a preferred treatment option for mercury contaminated sites. Typically, heat is applied to the exterior of the heating chamber and is transferred through the wall of the chamber to the waste material. Neither the burner flame nor the combustion gases come into contact with the waste material or the off-gases (Environment Agency UK 2012). This is important for treating mercury, dioxin and DL PCB contaminated matrices so the burner combustion products can be directly discharged to the atmosphere, as long as a “clean” fuel is used such as natural gas or propane. The objective of thermal desorption should be the maximisation of the recovery of the volatilised contaminants from the off-gases through condensation processes. A key operating principle that sets thermal desorption apart from waste incineration is based upon the optimised recovery of the desorbed contaminants from the gas rather than their destruction through combustion (Environment Agency UK 2012).

Direct thermal desorption – This process is not recommended for remediation of mercury contamination due to the high risk of fugitive mercury emissions during the process. However, it has been applied in the past at some sites. Heat is applied directly by radiation from a combustion flame and/or by convection from direct contact with the combustion gases. Systems employing this type of heat transfer are referred to as direct-contact or direct-fired thermal desorption systems (US Government 1998). The object of the operation is also to maximisation of the recovery of the volatilised contaminants from the off-gases through condensation processes. However, additional complexity arises due to the direct contact of the combustion gases with the waste vapor adding cost to the treatment of the system off-gases. Emissions of mercury vapor, dioxin and DL PCBs can be unacceptably high in systems that do not have very high levels of air pollution control (APC).

Batch retort– Retort ovens typically operate at temperatures of 425 to 540°C and under vacuum to increase mercury volatilization and reduce off-gases volumes (US

EPA 2007). They are typically used for smaller amounts of high concentration mercury contaminated soils (>260 ppm) and are limited to processing 1-2 tonnes per day (Merly and Hube 2014).

Incineration– Incineration is a destruction process using thermal combustion at elevated temperatures to destroy contaminants especially organic compounds. It has been used to treat low volumes of materials with low concentrations of mercury contamination but is not considered applicable to larger volumes of high concentration contaminated material due to the potential for mercury emissions and releases (Merly and Hube 2014).

7.2.4. Excavation and immobilisation technologies (excavation and disposal)

This method has been described in other literature as a ‘dig and dump’ process with the addition of immobilisation treatment. The waste removed can be contained on-site with capping or disposed off-site at an engineered hazardous waste landfill. Immobilisation of the mercury content refers to treatment that significantly reduces its ability to leach in soluble form or produce vapors. Immobilisation techniques include:

- a) amalgamation (with other metallic compounds);
- b) stabilisation
(usually through chemical reactions with sulphur compounds and polymers);
- c) solidification
(physical stabilisation through mixing with solid non-hazardous material.

7.2.5. Amalgamation

The US EPA (2007) *define amalgamation as the dissolution and solidification of mercury in other metals such as copper, nickel, zinc and tin, resulting in a solid, non-volatile product. It is a subset of solidification technologies, and it does not involve a chemical reaction. Two generic processes are used for amalgamating mercury in wastes: aqueous and non-aqueous replacement. The aqueous process involves mixing a finely divided base metal such as zinc or copper into a wastewater that contains dissolved mercury salts; the base metal reduces mercuric and mercurous salts to elemental mercury, which dissolves in the metal to form a solid mercury-based metal alloy called amalgam. The non-aqueous process involves mixing finely divided metal powders into waste liquid mercury, forming a solidified amalgam.*

The US EPA (2007) has identified amalgamation as the best demonstrated available technology (BDAT) for treatment of liquid elemental mercury contaminated with radioactive materials. This is an important consideration when developing remediation plans for sites with mixed contaminants that include mercury and radionuclides.

7.2.6. Stabilisation and solidification (S/S) without mercury recovery.

The processes of stabilisation involves chemical reactions that can reduce the mobility of waste and in some cases its toxicity. Solidification can change the physical properties from a liquid or sludge to a solid but does not change the chemical form of the waste. In combination these techniques can reduce the toxicity and mobility of the waste. S/S is commonly applied to contaminated soil, sludge, ash, and liquid (Basel Convention 2012). S/S involves physically binding or enclosing contaminants within a stabilized mass (solidification) or inducing chemical reactions between the stabilizing agent and the contaminants to reduce their mobility (stabilization).

The solidification process involves mixing contaminated soil or waste with binders such as Portland cement, sulphur polymer cement (SPC), sulphide and phosphate binders, cement kiln dust, polyester resins, or polysiloxane compounds to create a slurry, paste, or other semi-liquid state, which is allowed time to cure into a solid form (US EPA 2007).

Waste can be encapsulated in two ways: microencapsulation and macroencapsulation. Microencapsulation is the process of mixing the waste with the encasing material before solidification occurs. Macroencapsulation refers to the process of pouring the encasing material over and around the waste mass, thus enclosing it in a solid block (US EPA 2007).

The most common chemical conversion is dosing the waste with sulphur to create mercury sulphide. Conversion of all mercury to mercury sulphide (HgS) should be achieved to reduce leachability and volatility to acceptable levels. In general, HgS is produced by blending mercury and sulphur under ambient conditions for a certain time, until mercury (II) sulphide is produced. Isolation from the environment by encapsulation and disposal in a specially engineered landfill, or permanent underground storage may be necessary as elevated chloride levels in leachate can increase mercury release (Basel Convention 2012). Elevated chloride conditions are typically encountered in municipal landfills which are unsuitable for disposal of this form of waste.

Under certain circumstances HgS can be reconverted back to elemental mercury. If elemental mercury waste is intended to be converted to HgS for permanent disposal it should be recognised that at some future time this process could be reversed.

7.2.7. Sulphur polymer stabilization/solidification (SPSS)

The polymer stabilization process offers the additional advantage that it is difficult to reverse preventing the recovery of elementary mercury from the matrix. The SPSS process¹⁵ consists of two steps: mercury is stabilized with sulphur as the first step to form beta-mercury sulfide (meta-cinnabar dust); (López et al, 2010, López-Delgado et al, 2012) and, in a second step, this mercury sulfide is incorporated and microencapsulated in a polymeric sulphur matrix at 135 °C, obtaining a fluid that is cooled to room temperature in moulds, to obtain solid blocks (monoliths).

The second step of the process provides an additional barrier for mercury to prevent and avoid mercury releases to the environment minimizing with it the possibility of its conversion to other forms of mercury. Mercury is transformed in the process which has low energy consumption, low mercury emissions, no water consumption and no effluents, and generates no other wastes (Basel Convention 2012).

7.2.8. S/S with sulphur microcements

The treatment of mercury wastes with sulphur microcements is another stabilization and solidification technology, which results in a solid matrix that ensures the confinement of mercury because of its precipitation in the form of very insoluble compounds, as oxides, hydroxides and sulfides.¹⁶

7.2.9. In-situ containment

A process of creating engineered isolation of the mercury contaminated area from non-contaminated surrounds which includes capping to prevent vapor release. Physical barriers are engineered that can prevent re-mobilisation of mercury laterally and vertically (either through the soil profile or to air). There are many different varieties of contain-

¹⁵ For further information: www.ctndm.es

¹⁶ For further information: info@cementinternationaltechnologies.com; www.cemintech.com.

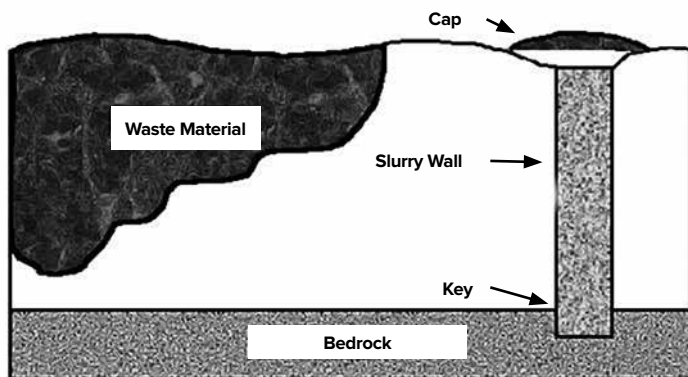


Figure 9: Section showing capped slurry wall isolation



Figure 10: Combined trenching and slurry insertion

ment with differing techniques including the installation of vertical slurry walls or grout curtains (also called cut-off walls) made by cutting deep trenches into the soil around the contamination and filling with slurries such as bentonite/cement and soil mixtures.

The benefits of this approach include relative simplicity and rapid implementation with cost reductions compared to excavation (and the hazards associated with excavation). Isolation through capping, vapor barriers and cut-off walls also permits control and management of mercury migration. There are limitations to this approach in that mercury toxicity and mass are not reduced, groundwater flow may be disturbed and potentially contaminated wastes may be generated during trench excavation (Merly and Hube 2014). The long-term effectiveness of such containment may also need to be monitored and such mechanisms may be unsuitable for areas with elevated seismic activity.

7.2.10. Off-site disposal

Mercury wastes and residues from remediation of contaminated sites that are to be disposed off-site must meet licence, regional and/or national acceptance criteria for the

waste facility that receives them. In general terms this does not apply to elemental mercury recovered from processes such as indirect thermal desorption or retorting. Elemental mercury is a commodity that may be traded for allowed use under the Minamata Convention on Mercury (with the exception of mercury recovered from former chlor-alkali facilities and produced from primary mining for certain uses). However, restrictions may apply in some jurisdictions to the export of elemental mercury such as in the US and EU.

For mercury wastes Europe has relatively strict acceptance criteria for waste facilities under regulatory frameworks - The European Directive 1999/31/EC and Decision 2003/33/E; Decision of 14/11/2008 1102/2008 and The EC Directive 2011/97/CE.

Off site disposal of mercury waste does have disadvantages such as the high cost for excavation and transport to disposal sites (and potential pre-treatment to meet acceptability criteria at the waste disposal site. In terms of sustainability this can create a high carbon footprint for the project especially when large volumes are transported.

The following table provides regulatory mercury leaching limits from waste for various types of waste disposal facilities (landfills) ranging from inert landfills through to hazardous waste landfills.

MERCURY LEACHING LIMIT VALUES FOR DIFFERENT LANDFILL TYPES ACCORDING TO DECISION 2003/33/EC, ANNEX			
Landfill Type	L/S =2 l/kg mg/kg dry substance	L/S =10 l/kg mg/kg dry substance	Co (percolating test) mg/l
Criteria for landfills for inert waste	0.003	0.01	0.002
Criteria for granular non-hazardous waste accepted in the same cell as stable non-reactive hazardous waste	0.05	0.2	0.03
Criteria for hazardous waste acceptable at landfills for non-hazardous waste	0.05	0.2	0.03
Criteria for waste acceptable for landfills for hazardous waste	0.5	2	0.3
Source: BiPro (2010) Requirements for facilities and acceptance criteria for the disposal of metallic mercury.			

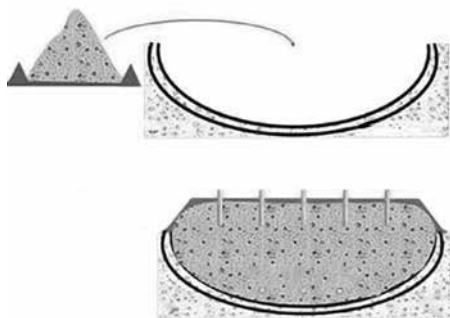


Figure 11: Schematic of on-site waste entombment. Source: Colom-bano et al (2010)

7.2.11. On-site disposal

Contaminated residues and soil remaining after mercury site remedial treatment are typically disposed of on-site via entombment. This is an engineered cell designed specifically to isolate the mercury contaminated waste from the environment. It has the advantage of saving transport costs to an off-site facility.

The key features of the ‘tomb’ include compacted low permeability clay base or cement base incorporating synthetic liners such as HPDE, capping, gas extraction and capture. This is designed to prevent gas escape, rainwater infiltration, groundwater infiltration and mobilisation of contaminants. There are significant costs associated with long-term monitoring of the structure to ensure its integrity and containment of contamination. This structure also relies on seismic stability.

7.3. Emerging mercury contaminated soil remedial technologies

7.3.1. Electrokinetic techniques

In the literature several different terms are used to describe techniques based on the same principle: electrokinetic remediation (EKR), electrokinetic extraction, electro-reclamation, electrorestoration or electrodialysis. Three transportation phenomena are responsible for electrokinetic mercury movement in soils. The transport mechanism for any particulate mercury with charged surfaces, Hg^0 or colloidal precipitates, for example, is called electrophoresis. By electromigration, all ionic species can be transported to the cathode or the anode. Charged as well as uncharged species present in the pore liquid of soil can be transported towards the cathode by electro-osmosis (Merly and Hube 2014).

Electroremediation of mercury contaminated soils, facilitated by the use of complexing agents (EDTA) proved to be an attractive alternative treatment for the removal of mercury from mercury contaminated mining soils (Robles et al 2012) (Garcia-Rubio et al 2011). The addition of complexing agents enabled the formation of coordination complexes that strengthen electromigration. (Garcia-Rubio 2011) demonstrated that, for relatively low hydraulic permeability soil, iodide - enhanced EKR allows the same recovery efficiency as an in-situ flushing with the optimum chelating concentration, but the full-scale remediation could be accomplished in time periods several orders of magnitude shorter.

7.3.2. Phytoremediation

Phytoremediation uses plants to remove, transfer, stabilize, or destroy contaminants in soil, sediment, and groundwater. Phytoremediation applies to all biological, chemical, and physical processes that are influenced by plants (including the rhizosphere) and that aid in cleanup of the contaminated substances. Plants can be used in site remediation, both through mineralization of toxic organic compounds and through accumulation and concentration of heavy metals and other inorganic compounds from soil into aboveground shoots.

Phytoremediation may be applied in situ or ex situ to soils, sludges, sediments, other solids, or groundwater (US EPA 2012). There are ongoing studies into the effectiveness of phytoremediation techniques using plants to strip mercury from soil and mixed environmental media such as rice paddies. This could have a direct application in ASGM areas where rice and fish (which are often grown in the same rice paddy) are the staple food source and subject to mercury contamination from ASGM activity. It may also prove useful in agriculture areas subject to periodic flushing where contaminated sediments are deposited in low lying areas.

Bench scale studies have shown that both genetically modified and wild rice were able to remove Hg^{+2} ions when grown in a mercury-spiked hydroponics medium (Meagher and Heaton 2005). Further investigation would be required to assess the impact of fugitive emissions from transpiration of the plants and to ensure that the contaminated rice was not permitted for human consumption. Careful attention to the full lifecycle and fate of mercury hyperaccumulator plants must be taken in cases where the plants may be harvested unintentionally as a food crop or for fuel to avoid ingestion or releases from combustion.

In addition to rice plants, cottonwood trees have been evaluated for their ability to remediate mercury. Eastern cottonwood trees (*Populus deltoides*) grow rapidly in a variety of conditions, including riverbanks and floodplains (APGEN 2003).

Phytoremediation may have applications in diffuse mercury contaminated sites such as the River Nura and surrounding agricultural land in the Nura valley where flooding has caused widespread contamination that is difficult to manage by conventional means. Planting crops that are mercury hyperaccumulators (plants that can take up and concentrate a particular contaminant up to 100 or 1,000 times greater than the concentration in soil) can have significant remedial benefits over time at a relatively low cost. Management of the arising biomass containing mercury should be carefully considered.

7.3.3. In Situ Thermal Desorption (ISTD)

In Situ Thermal Desorption (ISTD) is a technology that is applied in the cases of severe contamination of the soil with mixture of organic hazardous materials (dioxins, PAHs, PCBs) geotechnical constraint for large excavation and the need for a very short operation time (Merly and Hube 2014). It involves heat injection and vapor extraction from the soil and could be utilised for mercury contaminated sites or sites with a mercury/dioxin combination. Experiments have shown up to 99.8 % removal of the mercury from soil matrices using ISTD (Merly and Hube 2014) but the technology is still in the development stage.

This process has very high energy consumption and requires a dense network of bore holes to be drilled for heating and vapor extraction. Fugitive mercury emissions may also be difficult to control. In addition the large number of bore holes raises the risk of contaminant leakage to any underlying freshwater aquifer systems and must be closely monitored to ensure the integrity of bore case sealing.



Figure 12: Full-scale ISTD operation on organic compounds contamination in the USA. Source: Merly and Hube (2014)

7.4 Proven treatment technologies for water contaminated with mercury

7.4.1. Pump and Treat

This is the most commonly applied treatment for mercury contaminated groundwater. It has applications for the treatment of mercuric brine which is common at sites of mercury cell chlor-alkali plants. The method involves drilling bores into the contaminated groundwater zone, pumping contaminated water to the surface and treating the water with a range of filtration media. The design objective is to capture the whole contaminated plume (or at least the majority of it) over a given period of time (as ongoing maintenance costs are high) and to treat the water to a low level of mercury contamination.

The effectiveness of the pump and treat system depends on the hydrogeology and the type of contaminants and the process is very slow.

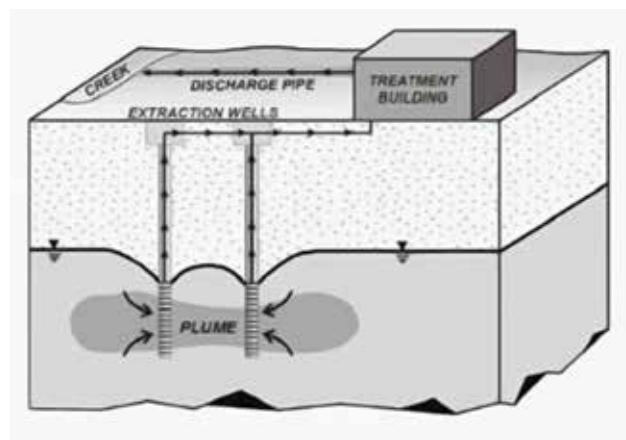


Figure 13: Pump and treat principles. Dept. of Geosciences Texas A&M University

7.4.2. Permeable Reactive Barriers

The other main technology used for the treatment of mercury contaminated water is permeable reactive barriers (PRB). PRB technologies consist of passive in-situ groundwater treatment based on the removal of mercury from groundwater flowing through an in-situ permeable reactive media involving sorption and or chemical reduction of mercury. The mercury plume is intercepted by an impermeable wall perpendicular to

the groundwater flow and designed to create a funnel, in the direction of the reactive permeable zone (“gate”) where mercury removal occurs. These lateral barriers are generally cut-off slurry walls (Merly and Hube 2014).

This technology has been used in Europe, Australia and the US at many sites to treat a range of contaminants including chlorinated solvents, hydrocarbons and inorganic compounds. Reactive materials including copper, pyrite and granular activated carbon (GAC) have been incorporated as filtration and conversion agents in the reactive ‘gate’ section of the barrier.

The main advantages of this system is the lower cost compared to pump and treat systems. However, the use of GAC to adsorb mercuric compounds requires regular monitoring and replacement upon saturation and must then be treated as a mercury waste with attendant costs.

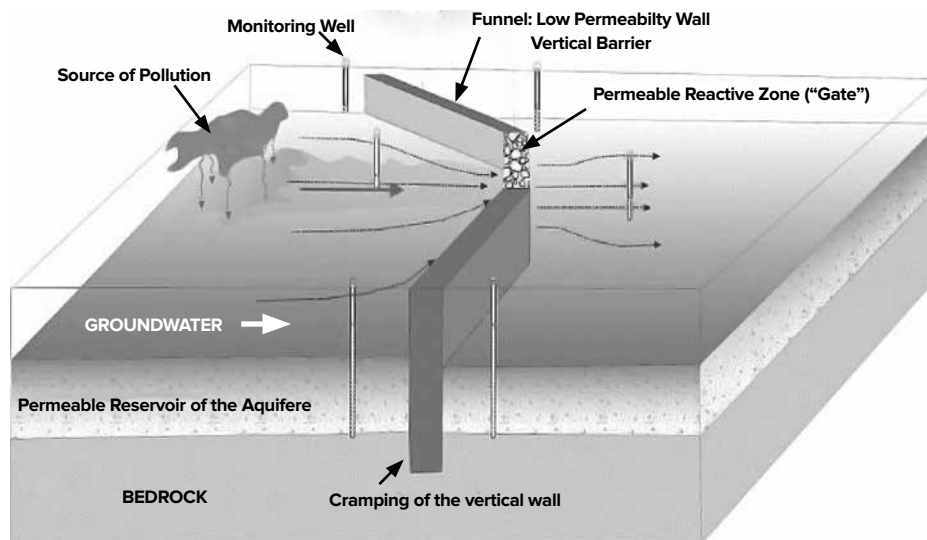


Figure 14: Pump and treat principles. Dept. of Geosciences Texas A&M University

7.5. Emerging water treatment technologies.

A number of water treatment technologies for mercury technology are being developed but are mostly in the experimental development phase. These include;

- » Bioremediation
- » Nanotechnologies
- » Alternative sorption materials
- » Alternative coagulation & flocculation

These are in the early development stage and are not detailed in this document however a discussion of their relative merits can be found in Dash and Das (2012) and Merly and Hube (2014).

8. DIOXIN AND PCB CONTAMINATION REMEDIATION

8.1. Non-incineration alternatives

The majority of this document is focused on remediation of mercury contaminated sites. However, a number of sites in Kazakhstan have been identified with dioxin and DL PCB contamination. While some of the remediation and treatment options identified for mercury are also relevant for dioxin and PCBs (in situ isolation, entombment etc.) the different chemical properties of mercury and dioxin can require different remedial options in terms of treatment. Mercury can be recovered through volatilisation and distillation processes including indirect thermal desorption. The recovered elemental mercury can then become a commodity or stored as waste. Dioxins and PCBs are scheduled for elimination under the Stockholm Convention on Persistent Organic Pollutants and must be destroyed or disposed of in an Environmentally Sound Manner (ESM).

In the past high temperature incineration has been used in an attempt to destroy PCBs and dioxins. This has been problematic because the residues of the process (especially fly ash) are highly contaminated and have to be stored permanently in isolated conditions. In addition, even optimal operation of the most advanced incinerators results in the release of some dioxin and DL PCBs to atmosphere through processes such as de novo synthesis post stack (Weber et al 2001). The fly ash is often buried deep in disused salt mines which have been subject to instability and concerns of leakage. There

are now a number of alternative technologies and processes, which have been commercially developed that can destroy PCB and dioxin contamination to levels approved by regulatory authorities. These include:

- » Gas Phase Chemical Reduction (GPR)
- » Sodium Reduction
- » Base Catalyzed Decomposition (BCD)
- » Solvated Electron Technology
- » Supercritical water oxidation¹⁷
- » Ball milling
- » Copper mediated destruction
- » Catalytic hydrogenation

Some of these technologies benefit operationally from a pre-treatment process units such as indirect thermal desorption units (ITDU). These technologies were evaluated by several expert panels since they were introduced and a lot of data is available about their practical use as well as potential risks (Luscombe 2001, IPEN Dioxin, PCBs and Waste WG 2010, US EPA 2010, UNEP 2004). Some of them are listed among environ-

¹⁷ for more details see Luscombe (2001) Non-incineration PCB Destruction Technologies. Greenpeace International. <http://www.istas.net/portada/cops8.pdf>



Figure 15: The Indirect Thermal Desorption Unit (ITDU) at Spolana Neratovice, Czech Republic.

mentally sound management (ESM) technologies for treatment of POPs containing wastes (Basel Convention 2007) and were evaluated by special Stockholm Convention expert group (UNEP – EG BAT/BEP 2006).

In some cases these need to be used in a treatment train where the PCB or dioxin is removed or separated from a larger matrix such as soil and then a much smaller amount of the concentrated contaminant is destroyed in one of the technologies listed above.

Example 1: Treatment train for HCH, HCB and dioxin waste from a contaminated

The thermal desorption unit heats contaminated materials to 500-600 °C stripping in absence of oxygen and POPs are collected in filter and condensation system. The BCD unit (see below) then destroys this concentrate.

Some technologies can operate in a singular manner to destroy PCB and dioxin wastes without the need for a treatment train.

8.1.1. Gas Phase Chemical Reduction (GPCR)

An Australian GPCR plant located in Kwinana, Western Australia, operated from May 1995 to December 2000, processing PCB and pesticide wastes (including DDT) for government and industry clients throughout Australia. A full scale treatability study was also conducted at this time to prove that the GPCR process could be used successfully for the destruction of highly chlorinated HCB. The plant in Australia closed and relocated overseas when all of the commercially available chlorinated hazardous waste in Australia was destroyed.



Figure 16: The BCD unit at Spolana Neratovice, Czech Republic in its building phase.

Around this time the company that developed the GPCR technology, Eco Logic, built several smaller scale demonstration plants and successfully treated many different types of organic wastes including chemical warfare agents, explosives, pesticides, brominated fire retardants, CFC refrigerants, HCB, and dioxins. The technology is proven suitable for the destruction of organic wastes in all matrices including soil, sediment, sludge, high-strength oils, tar, watery wastes, wood wastes, and bulk solids such as electrical equipment, equipment casings, and drums. The scientist that developed the technology Dr Doug Hallett has upgraded the GPCR system since the 1990's and currently markets the process through his company Natural Energy Systems Inc. Full details of the US EPA CLU-in assessment of this technology are available¹⁸.

18 US EPA CLU-IN http://clu-in.org/download/partner/vijgen/NATO_EcologFactSheet_3.pdf

DIOXIN DESTRUCTION RATES BCD AT SPOLANA		
Material	Inlet ng kg ⁻¹ I-TEQ	Outlet Oil Matrix ng kg ⁻¹ I-TEQ
Chemical waste	209,000	0
Chemical waste	200,000	4.3
Chemical waste	11,000	0.23
Chemical waste	47,000	0
Chemical waste	35,000	0
Dust	1,620,000	0.52

OVERVIEW OF NON-COMBUSTION TECHNOLOGIES					
	Capable of High DE*	Containment of all Residues and Wastes	Commercial Availability	Commercial Experience with POPs	Vendors
Ball milling	Yes	High	Yes	Moderate	Several
Base catalyzed Decomposition	Yes	High	Yes	Extensive	Several
Catalytic hydrogenation	Yes	High	Yes	Limited	Two
Copper Mediated Destruction	Yes	High	Yes	Very Limited	One
Gas Phase Chemical Reduction	Yes	High	Yes	Moderate	Onr
Solvated Electron Technology	Yes	High	Yes	Limited	One
Sodium Reduction	Yes	High	Yes	Extensive	Many
Super Critical Water Oxidation	Yes	High	Yes	Moderate	Several
<p>Note: Extensive = many years of commercial operation from multiple vendors. Moderate = many years of commercial operation from one or more vendors. Limited = some years of experience from at least one vendor. Very limited = only available from one vendor with limited commercial application.</p> <p>Destruction Efficiency (DE) – is calculated on the basis of the total mass of POPs fed into a process, versus the sum of the POPs in all products, by-products, and environmental releases (e.g. gaseous, solid and liquid) i.e. DE considers the total destruction of POPs in a given process.</p> <p>Destruction and Removal Efficiency (DRE) is calculated on the basis of total Pops fed into a process versus the concentration in the stack gases. It ignores releases in solid and liquid waste streams.</p>					

While GPCR is a proven non-combustion technology for the destruction of POPs such as dioxin and DL PCBs other non-combustion technologies have been developed that have a range of applications suitable for POPs destruction. The following two tables list the technologies, their applications and some limitations while providing some comparative data on costs. The tables are cited from a presentation prepared by Dr Darryl Luscombe given by Arnika representatives at the “Toxics Free Kazakhstan” Conference in Astana, Kazakhstan in August 2014.

In conclusion, non-combustion technologies are commercially available for POPs destruction and capable of meeting all the fundamental requirements of the Stockholm Convention for treatment of POPs wastes. Non-combustion technologies do not further promote the releases of dioxins and other POPs to the environment and are the preferred method of treatment for POPs wastes.

INDICATIVE COSTS OF TREATMENT					
Technology	Vendor	PCB Oils	Soils	Capacitors	Transformers
Ball milling ¹	EDL	\$300/ton	\$250/ton	\$300/ton	\$300/ton
Base catalyzed Decomposition ²	Multiple	\$0.7–2.2 kg depending on waste	\$300/m ³		
Catalytic hydrogenation ¹	Hydrodec Group PLCs	5–50 ppm PCB: \$0.40/L 50–500 ppm PCB: \$0.80/L >5.00 ppm PCB: \$4.00/L			
Gas Phase Chemical Reduction ¹	Natural Energy Systems Inc..	\$2,300/tonne - for 100% PCB waste	\$500/tonne - assumes low % of PCB	\$1,300/tonne - assumes 40% PCB	\$1,300/tonne - assumes 40% PCB
Solvated Electron Technology ¹	Oasis Systems/Commodore	\$5,512–\$6,614/tonne	\$5,512–\$6,614/tonne	\$5,512–\$6,614/tonne	\$5,512–\$6,614/tonne
Sodium Reduction ¹	Kinectrics Inc	\$0.9–\$7/litre		\$500 –1,700/tonne	\$500–1,700/tonne
Sodium Reduction ¹	ESI Group	\$0.35 to \$0.85/litre (up to 3,000 ppm)	\$680–\$1,700/tonne	\$1,700–\$4,250/tonne	\$800–\$1,200/tonne

Vendor supplied costing information all costs given in US dollars. Actual costs will depend on site-specific conditions.

Sources:

1. SNC LAVALIN Inc., PCB Management and Disposal Demonstration Project. Analysis of PCB Treatment & Disposal Options for the Socialist Republic of Vietnam. Final Report to The World Bank, July 20082.

2. Secretariat of the Basel Convention (ND). Destruction and Decontamination Technologies for PCBs and other POPs Wastes under the Basel Convention. A Training Manual for Hazardous Waste Project Manager. Volume C. Base catalyzed decomposition.

9. OCCUPATIONAL AND COMMUNITY SAFETY AND HEALTH MANAGEMENT FOR CONTAMINATED SITES

In line with the project objectives, building social capacity through the free flow of information is the basis for ensuring that occupational health and safety management is linked to community health and safety and all site investigation reports, health and safety plans, risk registers, remediation plans and waste transport and treatment plans are available to all stakeholders for discussion and amendment at the earliest possible time.

Contaminated sites remediation can involve a number of stages:

- » Preliminary site investigation
- » Detailed site investigation
- » Site management
- » Remediation, validation and ongoing management.
- » Waste transport and treatment.

Occupational and community safety and health issues are to be addressed throughout all stages of the process. It should also be recognized that site workers will have specialized protective and monitoring equipment that is not available to those outside the site boundaries as well as shorter exposure duration periods (<8 hours per day) on-site.

Monitoring trigger levels (alert levels) for fugitive emissions should be established that are protective for members of the public on the other side of the site fence line to reflect their lack of protective equipment and long exposure periods (up to 24hrs per day).

Any risk based calculation of acceptable air contamination concentrations and averaging periods should reflect this difference and be calibrated for sensitive receptors among the community (e.g. children, elderly, pregnant women and immune compromised individuals).

9.1. Overview

Contaminated sites may present health and safety risks to workers and community members during investigations and remediation and while these risks may vary between on-site and off-site impacts, they should be addressed in one framework to ensure transparency and accountability.

Hazards can be encountered at any stage of site works and may include other heavy metals in addition to mercury as well as volatile organic solvents, hydrocarbons, pesticides, industrial chemicals or even persistent organic pollutants and radioactive

materials These contaminants can be in a solid, liquid, vapor or dust form in the soil, air or groundwater. Other potential hazards include fires, explosions, confined spaces, gas lines and electricity, machinery, manual handling and transport risks. In some former and current conflict zones contaminated sites may also be impacted by buried unexploded ordinance (UXOs). Special precautions must be taken when investigating sites with UXOs and advice should be sought as early as possible from defense personnel with experience in screening for and neutralizing these devices. An extensive preliminary site investigation including all former uses of the site will assist in identifying the potential presence of radioactive material and UXOs and the need for more detailed screening for these materials.

Management of contaminated sites should ensure that all workers and potentially impacted community members are not exposed to hazards. While employers have a 'duty of care' to employees, total site management has a social responsibility to the broader community. Work on contaminated sites may involve risks from hazardous substances in an uncontrolled state with minimal or no information on their identity and concentration. Precautions must be taken and the assumption made that the site contains significant risks to the safety and health of workers and the broader community. Suspected contaminated areas should be viewed as hazardous unless proved otherwise by testing.

9.2. Duty of Care and Social Responsibility

Management of contaminated sites must ensure that:

- » There is full compliance with all relevant health and safety laws and consultation and cooperation is afforded to worker and government safety and health representatives;
- » Employees and other workers are provided with a workplace and safe system of work to protect them from hazards;
- » The community is informed of and protected from hazards emanating from the site. This includes dust, vapors, contaminated water flows and soils.
- » All workers receive relevant site-specific information, instruction, training and supervision to work in a safe manner without exposure to hazards;
- » Adequate personal protective clothing and equipment is provided without cost to the workers where hazards cannot be reduced to an acceptable level;
- » All plant is installed or erected so it can be used safely;

- » All handling, processing, storage, transportation and disposal of substances at the site are carried out in a manner that does not expose the workers or other community members to hazards.
- » All site investigation reports, health and safety plans, risk registers (see below), remediation plans and waste transport and treatment plans are freely available to all workers and other stakeholders.

9.3. Risk Registers

Management of contaminated sites must ensure that workers and the community have access to a regularly updated Risk Register, which sets out the identified hazards, the assessment of risk of injury or harm and the measures put in place to eliminate or reduce the risks. Workers and the community must be protected by hazard mitigation.

Application of a hierarchy of control measures ranging from the most effective to the least effective measures would include:

1. Elimination – removing the hazard or hazardous work practice.
2. Substitution – replacing a hazard or work practice with a less hazardous one.
3. Isolation – separating the hazard or work practice from people involved in the work (enclosing systems, remote access or physical barriers).
4. Engineering controls – modifications to tools or equipment or machinery guards.
5. Administrative control – work practices to reduce the risk, instruction, training and warning signs.
6. Personal protective clothing and equipment (PPE) – to be provided when other control measures have been applied and protection needs to be increased.
7. Continuous monitoring and review of control measures – to ensure continuing effectiveness and guard against unintended consequences.

The frequency of monitoring and review should be based on the level of risk, the type of work practice, the plant or machinery involved as well as environmental factors.

9.4. Information and Training

Management of contaminated sites must ensure that:

- » Information and education on all identified hazards in the form of a risk register be provided to the workers and broader community. This must include information

relating to known and suspected contaminants.

- » Induction, information, instruction, training and supervision in safe procedures are provided to all workers.
- » Specific training is provided to workers involved with hazardous substances, including health effects, control measures, emergency response and correct use of PPE.
- » Records kept of all induction and training for work with hazardous substances.
- » All workers are trained in emergency evacuation procedures and these are made available to communities at risk to help develop emergency response procedures should impacts occur off-site.

9.5. Supervision

All workers must be provided with adequate supervision to ensure they are not exposed to hazards and take reasonable care of their own and other's health and safety. This requires that:

- » Supervisors have the skills, knowledge and authority to fulfill the roles;
- » Training is ongoing and there is regular revision of safe procedures.
- » PPE is used and kept in adequate working condition.

9.6. Storage and transport controls for contaminants

General principles for storage and transport control:

- » Limit access to authorised people only.
- » Store contaminants in a cool secure, ventilated area with signage indicating material, concentration, risks and controls.
- » Monitor atmospheric contamination and temperature levels in storage areas to ensure they are within appropriate levels.
- » Choose an appropriate container for storage, such as corrosion or solvent-resistant.
- » Ensure all containers are labeled correctly and labels are kept intact.
- » Ensure all unknown substances are labeled as UNKNOWN SUBSTANCES – TREAT WITH EXTREME CAUTION;
- » Check the compatibility of substances stored together and separate if required. Avoid risks of mixing and cross contamination.
- » Check all containers against leakage or seepage.

- » Ensure appropriate fire fighting and emergency equipment is available.
- » Ensure a well developed evacuation procedure with regular drills for emergency situations.
- » Ensure all contaminants are secured before and during transport.
- » Ensure all plant and equipment is decontaminated before leaving the site.

All chemicals, contaminated soils and liquids must be stored and transported according to the relevant laws.

9.7. Workplace amenities and first aid facilities

Specific requirements for amenities relevant to the contaminated site should be established as part of the site specific safety and health planning. Where applicable, clean decontamination facilities should be provided which include, but are not limited to:

- » showers;
- » hand washing facilities;
- » eye wash facilities;
- » separate clean area;
- » areas for decontamination of all equipment, including washdown areas for trucks. If there is a high level of contamination then a separate decontamination unit should be provided for workers, in addition to and separate from other sanitary and washing amenities.
- » Mercury intoxication requires specialist medical intervention and treatment including chelation (treatment to accelerate mercury excretion from the body) and requires the worker to be removed from the source of exposure until treatment is completed and the exposure source investigated and removed.

9.8. Exposure monitoring

Exposure monitoring is means of measuring the exposure to contaminants experienced by people working on the site. In some cases this may also be considered appropriate for community members. Exposure monitoring should be carried out by a competent person to recognized monitoring standards. All exposure monitoring results are to be made available to anybody likely to be exposed to hazardous contaminants. In the case

of mercury contaminated sites biological monitoring via hair sampling on a regular basis may form part of the exposure monitoring program performed by an accredited laboratory with QA/QC procedures and experience in interpretation of analysis results.

9.9. Health surveillance programs

In addition to the requirements for hazardous substances already outlined, health surveillance programs should be undertaken for workers and community members known to have been exposed to 'high concern' hazardous substances. These include, but are not limited to:

- » asbestos;
- » inorganic arsenic;
- » inorganic chromium;
- » inorganic mercury;
- » cadmium
- » lead

- » methylmercury
- » polycyclic aromatic hydrocarbons (PAH);
- » crystalline silica;
- » thallium; and,
- » organophosphate pesticides
- » Persistent Organic Pollutants (POPs)

A health register can be established by local health workers under supervision of experienced clinicians and toxicologists. Workers and/or residents at risk of exposure can be added to the register and their medical condition monitored over time. The benefit of this approach is that local health workers can be trained to identify sentinel symptoms of exposure to specific contaminants and identify the early stages of the symptoms in patients that would otherwise go undetected. A register can also help to identify any clusters of contamination related health problems in a locality that may have legacy sites leading to long term exposure of residents.

10. KAZAKHSTAN CONTAMINATED SITES – CASE STUDIES SITES

The following section of this report considers several case studies of contaminated sites in Kazakhstan that are impacted by mercury, dioxin and DL PCBs. A brief description is provided of the location and the contamination and remedial actions are suggested in the context of civil participation and long term goals for social improvement through environmental rehabilitation of affected areas. Rather than considering the remediation of sites in a strictly science based framework this section discusses a collective impact approach and raises the benefit of free dissemination of information within society about the problems caused by the contamination and collective social responses to address the situation which build social capital and makes for more resilient communities.

10.1 Large Scale Mercury Contamination in Kazakhstan and the Mercury Treaty: developing a collective impact approach to civil society engagement.

The process of addressing the human health, environmental and economic impacts from mercury contaminated sites through collaboration and co-operation between a broad range of civil society organisations and communities will, with the aid of increased public access to information, raise community awareness, build capacity and empower civil society.

Collective impact involves the commitment of a diverse range of actors from different sectors to a common agenda for solving a specific problem (Kania and Kramer 2011). Unlike most collaboration, collective impact initiatives involve a centralized infrastructure and a structured process that leads to mutually reinforcing activities. While this approach has mostly been used to address complex social problems, it has also been used to clean and restore the Elizabeth River watershed in Virginia (Kania and Kramer 2013).

Kazakhstan faces a significant threat from the historical legacy of Soviet era military and industrial pollution (and many of these industries are still operational) with adverse consequences for human health, the environment and economic development. Of particular concern is the threat from mercury impacts arising from two specific examples of legacy industrial pollution. The first example is from an acetaldehyde plant on the River Nura in the city of Temirtau in north-central Kazakhstan and the second from a chlor alkali plant near the city of Pavlodar in north eastern Kazakhstan. These events show extensive and pervasive ongoing impacts from mercury pollution with serious risks for human health and ecological health, as well as adverse consequences for local economies. Developing an understanding of the nature and extent of mercury pollution impacts provides an indication of the potential for cross sector collaboration and civil society partnerships in addressing mercury pollution at a national, regional and local level.

10.1.1. Environmental Health

When mercury is released into the environment it starts the process of methylation to become methylmercury (MeHg), the most hazardous form of mercury to human and ecological health (Ullrich et al 2007). Inorganic mercury is readily converted to methylmercury in aquatic systems, accumulated by aquatic biota and biomagnified along the food chain where it presents as a risk to reproductive and neurological impairment in fish eating birds and mammals, even at low concentrations (WHO 1990). Wildlife exposure to methylmercury can cause death, reduced fertility, slower growth and abnormal development and behaviour that may affect survival. In addition methylmercury may affect the endocrine system of fish and potentially disrupt development and reproduction (US EPA 2014).

Aquatic food webs are known to be an essential pathway for mercury to accumulate in human bodies. Methylmercury is almost 100% absorbed by human bodies and exposure results in a range of neural problems including ataxia, visual field constriction, mental retardation, cerebral palsy and seizures (WHO 1990). Methylmercury in pregnant women can be passed to the fetus where the effects may range from subtle delays in cognitive and motor development to cerebral palsy, depending on how much and the period during the pregnancy that the methylmercury was consumed (Marsh et al 1995, Boishio and Henschel 2000). Developmental exposure to methylmercury is known to be linked to a loss in Intelligence Quotient (IQ), with associated lower school performance and educational attainment (Bellanger, M, et al, 2013).

10.1.2 Case Study 1: Mercury pollution in the River Nura and surrounds

The River Nura flows from the mountainous region in the east of Kazakhstan through the heavily industrialised Karganda region and nearly one thousand kilometres into the terminal lakes of the internationally important Korgalzhyn wetlands. These wetlands became Kazakhstan's first designated Ramsar site and Lake Tengiz has recorded over 300 species of migratory waterfowl, many of which are endangered. For decades an acetaldehyde plant in Temirtau, a city on the Nura river, known as 'Karbid' discharged large volumes of mercury waste and other pollutants into the river before being closed down in 1997 (Ullrich et al 2007, Šír 2015 a).

In the river the mercury became associated with millions of tonnes of power station fly ash forming a highly contaminated 'technogenic silt' which disperses over the

floodplain during spring floods (Heaven et al 2000). In 2003 the World Bank loaned the Kazakhstani Government \$40 million to undertake a long-term remediation of the mercury impacts. Work began in 2007 and was completed in 2013 (Šír 2015 a). Prior to the remediation program the topsoils of the floodplain contained an estimated 53 tonnes of mercury, and silt deposits along the banks of the river contained about 65 tonnes, with an additional 62 tonnes in Zhaur Swamp approximately 1.5 km from Temirtau city.

Seasonal hydrological conditions in the River Nura control mercury concentrations in surface waters, with the majority of mercury mass flow during the annual spring flood when contaminated bed sediments are remobilized (Ullrich et al 2007). The sediments within a 20 km section of the river downstream from the effluent outfall were highly polluted. Concentrations exceeding the legally allowable Kazakhstani limit value of 2.1 mg kg⁻¹ were found 75 km downstream of Temirtau in Intumak Reservoir and concentrations above 10 mg kg⁻¹ total mercury (Dutch intervention value) were found 60 km downstream (Heaven et al 2000)

Zhaur Swamp, just outside the city of Temirtau and less than 1 km from the nearest villages, was found to have extremely high concentrations of mercury and concerns have been raised regarding the long term viability of the villager's drinking water supply. Concentrations of mercury in fish were shown to still be elevated more than 100 km downstream from the source and for most species there was no significant decrease in mercury levels over this distance. It has been suggested that this could reflect fluvial transport of methylmercury from upstream sites or increased in-situ production of methylmercury downstream (Ullrich et al 2007).

A 2009 study of mercury concentrations in hair samples involved analysis from Temirtau town and four floodplain villages (Chkalovo, Gagarinskoye, Samarkand and Rostovka) ranging from 1.5 to 35 km from the outfall. From this study it was determined that 17 % of the population exceeded the safety standard of 1 µg g⁻¹ for hair mercury developed by the US EPA and these people were considered at risk (Hsiao et al 2009).

In the two largest of these population centres (Temirtau and Chkalovo) many residents reported they were concerned about mercury contamination and did not eat river fish that they caught. Discussions with market fish vendors indicated that they recognized the sensitive issue of mercury in fish and often advertised the fish origin of their stock (Hsiao et al 2009). While there may have been a local consciousness of mercury

pollution and possibly lower consumption in the two largest centres, the three riverine villages consumed significantly more local caught fish than commercially purchased, up to 80% of all fish meals. In conjunction with this study it was found that about 84 % of all fish samples exceeded the Kazakhstani safety level of $0.3 \mu\text{g g}^{-1}$ and 33 % exceeded the threshold levels of $0.5 \mu\text{g g}^{-1}$ (Hsiao et al 2009).

Summary of outcomes and impacts from mercury contamination of River Nura:

- » Unsafe levels of mercury contamination in river sediment, floodplain soils and fish, with the loss of clean water, clean fish and clean agricultural land resulting in associated adverse economic impacts.
- » Potential mercury related health impacts in adults.
- » Potential neurotoxic health impacts in children, and associated educational and economic consequences.
- » Potential for further dispersion of mercury loaded sediments to accumulate in the Ramsar wetlands where the river terminates with risks to endangered wildlife.

10.1.2.1. Remedial actions and outcomes:

The remediation activities undertaken between 2007 and 2013 were known as the “Nura River clean-up project”. While significant amounts of mercury pollution were remediated concerns remain as to whether the fundamental goals of the project were achieved.

The main goals of the project were to clean up the Nura riverbed, ensuring effective management of the landfill site where contaminated soil was contained, as well as to rehabilitate the Intumak dam, which provides flow control downstream and functions as a pollution trap of mercury contaminated reservoir sediments (Šír 2015 a).

The dredging of the riverbed and cleanup of the riverbanks (to remove mercury contaminated technogenic silt) has improved environmental conditions on the Nura River. At the beginning of the project the mercury pollution levels in soils and sediments ranged from $50\text{--}1,500 \text{ mg kg}^{-1}$. In 2012, mercury polluted soil has been removed to meet internationally accepted safe levels for upper soils 2.1 mg kg^{-1} for agricultural use and 10 mg kg^{-1} for other land use. Remote areas were cleaned to 50 mg kg^{-1} (Šír 2015 a). Water quality in the river has improved and mercury levels are now below water quality guidelines for drinking water. The Karbid factory site has been remediated and 2 million tonnes of contaminated soil disposed of to a dedicated hazardous waste landfill which

has capacity to receive further wastes in the event of additional remediation activity.

A 30 km long section of the Nura River, from the Samarkand reservoir to Rostovka village, was cleaned of mercury contamination including the impacted area of locality of Zhaur Swamp. This remedial action made approximately 6,234 hectares of land available for agricultural and cattle grazing purposes which will be a major benefit to the communities along the Nura river for the foreseeable future. Air quality has also improved considerably with mercury vapor levels dropping from a range of $6,000\text{--}140,000 \text{ ng m}^{-3}$ down to below the regulatory limit of 300 ng m^{-3} (Abdullah et al. 2013).

In 2013–14 a partial validation sampling survey was conducted by Arnika Association of the Czech Republic and two Kazakhstani NGOs EcoMuseum and CINEST to assess post remediation contamination impacts. The NGOs testing revealed elevated amounts of certain heavy metals (mercury, chromium, lead and cadmium) in some of the sediment samples, elevated levels of mercury in fish meat samples and elevated levels of PCDD/Fs and DL PCBs in some egg samples (Petrlík 2015). This indicates that more action needs to be taken to ensure that the river is cleaned up to a satisfactory standard. A comprehensive account of the sampling regime and a detailed site history of the mercury pollution of the Nura River are included in the reports by Šír (2015 a) and Abdullah et al. (2013).

The remediation did lower mercury contamination in many parts of the Nura river and surrounds however many sites are still polluted and exceed the remediation limits established for the clean up project. In Rostovka, Temirtau including Krasniye Gorki, Chkalovo, Samarkand and Gagarynskoe, mercury levels are still too high, as well as the levels of copper, chromium and zinc (Šír 2015 a).

Mercury levels in fish from the river still exceed the safe consumption guidelines and warnings should be issued to protect sensitive sub-populations (pregnant women and children). Due to the hotspots of contamination detected by the NGO Arnika and ongoing indirect contamination of fish it is recommended that ongoing soil, water and biota sampling take place to assess the need for further clean up activities.

10.1.3. Case Study 2: Mercury contamination in the vicinity of Pavlodar

Pavlodar is a city of over 300,000 people located on the Irtysh River in north-eastern Kazakhstan. The Pavlodar Chemical Plant operated a mercury-cell chlor-alkali plant that produced chlorine and alkali between 1975 and 1993, resulting in widespread mercury

contamination of the surrounding environment (Randall et al 2007). It has been estimated that in excess of 1,300 tons of mercury may have polluted the environment during the years of operations. In 2006 the Pavlodar Chemical Plant, owned as a joint venture with the municipality of Pavlodar as one of the major stockholders, was intending to equip the plant with new chlorine production lines using membrane technology (Randall et al 2007). The exact status of current ownership and investment plans are not known.

Building 31 where the mercury electrolysis cells were located has been identified as a principle mercury hotspot (1 km²), with mercury concentrations in the top 50 cm of soil exceeding the Kazakhstani standard of 2.1 mg kg⁻¹ and an estimated 20,000 m³ above 10 mg kg⁻¹. The highest concentrations of mercury were in excess of 2 mg kg⁻¹ (Ullrich et al 2004). Soviet government investigations included an estimate of 1,000 tons of metallic mercury deposited under Building 31 and in its concrete basement (Randall et al 2007).

Groundwater modelling has shown a plume beneath the plant moving north in parallel with the Irtysh River comprised of soluble compounds of inorganic mercury such as chlorides, sulfates and complexes of organic acids (Randall et al 2007). Mercury concentrations within the groundwater are as high as 150 µg l⁻¹ in the plume beneath Building 31 and also near the waste lagoons, although the contamination did not appear to have spread more than 2.5 km from the site during studies from 2004 (Ullrich et al 2004).

When the roof of Building 31 was removed in 1998 in order to commence the site clean-up, extensive mercury vaporization occurred and the city of Pavlodar declared a state of emergency. Public and media pressure forced the government to allocate funds for dismantling Building 31 and mercury separation and collection, however, after the funds were spent the remediation effort halted. The footprints for Building 31 and the sludge collecting ponds have been sealed and capped with a clay barrier and a 3588 m long cement/bentonite cutoff wall has been constructed around this area (Randall et al 2007).

Untreated wastewaters from the chlor-alkali plant were discharged into the nearby shallow and impounded Lake Balkyldak, which constitutes a second major hotspot of mercury contamination. A 2007 study showed that sediments from the lake were heavily contaminated with mercury concentrations in the surface layer as high as 1,500 mg kg⁻¹ near the wastewater outfall pipe (Ullrich et al 2004). Re-suspension of lake sediments through wind action is acting as a strong source of mercury to the water

column, which raises the mercury levels at the outfall from 1.39 µg l⁻¹ to 7.3 µg l⁻¹. Fish from the lake were sampled and found to be unfit for human consumption, with mercury concentrations ranging from 0.16–2.2 mg kg⁻¹ (Ullrich et al 2007).

Lake Balkyldak is recognized as being highly contaminated and in need of remediation and that exposure routes for mercury through the consumption of contaminated fish is a real risk.

Concentrations of mercury in sediments from the River Irtysh ranged from 0.046 mg kg⁻¹ in the old river channel to 0.36 mg kg⁻¹ in the floodplain oxbow lakes, also the site where the only trace concentrations of 3 to 9 ng l⁻¹ of mercury were found in the water (Ullrich et al 2007). At this stage according to the studies done, the River remains only slightly impacted by mercury.

The northern outskirts of Pavlodar is still at risk from a possible change in the groundwater plume direction as well as upward movement of the mercury pollution to the surface of the pastures next to Lake Balkyldak. The US EPA had funded a number of additional mercury studies in 2006 to, amongst other work, improve the accuracy of the forecast for the mercury contaminated groundwater into the northern industrial area of Pavlodar (Randall et al 2007).

With important implications for mercury remediation efforts, a study (Kajenthira et al 2012) investigated stakeholder risk perceptions associated with the chlor-alkali site and found that the indifference of the local population to the possibility of health risks could pose a barrier to successful site remediation. The authors recommended that prioritizing the engagement of the local population would be critical for remediation success.

Summary of the outcomes and impacts of mercury contamination in the vicinity of Pavlodar:

- » 'Containment' of mercury contamination from chlor-alkali plant behind cut-off wall and under clay capping. This is not considered a long term solution and will require monitoring to detect failure.
- » Unsafe levels of mercury contamination in the sediments of Lake Balkyldak and high levels of mercury contamination in the fish making them unfit for human consumption.
- » Loss of commercial and subsistence fishing activity and social activities related to community use of the lake.

- » Potential mercury related health impacts in adults.
- » Potential neurotoxic health impacts in children, and associated educational and economic consequences.
- » Potential groundwater plume contamination of pastures next to Lake Balkyldak.

10.1.3.1. Potential remedial actions:

Although some preliminary remedial action has taken at the source of the mercury contamination to cap hotspots and prevent vapor release extensive monitoring will need to remain in place to ensure the integrity of the capping and the operation of the cut-off wall. Investigations should take place as to whether remaining soil contamination at the chlor-alkali site is amenable to ex-situ indirect thermal desorption (ITD) either on-site (to reduce costs and transport) or ex-situ.

The confirmed contamination of Lake Balkyldak is more problematic. While it is possible to dredge the lake sediments and subject them to treatment (ITD), entombment and isolation or other methods remobilization of mercury during the dredging process could prove an unacceptable risk. In some situations mercury contaminated sediment can be left in situ and methylmercury releases diminish over time as siltation progressively reduces exposure of the contaminated sediment to receptors such as aquatic biota. However, in the case of Lake Balkyldak re-suspension of mercury through wind effect is raising mercury levels from $1.39 \mu\text{g l}^{-1}$ to $7.3 \mu\text{g l}^{-1}$ near the out-fall. This will continue to cause fish contamination for the foreseeable future. Fish from the lake are already mercury contaminated and unfit for consumption. An investigation of remediation options should be considered including the potential for dredging of contaminated sediments and subsequent treatment as well as less invasive options such as bioremediation trials.

Most importantly there is need for a public awareness campaign to inform the public of the dangers of the mercury contamination and highlight the need for risk related behaviour management such as avoiding consumption of contaminated fish, restricting water based activities in the contaminated lake (specifically swimming and other direct contact exposures). The future of Lake Balkyldak should be discussed through public forums that consider its current constraints and the potential benefits or problems associated with a range of remedial options.

10.2. Dioxin and Dioxin-like PCB contamination in Kazakhstan

While the main focus of this report is on mercury contamination in Kazakhstan, former and current industrial activity has left a legacy of dioxin and PCB contaminated sites and ongoing contamination issues. The need for remediation of these sites and community engagement and awareness raising are similar for these contaminants.

10.2.1. Health effects of dioxins (PCDD/F) and DL PCBs

Dioxins (*polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans or PCDD/F*) are a group of chemically-related compounds that are persistent environmental pollutants (POPs). Certain dioxin-like polychlorinated biphenyls (PCBs) with similar toxic properties are also included under the term “dioxins”. They are found throughout the world in the environment and they accumulate in the food chain, mainly in the fatty tissue of animals. More than 90 % of human exposure is through food, mainly meat and dairy products, fish and shellfish (WHO 2010).

Dioxins are highly toxic and can cause reproductive and developmental problems, damage the immune system, interfere with hormones and also cause cancer. Prevention or reduction of human exposure is best done via source-directed measures, i.e. strict control of industrial processes to reduce formation of dioxins and DL PCBs. Dioxins are released from waste incinerators, cement kilns, medical waste incinerators, metal smelting operations, paper pulp manufacturing and pesticide manufacture. Dioxins are listed for elimination under the Stockholm Convention on Persistent Organic Pollutants.

10.2.2. Case Study 3: Balkhash city (including the Kazakhmys tailings dump), Karagandy Oblast, Kazakhstan.

Balkhash is a city in Karagandy Oblast, located on the northern shore of the Lake Balkhash at the Bay Bertys. An industrial area near the city has a range of metal ore processing and refining operations established in the Soviet era and now operating under Kazakhmys Corporation LLC. The collective name of the operations at the industrial zone is ‘Balkhashtsvetmet’ and includes the Balkhash Non-Ferrous Metals Processing Plant. The metallurgical operations are the main source of pollution contributing non-ferrous metals (Cu, Pb, Zn, Cd, As), large emissions of sulphuric acid gas and dioxin

contamination to the area. The Balkhashtsvetmet also has an adjacent waste dump 25 km² in size (twice the size of the city itself).

Concerns over the health of Balkhash residents have grown in recent years due to a significant spike in health issues believed to be related to pollution. In an assessment over a five year period, the birth of the children with congenital developmental anomalies is 2.7 times higher than in Kazakhstan overall. The level of hormone-dependent congenital developmental anomalies (14.4%) is more than twice the national reference level. There are also high cancer rates. Morbidity of a majority of hormone-dependent cancers are 1.5–2 times above the average for national Kazakhstan (Dyusembayeva 2014). Preliminary sampling suggest that there may be a link between these illnesses and heavy metal and dioxin contamination from the Balkhashtsvetmet, associated operations and the massive waste dump.

NGO sampling:

The highest level of lead observed in soil samples from Balkhash has exceeded US Regional Screening Levels (RSL) for all uses by 10 fold. The limit value of 400 ppm of lead was exceeded in 5 of 14 sediment samples and in 5 samples of 15 samples of soil. Arsenic RSL was exceeded in 3 samples of soils as well as in 3 samples of sediments (up to 900 fold in soils and 1,250 folds in sediments). The highest level of copper in sediment sample has exceeded RSL by 17 fold (Šir 2015).

Sampling for dioxin in wall dust scrapings at a copper smelting shop in the industrial zone reported I-TEQ 263.78 pg g⁻¹. Soil dioxin screening levels for residential area in many countries are 10 I-TEQ pg g⁻¹ (US EPA 2009). Values in soils in the city (The Central Park) reported more than 6 I-TEQ pg g⁻¹. Soils from 1–3 km from the site reported PCCDD/F of around 1 I-TEQ pg g⁻¹ indicating that airborne deposition is limited. However, smelting activities appear to be the source of localised dioxin contamination at the industrial centre.

10.2.2.1. Potential Remedial Actions:

Further investigation and characterization of the emissions from the Balkhashtsvetmet, and associated operations are warranted. In addition the large waste dump should be subject to a Detailed Site Investigation to characterise exposure pathways for heavy metals and PCDD/Fs release. A remediation plan should be developed combined with a

community engagement program to raise awareness of the issues. Further groundwater investigations should also be considered. A population health study in conjunction with a hair sampling program could be established to ascertain to what degree non-ferrous metal contamination is impacting on the Balkhash residents given the extremely high levels of arsenic and lead detected. The very high lead levels are also a significant concern for developmental issues in children.

Similarly a dioxin sampling program utilizing breastmilk from women of child-bearing age should be considered as it is less invasive than other biological sampling and may provide an indication of dioxin/PCB body burden among mothers. This may provide some indication of dioxin contribution to the elevated hormone-dependent congenital developmental anomalies in Balkhash.

10.2.3. Case study 4: Abandoned electric substation, Ekibastuz city, Pavlodar Province, Kazakhstan. PCB contamination.

The substation was constructed for rectifying AC to DC using 15,000 capacitors on two outdoor areas. After the collapse of the Soviet Union the substation was abandoned and local residents dismantled the capacitors for scrap copper causing significant PCB oil spills. A poorly conducted emergency clean-up took place in 2002 where capacitors were partially dismantled and sealed. PCB contaminated soil was removed and packed in bags. The capacitors and contaminated soil were removed and placed in underground storage ATB in the former Semipalatinsk nuclear Test Site (technical test area Opytnoe Pole).

Following the rudimentary clean-up 2002 the level of PCBs in the soil substation was 26,200 mg kg⁻¹, while the acceptable level for agricultural soil in Kazakhstan is 0.06 mg kg⁻¹ compared to 40 mg kg⁻¹ for soil in industrial areas in Germany. There is no PCB value established in Kazakhstan as yet for remediation or other purposes for industrial areas. 50 mg kg⁻¹ of PCBs is provisional low POPs content value established by Basel Convention. All wastes (including contaminated soils) above this level should undergo POPs destruction or irreversible transformation according Stockholm Convention (Basel Convention 2007).

The site has been investigated and partially characterized with quantification of soil contamination volumes (SNC-Lavalin International Inc 2010). It was estimated that 2,800 cubic metres of material are classified as hazardous waste due to PCB concentra-

tions. A further 5,200 cubic metres were designated ‘heavily contaminated soil’ while a further 125,000 cubic metres was designated as ‘weakly contaminated soil’. The estimates suggest the volumes could be 3 times higher but could only be confirmed by further study and potentially excavation.

PCB contamination in one sample of groundwater (downstream) on the eastern boundary of the site found PCB concentration of $1.1 \mu\text{g l}^{-1}$.

10.2.3.1. Potential Remedial Actions:

The contamination at the electrical substation near Ekibastuz city could have a much wider influence than the site-specific contamination due to the extensive community vegetable production gardens (‘dachas’) around the site. The ‘dachas’ are sited 500 m from the boundary and occupy around 3 km² of land and are farmed by up to 5,000 people. While the substation is fenced and has security, wind and water borne contamination may affect these crops and any livestock grazed in the vicinity. This includes a family that act as caretakers on the site and raise cows, sheep and poultry. More broadly it is estimated up to 30,000 people purchase and consumed food from the dachas potentially amplifying the impacts of the contamination.

Initially, sampling of produce from the dachas should be conducted to ascertain if PCBs are elevated –especially among livestock and dairy produce. A community awareness program should be initiated to inform dacha owners of the potential for contamination and ensure they do not use soil from impacted areas on their crops and to source irrigation water from sites not associated with the sub-station.

Wind erosion is the most likely pathway for the spread of contamination in natural circumstances in Kazakhstan, and this should be considered in any models of risk assessment. Elevated levels of PCBs have been found in sediments in the direction of prevailing winds nearby the substation (Petrlik 2014).

The contaminated soil from the site could be excavated and treated with a treatment train consisting of indirect thermal desorption (on site depending on accessibility) to remove/separate the PCBs from the soil and then Gas Phase Chemical Reduction (off site) could be used to destroy the concentrated PCBs.

Further groundwater monitoring may be required to ascertain the extent and movement of any PCB plume. However, PCBs are a dense non-aqueous phase liquid (DNAPL) and tend to form a pool or ‘fingers’ in groundwater below the surface rather than highly mobile plumes and may be amenable to short term pump and treat solutions depending on the hydrogeology at the site.

11. COMMUNITY ENGAGEMENT ON CONTAMINATED SITES:

EMPOWERING CIVIL SOCIETY THROUGH INFORMATION SHARING AND RAISING AWARENESS.

In the process of addressing the economic, human health and environmental impacts from mercury and POPs contaminated sites, collaboration and cooperation between a broad range of civil society organisations and communities will, with the aid of increased public access to information, raise community awareness, build capacity and empower civil society.

With the increased availability and dispersal pathways of information on chemical safety and the application of demonstration projects to engage with affected communities and provide health, environmental and economic outcomes, there will be greater impetus for implementing legislative change to further address chemical safety at a local, regional, national and international level.

An empowered and resilient civil society, with ongoing international support, will be well placed to undertake direct monitoring, evaluation and verification of con-

taminated sites clean-up and continuing improvements in broader chemical safety. Outcomes for mercury and POPs contaminated sites clean-up and safe disposal will include health, educational, agricultural and fishery benefits and associated positive economic impacts.

11.1. Contaminated sites and the Requirements of the Minamata Convention on Mercury: Engaging the Public.

The Minamata Convention on Mercury outlines activities parties can undertake to address contaminated sites and generate information for the public to raise awareness about their implications for human health and the environment. Kazakhstan is not yet a signatory to the convention and will need to take further steps at a national level to prepare for the necessary requirements. In the meantime guidance such as this document

can assist to build capacity within the community, among NGOs and policy makers to address mercury and POPs contaminated sites within Kazakhstan.

At this point the parties to the convention have not yet developed specific guidance for contaminated sites but this does not prohibit national governments from developing their own management frameworks, policies and legislation to assess identify, characterize and remediate contaminated sites. As Kazakhstan makes progress toward ratification of the Minamata Convention on Mercury it is important to be aware of the specific statements made in the treaty about mercury contaminated sites and the need for public engagement.

Under Article 12 “Contaminated sites”, the Conference of Parties are required to prepare guidance on managing contaminated sites that include methods and approaches for “Engaging the Public” (UNEP 2013).

In addition, under Article 18 “Public information, awareness and education”, each Party is required to provide to the public information on mercury pollution as well as the “results of its research, development and monitoring activities under Article 19”. Parties are also required to provide education, training and public awareness related to mercury health effects in collaboration with relevant intergovernmental and NGOs and vulnerable populations.

Public engagement and the empowerment of civil society through cross-sector collaboration and cooperation requires an integrated two way approach between a national and regional level engagement of civil society and a local site specific process of stakeholder engagement. Each process should have the capacity to inform and adapt the other. However, public engagement needs also to take into consideration the specific cultural, social and political context to be most effective.

11.2. National Engagement of Civil Society on Contaminated Sites.

At a national and regional level there is an opportunity to utilize the principles involved in a collective impact approach, which would assist in the process of cooperation and collaboration between NGOs and across sectors.

The process of accessing and disseminating relevant information, identifying, cleaning up and safely disposing of mercury contamination and restoring river and lake ecology is an adaptive problem with relevance to a variety of civil society organisations

and communities, government departments and private sector interests. The negative economic, health, environmental and social impacts from mercury contamination represent an opportunity to engage a broad coalition of interests, ranging from health and education services to academic and research institutions to agricultural, fishery and environmental stakeholders along with government and union interests.

Five conditions required for successful collective impact include:

- » a common agenda,
- » shared measurement systems,
- » mutually reinforcing activities,
- » continuous communication and
- » backbone support organisations.

Collective impact requires the participants to have a shared vision for change with a common understanding of the problem and agreed actions to a joint solution (Kania and Kramer 2011). The agenda may, for example, be framed in the context of environmental health and local economic benefits rather than contaminated sites remediation.

Shared measurement systems are essential for agreement on measuring success and this process ensures that all efforts remain aligned. An overarching plan to coordinate the differentiated activities of participants allows for mutually reinforcing action, but enables each organization to determine a course consistent with the agenda and informed by shared measurement of results (Kania and Kramer 2011). Depending on the common agenda, measurement systems in the Kazakhstan context may apply, for example, to contaminated fish, drinking water or area of remediated agricultural land or all three. Shared measurement, mutually reinforcing activities and continuous communication enable participants to react consistently with the common agenda to emerging problems and opportunities (Kania and Kramer 2013).

Coordination and collaboration require supporting infrastructure such as a separate organisation and staff to serve as the backbone for the duration of the collective impact and plan, manage and support the initiative. In some instances this has been simplified to three roles: project manager, data manager and facilitator (Kania and Kramer 2013).

The advantage of using a collective impact approach is that it actively engages cooperation, collaboration and coordination, which in turn builds civil society capacity and

greatly assists in disseminating vital information on chemical safety. However, building a partnership of this nature requires additional lead-up time and resources.

In terms of mercury remediation in Kazakhstan there is a clearly identified need for site specific stakeholder engagement (Kajenthira et al 2012) and this should have a two way interaction with a national or regional level collaboration. This would facilitate adaptation and responsiveness to changing circumstances.

11.2.1 Guidance for Site Specific Stakeholder Engagement

Stakeholder engagement in the identification, assessment and remediation of mercury contaminated sites involves the deliberate participation of individuals, communities, NGOs, government authorities and others who may have an interest in, or be potentially affected by, the contaminated site and the clean up activities. Stakeholders may include; landowners and residents living near the site; communities and industries affected by the ongoing impacts of mercury pollution; public health, environmental and other regulatory authorities; NGOs and site management and workers.

Stakeholders have a right to information about environmental health factors that affect their lives, the lives of their children and families and the future of their communities.

The aim of stakeholder engagement is to improve the quality of the decisions made for the particular remediation project as well as also improving the decision-making process itself. Two-way engagement, which effectively conveys information and enables stakeholder participation in the decision making process, can provide significant cost savings and improve credibility for organisations involved in contaminated sites management. Stakeholders benefit by contributing to improved risk management decisions and more acceptable site management options which deliver improved health, safety and amenity benefits.

11.2.2. Stakeholder Preparation

Stakeholder engagement should start as early as possible and continue throughout the identification, assessment, remediation and management of the contaminated site. In addition, stakeholders should be engaged whenever a new issue is identified that may pose a risk to health or the environment or raise public concern.

Preparation and research for stakeholder engagement can be integrated into the process of site identification and characterization as there is considerable potential for

information from each process to inform the other. Stakeholder preparation can involve a number of components.

11.2.3. Understanding the issues

Ensure there is a clear understanding of the key issues to be addressed through the site assessment, remediation and management. These can include a range of events or actions where decisions are being made. In addition there should be an understanding of the extent of existing off site impacts and affected communities.

11.2.4. Ethnographic assessment

Ethnographic assessment can be undertaken to determine the nature and extent of community interactions with the suspected or known mercury contaminated site as well as demographic information on those interactions. It is important that ethnographic surveys are conducted across a broad time spectrum (not just office hours) and include seasonal variations. Is the site a source of salvage materials or other resources or a commonly used site for waste disposal? Is the site an informal gathering or meeting place or part of a transport link (commonly used shortcut)? Are there seasonal factors in the community interactions with the site? An ethnographic assessment will also identify whether areas adjacent, downstream or downwind to the site are actively used or accessed by members of the community. Identification of sensitive receptors, contamination vectors and people potentially requiring follow-up health survey and investigations will all benefit from undertaking an ethnographic assessment.

11.2.5. Potential stakeholders

In general, stakeholders will come from the following sectors and initial contacts may yield additional information on organisations and individuals with a relevant interest;

- » Landowners, residents and their representative organisations and community leaders.
- » Non-government organisations. These may include environment groups, public health groups, agricultural and fishery groups and others whose interests may overlap with the benefits of reducing mercury contamination in the environment.
- » Local, regional and national government agencies and representatives.
- » Local businesses, public services (school, utilities etc) and their representative or-

ganisations who may be affected by the remediation.

- » Workers, unions and associations.

In addition to the above, further stakeholders may be identified by considering the following questions;

- » What is the project's geographical area of impact, including off site impacts?
- » Who is currently affected by the issues, including off site mercury pollution?
- » Who are the representatives of those likely to be affected?
- » Who are the 'voiceless' for whom special efforts may have to be made?
- » Whose absence from participation would detract from the final results?

The list of potential stakeholders will form the basis for the development of a stakeholder engagement plan, although any subsequently identified stakeholders should be included and the plan adapted.

11.2.6. Stakeholder Planning

Development of a stakeholder engagement plan should take place at an early stage of the preliminary assessment of site contamination. The plan should include a description of the overall remediation and management project.

When there is clarity about the issues and stakeholders involved, the objective/s of the program should be set out, including information about the purpose of the engagement as a whole as well as specific objectives relating to engagement activities planned to address particular issues. Different approaches to stakeholder engagement for various activities should be clarified and may include:

- » Inform – promote awareness and educate.
- » Consult – seek input and feedback.
- » Involve – two way discussion where there is a real opportunity to influence the final outcome.
- » Collaborate – facilitate consensus so that stakeholders shape decisions that affect them.
- » Empower – provide a forum for stakeholder decisions where there is an agreement to implement these outcomes.

The stakeholder engagement plan should be flexible and responsive to changing circumstances and stakeholder input. Before engagement activities commence, the plan should be tested to ensure the appropriate stakeholders have been identified and the plan is likely to meet expectations of the engagement process.

11.2.7. Stakeholder Implementation

A concise summary of the stakeholder engagement plan should be provided to all stakeholders in the form of a 'statement of intent'. This would include the following:

- » background information about the site, a statement about the project and the purpose and objectives of the engagement process;
- » a description of the major issues likely to be addressed;
- » a description of stakeholders;
- » a statement on the kind of involvement that is being sought;
- » a list of key engagement techniques that will be used;
- » a commitment on how the information from the process will be used
- » a commitment on how feedback will be given to stakeholders on how their input was used and the reasons for decisions;
- » a timeline for the engagement program that allows sufficient time for stakeholders to discuss and form opinions on the issues;
- » a list of staff and funding resources available for the engagement program;
- » sources of further information, including contact details for relevant staff and stakeholder representatives.

Stakeholder engagement techniques will need to be designed for the local context and consider cultural, social and seasonal factors that may influence participation.

Examples of techniques include:

- » individual consultations with community leaders and organizational representatives;
- » public meetings;
- » on-site meetings;
- » printed information;
- » workshops;
- » design meetings

Feedback to stakeholders should be provided at each stage of the engagement process, following engagement activities and at the completion of the program. Timely reporting back to stakeholders validates information as it is gathered as well as encouraging continued involvement. In addition to the opportunity for people to hear other people's views, evidence is provided that stakeholder's views, comments and suggestions have been recorded accurately and received attention.

When reporting back to stakeholders, feedback should include details about:

- » the rationale for, and extent of, the engagement process undertaken;
- » stakeholders who were identified and invited to participate and those who actually participated;
- » how, when and where the engagement activities were carried out;
- » the information that was provided to stakeholders;
- » input provided by stakeholders;
- » the decision that was made;
- » how the stakeholder's input was considered and incorporated into the decision making process;
- » other factors that may have influenced the decision that was made;
- » availability of any relevant documentation.

11.2.8. Stakeholder Evaluation and Reporting

Evaluation of the processes and outcomes is an integral part of a stakeholder engagement program and can help to:

- » identify if stakeholders are satisfied that the process is fair and fulfills expectations;
- » improve future stakeholder engagement activities and programs;
- » establish if there is a need for ongoing engagement activities;
- » improve the cost-effectiveness of future processes.

All stakeholders should be involved in the evaluation and feedback on the effectiveness of the program throughout the implementation of the stakeholder engagement plan, as well as after the conclusion of the process. This will allow for an adaptive management approach and improvements to be made where necessary.

When designing an evaluation strategy for inclusion in the stakeholder engagement plan, the following steps may be useful:

- » 1. Identify the purpose of the evaluation in order to clarify how it should be conducted and how the results should be used.
- » 2. Identify the parties with an interest in the evaluation and how they might use the information.

Consideration should be given to whether evaluation tasks are better allocated to a separate organization in order to more objectively analyse the success of the program.

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