Monitoring Reports

TOXIC HOT SPOTS IN KAZAKHSTAN

The European Union's Non-State Actors in Development - Actions in Kazakhstan programme

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Toxic Hot Spots in Kazakhstan

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CONTENT

ABBREVIATIONS

AAC – Approximately allowed concentrations (Ориентировочно-допустимая концентрация (уровень))
ADI – Acceptable Daily Intake
AMA – Advanced Mercury Analyser
BDS – BioDetection Systems (laboratory in Netherlands)
BGMK – Balkhash Non-Ferrous Metals Processing Plant
BEQ – bioanalytical equivalent
CALUX - Chemically Activated Luciferase Gene Expression
CAS – Chemical Abstracts Service Registry Number (a unique numerical identifier asigned to every chemical substance described in the open scientific literature)
CEE – Central and Eastern Europe
CDI – Chronic Daily Intake
CINEST - Center for Introduction of New Environmentally Safe Technologies
DDD – dichlorodiphenyldichloroethane (a metabolite of DDT)
DDE – dichlorodiphenyldichloroethylene (a chemical compound formed by the loss of hydrogen chloride from DDT)
DDT – dichlorodiphenyltricholoroethane (pesticide)
DL PCBs – dioxin-like PCBs
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
GPS – Global Positioning System
HCB - hexachlorobenzene
HCHs – hexachlorocyclohexanes (pesticides and their metabolites)
HpCDD – heptachlorodibenzo-p-dioxin
HpCDF – heptachlorodibenzo-p-furan
HQ – a hazard quotient
HRGC-HRMS – high resolution gas chromatography – high resolution mass spectroscopy
HxCDD – hexachlorodibenzo-p-dioxin
HxCDF – hexachlorodibenzo-p-furan

IARC – International Agency for Research on Cancer
INC – Intergovernmental Negotiating Committee (normaly set up for negotiations of new international convention)
IPEN – International POPs Elimination Network
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
ML – maximum level
MRL – maximum residue level
NA – not analyzed
NGO – non-govermental organization (civil society organization)
NIP – National Implementation Plan
NOAEL – No Observed Adverse Effect Level
OCPs – organochlorinated pesticides
OCDD – octachlorodibenzo-p-dioxin
OCDF – octachlorodibenzo-p-furan
PCBs – polychlorinated biphenyls
PCDD/Fs – polychlorinated dibenzo-p-dioxins and furans
PCDDs – polychlorinated dibenzo-p-dioxins
PCDFs – polychlorinated furans
PeCDD – pentachlorodibenzo-p-dioxin
PeCDF – pentachlorodibenzo-p-furan
POPs – persistent organic pollutants
RfD – Reference Dose
RISC - Risk-Integrated Software for Cleanups
RSL – Regional Screening Levels
SC – Stockholm Convention on Persistent Organic Pollutants
SF – Slope Factor
SOP – standard operating procedures
TCDD – tetrachlorodibenzo-p-dioxin
TCDF – tetrachlorodibenzo-p-furan
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
US EPA – United States Environmental Protection Agency
WHO-TEQ – Toxic equivalent defined by WHO experts panel in 2005
w.w. – wet weight

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

This series of studies is focused on the presentation and discussion of the data related to contamination of soils and sediments and pollution of free range chicken eggs, cow milk and fish by heavy metals and persistent organic pollutants. Environmental samples were obtained during two field visits conducted in Kazakhstan in July–August 2013 and July–September 2014.

Sampling campaigns represent an important part of the project "Empowering the civil society in Kazakhstan in improvement of chemical safety". This is a joint project of the Czech not-for profit organization Arnika Association and two Kazakhstani partners, the Karaganda Regional Ecological Museum (EcoMuseum) and the Center for Introduction of New Environmentally Safe Technologies (CINEST). The main goal of the project is to reduce the level of poverty in Kazakhstan (mainly in poor local communities) by focusing on its environmental and chemical safety factors. Specific project objectives comprise (a) the strengthening of cooperation and building of capacities of environmental civil society organizations to support their involvement in decision making, (b) increasing public access to information and raising awareness on chemical safety issues and (c) initiating legislative changes related to chemical safety and developing replicable model examples. The project also aims to help Kazakhstan to implement the Stockholm Convention on Persistent Organic Pollutants and the UNECE Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters, usually known as the Aarhus Convention. The project started in November 2012 and will be finished at the end of April 2015.

A selection of further presented localities was based on preliminary analyses, reports in literature and personal experience of members of the team from EcoMuseum and CINEST, and on suggestions by other NGOs based in Kazakhstan which took part in small grants programme of the project. Three locations with heavy metallurgic industry (the cities of Balkhash and Temirtau, and Glubokoe), four potentially contaminated sites/areas due to historic environmental burdens (Ekibastuz – electrical power substation, river Nura, Daryal and Orta Deresin, two abandoned military bases on the banks of Balkhash lake), and two sites potentially influenced by mining activities (Akchatau in Karagandy Oblast and the former uranium mining area of Stepnogorsk) were chosen for sampling. The villages of Akchatau in Karagandy Oblast, Shabanbai Bi in Kyzyl Arai nature protected area, lake Dubygalinskoe in Eastern Kazakhstan and the shore of Balkhash lake opposite Balkhash city were chosen as sites for sampling in order to find background levels of pollutants, although some of them didn´t show as clean as anticipated.

The results presented in following reports are based on the analyses of 191 samples in total. Soil, sediments, waste and biological (food) samples were taken and you can find the specification for each location in Tables 1 – 12. Samples were analyzed for

» 10 OCPs (organochlorine pesticides) and their metabolites
» 7 PCBs congeners
» PCDD/Fs and DL PCBs for both bioassay analyses, and for chosen samples congener specific analysis (rather for samples from a second field sampling visit)
» brominated flame retardants (including PBDEs) in a few selected samples
» mercury and methylmercury
» other heavy metals (lead, cadmium, copper, chromium, zinc, arsenic).

We believe that the work presented in the following reports will contribute to implement the Stockholm 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.

Prague, April – 25, 2015

Jindrich Petrlik, Executive Director
Arnika – Toxics and Waste Programme
on behalf of the joint Arnika – EcoMusuem – CINEST project team

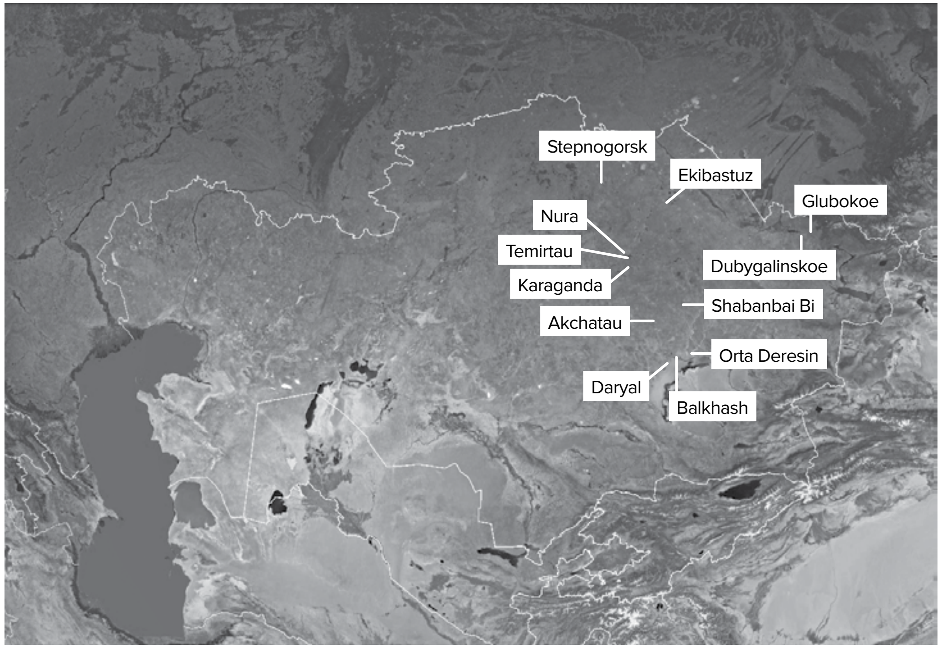
2. SAMPLING

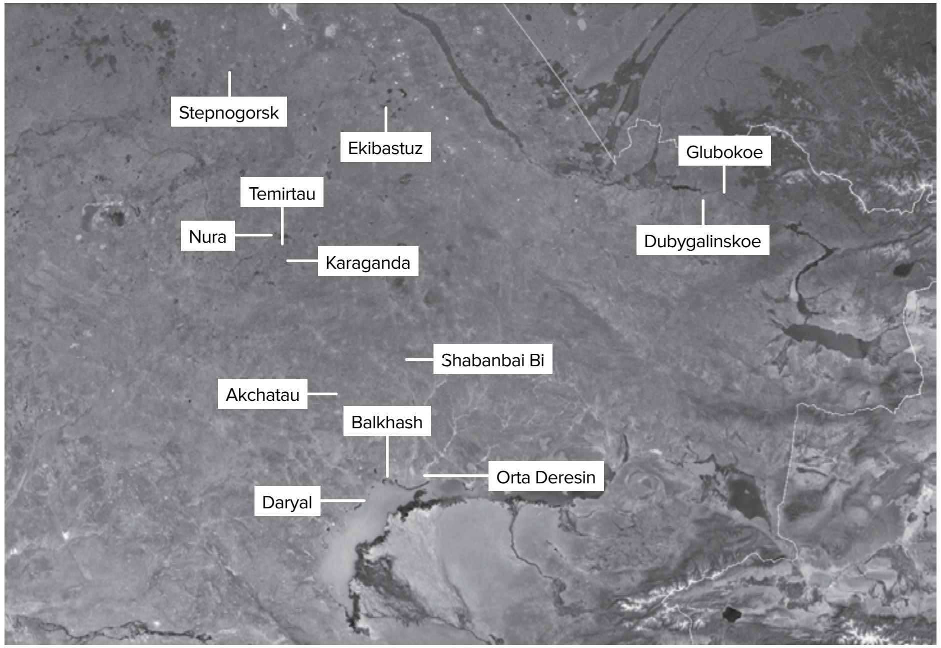
Samples of solid matrices were usually taken as mixed samples from the top layers. They were formed by several partial samples taken in various places of the given locality. Soil samples were taken by means of a shovel into polyethylene containers (V = 500 ml) with screw lids or into polyethylene bags. Samples of sediments were taken by a core sampler into polyethylene containers (V = 500 ml). During soil sampling, the sampling shovel and core sampler were washed with tap water or with available river or lake water. The sampling person changed gloves after taking each sample. The mixing bowl was rinsed with tap water for soil samples and with stream/lake water, dried with a towel and cleaned with technical alcohol respectively for sediment samples. After leaving each sampling area, the boots of sampling and assisting persons were rinsed with tap water such that the contamination from one sampling spot did not affect the subsequent sampling.

Cases with sediment and biofilm samples were wrapped in aluminium foil. Eggs were stored in egg boxes wrapped in two polyethylene bags and cooked for 10 minutes. The milk sample was stored in a PET bottle. Fish samples were wrapped in two polyethylene bags. Soil and other solid matrices samples were kept at room temperature, while sediment and eggs were stored in a fridge at 4–8 °C during the stay in Kazakhstan. Fish and milk samples were stored in a freezer.

3. SAMPLED SITES

Detail description of the sampled sites and information about samples taken are provided in the following text and tables. The location of sampled localities is also shown on the maps of Kazakhstan in Figures 1 and 2.





Figures 1 and 2: Maps with locations where the samples were taken.

TABLE 1. DESCRIPTION OF SAMPLE TAKEN IN AKCHATAU.						
Sample code	**Date**	**GPS**	**Sampling spot**	**Sample material, preparation**	**Type of sample**	**Comment**
Akchatau 1	5/9/2013	+ 47° 59' 06.2" + 74° 02' 43.7"	Children's playground in the centre of the village	Sandy soil upper layer, light brown and dry, sieving, homogenization	Soil, mixed sample out of 5 partial samples. 15×20 m rectangle, 10×10 cm squares sampled, sampling depth 2–10 cm	

3.1 Akchatau

Geographical coordinates – 47°59'06.2" N 74°02'43.7" E

Akchatau/Aqshatau is a village in Karagandy Oblast in Central Kazakhstan. It is also the location of the first major tungsten deposit discovered in Central Kazakhstan (Laznicka 2010). The deposit also contains a recent reserve of 16 kt beryllium in addition to 52.4 kt 52.4 kt tungsten (wolfram) and 17.5 kt molybdenum, in a system of more than 300 greisen veins.

Only one sample was taken in Akchatau, at a playground in the centre of the village.

3.2 Balkhash

Geographical coordinates – 46°32'27" N 74°52'44" E

Balkhash is a city in Karagandy Oblast, located on the northern shore of Lake Balkhash, at the Bay Bertys. Balkhash city (76,000 inhabitants) and its surroundings (30-50,000 inhabitants) are dominated by mining and nonferrous metallurgical enterprises. The major enterprise is Balkhashtsvetmet (the earlier Russian Balkhash Gorno-Metallurgical Combinat, BGMK). Further, the Balkhash Non-Ferrous Metals Processing Plant (Russian Zavod Obrabotki Tsvetnych Metallov, ZOCM) is part of the Kazakhmys Corporation LLC. Kazakhmys is a UK-registered copper mining company and the largest producer of copper in Kazakhstan. The Balkhash smelter is estimated to be the 22nd largest in the world and is one of only three plants in the world which still use the stationary Vanyukov submerged-tuyere furnaces developed in the former Soviet Union (Schlesinger 2011). In the early 1990s, production levels were reported to be 280–320 thousand tonnes per year, depositing 76 tonnes of copper, 68 tonnes of zinc and 66 tonnes of lead on the surface of the lake. Since then, emissions have almost doubled (Wikipedia 2015).

Among the largest enterprises, the Balkhash Non-Ferrous Metals Processing Plant is considered to be the largest atmospheric polluter and contributes about 20% of all pollution in the Republic (UNECE and KAZHYDROMET 2003); in spite of this the city is only ranked 16th on the UNECE priority list. Wikipedia confirms that emissions due to mining and metallurgical processes are a key factor affecting the ecology of the Ili-Balkhash basin and that it is mainly associated with pollution from the Balkhash Non-Ferrous Metals Processing Plant operated by Kazakhmys (Wikipedia 2015).

Chemicals unintentionally produced in these industrial processes that are subject to Annex C of the SC (PCDD/Fs, PCBs and HCB) are reported to be one of major subjects of health concerns in Balkhash city.

The waste of the Balkhash Non-Ferrous Metals Processing Plant is stored at tailing ponds occupying the 25 km^2, twice as large as Balkhash city itself.

TABLE 2: DESCRIPTION OF SAMPLES TAKEN IN THE BALKHASH CITY AND LAKE.						
Sample code	**Date**	**GPS**	**Sampling spot**	**Sample material, preparation**	**Type of sample**	**Comment**
			Soil			
BAL 1/1	21/8/2013 10:50	+46° 51' 11.2" +74° 58' 21.2"	City dacha area, 3rd micro-radon, Dom 18 – children's playground	Sandy soil upper layer, light brown and dry, sieving, homogenization	Soil, mixed sample out of 5 partial samples. 15×20 m rectangle, 10×10 cm squares sampled, sampling depth 5 cm	
BAL 1/2	21/8/2013 11:25	+46° 49' 52.5" +74° 58' 04.4"	City, small rocky hill near east of Balkhash Mining-and-Metallurgical Integrated Works (BGMK)	Sandy soil upper layer, light brown and dry, homogenization	Soil, mixed sample out of 3 partial samples. 10×10 cm squares sampled, sampling depth 5 cm	
BAL 1/3	21/8/2013 11:45	+46° 50' 00.5" +74° 58' 02.1"	City. Children's playground east of Balkhash Mining-and-Metallurgical Integrated Works (BGMK) (Alimzhanova 6-8)	Grey-brown sandy, dusty and dry sample, sieving, mixing, homogenizaton.	Soil, mixed sample out of 5 partial samples. 10×15 m rectangle, 10×10 cm squares sampled, sampling depth 5 cm	Sand was brought 4 years ago.
BAL 1/4	21/8/2013 12:00	+46° 50' 23.4" +74° 57' 52.3"	City. Children's playground with fountain close and north-east of the Balkhash Mining-and-Metallurgical Integrated Works (BGMK) (Nikolaya Ostrovskovo 9 / Alimzhanova 19)	Soily with rubble, brown-grey homogeneous dry sample, ‚sieving, mixing, homogenizaton	Soil, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	
BAL 1/5	21/8/2013 12:20	+46° 50' 43.5" +74° 57' 27.2"	City suburbs. Older family houses close and north of the Balkhash Mining-and-Metallurgical Integrated Works (BGMK)	Grey-brown soil, dry sample. Occasionally spread little,. homogenization	Soil, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	
BAL 1/6	21/8/2013 13:05	+46° 48' 19.0" +74° 57' 02.3"	Southern city rural suburbs. South of the Balkhash Mining-and-Metallurgical Integrated Works (BGMK).	Brown-black soil with many roots, plants, upper layer different, homogenization	Soil, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	Plants removed, septic tank smell
BAL 1/9	21/8/2013 15:45	+46° 48' 45.0" +74° 56' 46.2"	Southern city rural suburbs. Dacha close to electrical power station.	.	Soil, mixed sample out of unknown number of partial samples	
BAL 1/10	21/8/2013 16:15	+46° 49' 20.2" +75° 00' 1.4"	East of the city Balkhash, lake shore	Light brown soil, homogenization	Soil, mixed sample out of 5 partial samples	Old sand pit close to the site
BAL 1/13	21/8/2013 17:00	+46° 47' 31.3" +74° 59' 07.4"	Dacha area, lake shore		Soil, mixed sample out of 5 partial samples	

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
BAL-GR-23/1	23/8/ 2013	+46° 47' 23.4" +75° 00' 11.3"	Dacha area, east of the lake bay	Light brown soil, homogenization	Soil, mixed sample out of 5 partial samples	Surface polluted by animal faeces
BAL-GR-23/2	23/8/2013 12:45	+46° 49' 00.7" +74° 56' 49.6"	Dacha area, southern from the BGMK	Light brown, sandy soil, homogenization	Soil, mixed sample out of 5 partial samples	
BAL-HOT-GR-1	21/8/2013 13:25	+46° 47' 27.5" +74° 50' 17.6"	Near discharge from tailing pond of BGMK		Soil, point sample, top layer	Surface covered with green and blue salts
BAL-HOT-GR-2	21/8/2013	+46°47'30.86" +74°50'33.28"	Under the tailing pond of BGMK		Soil, point sample, top layer	
BAL-HOT-GR-3	21/8/2013 13:35	+46° 47' 27.5" +74° 50' 17.6"	Near discharge from tailing pond of BGMK		Soil, point sample, top layer	Surface covered with salts
BAL-HOT-GR-4	21/8/2013	+46° 47' 30.86" +74° 50' 33.28"	Under the tailing pond of BGMK		Soil, point sample, top layer	
BAL-PG-30-1	30/7/2014 10:40	+46° 50' 12.73" +74° 57' 52.78"	City, Seifulina 14, Children's playground	Sandy and gravelly dry sample, sieving, quartation, homogenizaton	Soil, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	
BAL-PG-30-2	30/7/2014 10:40	+46° 50' 25.96" +74° 58' 22.94"	City, Agibay biatyr street 22, children's playground	Sandy and gravelly dry sample, sieving, quartation, homogenizaton	Soil, mixed sample out of 5 partial samples. 10×10 m square, 10×10 cm squares sampled, sampling depth 5 cm	
BAL-PG-30-3	30/7/2014 12:40	+46° 50' 35.9" +75° 00' 12.66"	City, children's playground near supermarket center and mosque	Sandy and gravelly dry sample, sieving, quartation, homogenizaton	Soil, mixed sample out of 5 partial samples. 8×8 m square, 10×10 cm squares sampled, sampling depth 5 cm	
			Sediments			
BAL 1/7	21/8/2013 13:25	+46° 48' 14.20" 74° 57' 12.80"	Southern city rural suburbs, pasture close to factory.	Sandy clayey black sediment, homogenization	Sediment, 30 m line along shore sampled, 10 cm depth. Mixed sample out of 7 partial samples.	
BAL 1/8	21/8/2013 14:45	+46° 49' 09.1" +74° 56' 51.5"	South of the Balkhash Mining-and-Metallurgical Integrated Works (BGMK). Beach next to electrical power station canal.	Sandy black sediment, homogenization.	Sediment, mixed sample out of 5 partial samples.	Water discharge from electrical power station.
BAL 1/11	21/8/2013 17:30	+46° 47' 35.4" +74°59' 19.6"	Southern lake shore	Sandy sediment	Sediment, mixed sample out of 5 partial samples	
BAL-HOT-SED-1	21/8/2013 13:30	+46° 47' 27.4" +74° 50' 18.2"	Canal from BGMK wastepond.		Sediment, mixed sample out of 5 partial samples	Strange smell and hue

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
BAL-HOT-SED-2	21/8/2013	+46° 47' 27.5" +74° 50' 17.6"	Little lake next to BGMK wastepond		Sediment, mixed sample out of 5 partial samples	
BAL-SED-1	21/8/2013 12:00	+46° 46' 53.3" +74° 51' 36.8"	Desiccation basin south to BGMK wastepond.	Black sediment, mixing	Sediment, mixed sample out of 5 partial samples	Smelly, reed. Grazing cows spotted around
BAL-SED-2	21/8/2013 12:30	+46° 47' 30.0" +74° 51' 28.6"	Lake shore, overflow area.		Sediment, mixed sample out of 5 partial samples	
BAL-SED-3	21/8/2013 12:30	+46° 47' 31.4" +74° 51' 31.1"	Lake beach.	Sandy, black sediment, mixing	Sediment, mixed sample out of 5 partial samples, upper 5–10 cm layer removed	Without smell
BAL-SED-5	21/8/2013 15:02	+46° 48' 19.2" +74° 51' 44.8"	Lake shore.	Black sediement, coarse structure, homogenization	Sediment, mixed sample out of 5 partial samples	Water polluted by animal faeces.
BAL-SED-6	21/8/2013 16:40	+46° 48' 19.3" +74° 54' 19.9"	Salt marsh under BGMK wastepond.	Sediment, quartation, mixing	Sediment, mixed sample out of 5 partial samples	
BAL-1-SED-REF	30/7/2014 9:40	+46° 39' 32,7" +75° 34' 45,0"	Fishing settlement Sasi kol, part of the lake with a mixture of salt and fresh water	Sandy and loamy sediment, homogenization, quartation	Sediment, mixed sample out of 3 partial samples	Backgroud sample
BAL-2-SED-REF	30/7/2014 10:40	+46° 40' 12,1" +75° 27' 50,2"	A bend in the narrowest part of the lake with fresh water	Sandy sediment, homogenization, quartation	Sediment, mixed sample out of 5 partial samples	Backgroud sample
BAL-SED-14-1	30/7/2014 18:00	+46° 47' 29,1" +74° 51' 27,5"	Balkhash-wetland, side of the road along the shore, side closer to ash ponds	Black sediment, quartation, homogenizaton	Sediment, mixed sample out of 5 partial samples, sampling depth 30 cm, distance between points 1 m	Covered by faeces and plants, fecal smell
BAL-SED-14-2	30/7/2014 18:15	+46° 48' 01,2" +74° 51' 26,6"	Balkhash-wetland, lake shore south from ash pond	Black sediment, quartation, homogenizaton	Sediment, mixed sample out of 5 partial samples, sampling depth 20 cm, distance between points 2 m	Fecal smell
BAL-SED-14-2	30/7/2014 18:30	+46° 48' 34,90" +74° 53' 44,43"	Balkhash-wetland, channel under the ash pond	Grey and brown sediment, homogenization	Sediment, mixed sample out of 3 partial samples, sampling depth 15 cm, distance between points 2 m	Acid smell
Other solid materials						
POP-BAL	21/8/2013 17:00	+46 49' 23.65" +74 56' 52.34"	City. Below electric power station, nearby to the road to the Balkhash Mining-and-Metallurgical Integrated Works (BGMK) factory	Fly ash	Fly ash, point sample	

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
			Eggs			
B-1	23/8/2013	+46° 47' 31.3" +74° 59' 17.7"	Lake shore. Close to dacha	Free range chicken eggs	Mixed sample out of 6 subsamples.	
B-2	23/8/2013	+46° 47' 23.4" +75° 00' 11.3"	Dacha area eastern from lake bay.	Free range chicken eggs	Mixed sample out of 6 subsamples.	Hens occasionally freely roaming.
B-3	23/8/2013	+46° 49' 00.7" +74° 56' 49.6"	South from the Balkhash Mining-and-Metallurgical Integrated Works (BGMK) factory	Free range chicken eggs	Mixed sample out of 6 subsamples.	
B-4	21/8/2013 12:20	+46° 50' 43.5" +74° 57' 27.2"	Dacha between electrical power plant and lake, Berzakova 11	Free range chicken eggs	Mixed sample out of 4 subsamples from one fancier.	Hens roaming in garden, fed by corn.
B-5	21/8/2013 15:15	+46° 48' 21.5" +74° 56' 52.2"	Southern city rural suburbs. Dacha between electrical power station and lake. Bought from store selling local products.	Free range chicken eggs	Mixed sample out of 10 subsamples.	Same place as for sample BAL-M
bal-EGG-14-1	25/9/2014	+46° 48' 59.6" +74° 56' 46.9"	South from the Balkhash Mining-and-Metallurgical Integrated Works (BGMK) factory	Free range chicken eggs	Mixed sample out of 6 subsamples.	Chicken are fed with bought feeding (from Karaganda shops); approximate age of chicken – 1 year; chicken can easily eat soil organisms. Sampled very close to sample B-3
bal-EGG-14-2	25/9/2014	+46° 48' 21.4" +74° 56' 46.9"	Southern city rural suburbs.	Free range chicken eggs	Mixed sample out of 6 subsamples.	Chicken are fed with vegetables and fruits from the garden and bought grain (shops); approximate age of chicken – 2–3 years; chicken can easily eat soil organisms. Sampled very close to samples B-5 and BAL-M
bal-EGG-14-3	25/9/2014	+46° 48' 43.35" +75° 00' 39 00"	Green area close to lake shore, west of Shashubay, Rembaza 5 street.	Free range chicken eggs	Mixed sample out of 6 subsamples.	12 chicken are fed with bought feeding; approximate age of chicken – 3 years; chicken can easily eat soil organisms, fed with herbs from garden and bought millet. Walking area – 5×6 m. Household waste is composted, not incinerated. Consumers: 6 people, 1 child (13 years), eggs are also for sale.
bal-EGG-14-4	25/9/2014	+46° 47' 26.6" +74° 59' 01.4"	Lake shore. Rembaza 21 street, west of Shashubay.	Free range chicken eggs	Mixed sample out of 6 subsamples.	10 chicken are fed with vegetables and fruits from the garden and bought grain (millet); approximate age of chicken – 3 years, walking area – 3×4 m, sand from the lake. Possible contamination source – waste incineration. Sampled very close to sample B-1. Consumers: 9 persons, 3 children (age 10, 3 and 4 years).

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
			Fish			
BAL FISH 1a		+46°47' 31.81" +74°59' 7.55"	Lake	Fish	Perch	
BAL FISH 1b		+46°47' 31.81" +74°59' 7.55"	Lake	Fish	Perch	
balchas ryby	22/8/2013 9:00	+46°47' 31.81" +74°59' 7.55"	Lake	Fish	Pikeperch. Muscle meat sampled.	1+ years old, 300 mm length
bal-FISH-14-1	30/7/2014	n/a (approx. +46° 33' 48.82" +75° 6' 33.71")	Karakulum municipality, 20–25 km direction Saiak, bought from Balkhash local market	Fish	Catfish bought already chopped	Piece of 55 cm length (approx. half of fish between head and tail)
bal-FISH-14-2	30/7/2014	n/a (approx. +46°33' 48.82" +75° 6' 33.71")	Karakulum municipality, 20–25 km direction Saiak, bought from Balkhash local market	Fish	Catfish bought already chopped	Filet of 25×25 cm size (approx. 1/3 or ¼ of fish)
bal-FISH-14-3	30/7/2014	n/a (approx. +46° 31' 23.25" +75° 9' 24.13")	Southern shore of Balkhash lake, bought from Balkhash local market	Fish	Frozen catfish or sole	Measures: 53–59, age: 4+
bal-FISH-14-4	30/7/2014	n/a (approx. +46°46' 4.07" +75° 0' 53.28")	Southern shore of Balkhash lake, bought from Balkhash local market	Fish	5 zander fish already chopped	17cm out of approx. 2/3 lenght of first fish, then: 10 cm out of ½, 13 cm out of ½, 11 cm out of 3/4 and 15 cm out of ½
bal-FISH-14-5	30/7/2014 17:00	+46°49' 21" +74°56' 52"	City. Electric power station discharge, bought from local fishermen	Fish	3 carp fish	1st fish measures: 24/29, age: 4+; 2nd fish measures: 23/28, age: 5+; 3rd fish measures: 19/23, age: 3+
			Milk			
BAL-M	21/8/2013 15:15	+46° 48' 21.5" +74° 56' 52.2"	Southern city rural suburbs. Dacha between electrical power station and lake. Bought from store selling local products.	Cow milk	1 sample	Same place as for sample B-5

3.3 Daryal – former military base

Geographical coordinates – 46°35'20.38"N 74°27'59.89"E

Daryal U is an abandoned and destroyed military radar station in Aktogaysky district, Karagandy oblast, Kazakhstan. The nearest municipality is the village of Gulshad (1,000 people) – 5 km. Balkhash city is 35 km away. Daryal-U is located directly on the northern shore of Lake Balkhash

In 2004 EcoMuseum found more than 15,000 electrical capacitors at the former Early Warning System Daryal-U radar station (RS); these were manufactured at the Ust-Kamenogorsk Capacitor Plant (Ust-Kamenogorskiy kondensatornyi Zavod) and filled with PCBs. Ministry of Environmental Protection (MEP, "MOOS" *in Russian*) has provided funding for the project of dismantling, packing and transboundary export of capacitors to destruction, and about 10,000 capacitors have been exported for this purpose to Germany (Envio company). About 5,000 capacitors are still kept in the one of remained building on the former radar station territory that is located 230 metres from Balkhash Lake. Around the storage building and ruins of the station buildings there is the smell of PCBs. Local residents illegally dismantled capacitors in order to extract nonferrous metals; as a result, a lot of PCBs have been spilled.

We were not allowed to take samples in the area of destroyed station as we didn't get the required permission. We could only sample the area at a certain distance from Daryal U.

TABLE 3: DESCRIPTION OF SAMPLES TAKEN IN THE LOCALITY OF DARYAL.

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Soil						
DAR-01	31/7/2014 18:30	+46° 35' 37.23" +74° 28' 37.73"	Former military base Daryal, seasonal wetland reeds on the shore	Soil, homogenization, quartation	Soil, mixed sample out of 5 partial samples, sampling depth 5 cm	1 cm of surface removed
DAR-02	31/7/2014 18:50	+46° 35' 26.3" +74° 28' 12.7"	Former military base Daryal, heap next to the flooded pit	Brown and grey, sandy and loamy soil, homogenization, quartation	Soil, mixed sample out of 5 partial samples	Near DAR-SED-03, slightly chemical smell
DAR-03	31/7/2014 20:00	+46° 35' 37.1" +74° 28' 08.1"	Former military base Daryal	Sandy and loamy soil, homogenization, quartation	Soil, mixed sample out of 5 partial samples, sampling depth 5 cm	Slightly chemical smell
Sediments						
DAR-SED-01	31/7/2014 18:00	+46° 35' 37.81" +74° 28' 54.58"	Former military base Daryal, small lake near Balkhash lake	Black sediment, homogenization, quartation	Sediment, mixed sample out of 10 partial samples	Polluted by faeces, fecal smell
DAR-SED-02	31/7/2014 18:50	+46° 35' 28.2" +74° 28' 14.8"	Former military base Daryal, about 30 m from the lake shore, 3 m water depth	Light brown to gray sandy sediment, homogenization,	Sediment, mixed sample out of 3 partial samples,	Sediment with colored stones, fecal smell
DAR-SED-03	31/7/2014 19:00	+46° 35' 26.3" +74° 28' 12.7"	Former military base Daryal, flooded pit possibly former drainage channel	Black sediment, homogenization	Sediment, mixed sample out of 5 partial samples	

TABLE 4: DESCRIPTION OF SAMPLES TAKEN IN THE LOCALITY OF DUBYGALINSKOE.						
Sample code	**Date**	**GPS**	**Sampling spot**	**Sample material, preparation**	**Type of sample**	**Comment**
Soil						
DUB-SOIL-1	26/7/2014 19:00	+50° 04' 08.5" +81° 48' 02.3"	Near the shore of the lake on the right side of the beach	Light brown, loamy soil, homogenization, quartation, sieved	Soil, mixed sample out of 3 partial samples representing 1.5 m×1.5 m, depth 5 cm, 1 cm of top layer removed	Background sample, possible fecal pollution
Sediments						
DUB-SED-1	26/7/2014 19:00	+50° 04' 08.5" +81° 48' 02.3"	On the shore of the lake on the right side of the beach	Black sandy sediment, homogenization, quartation	Sediment, mixed sample out of 5 partial samples	Background to Irtysh River
DUB-SED-2	26/7/2014 19:15	+50° 04' 50.6" +81° 47' 54.0"	Utinoye lake (Goose lake), side lake near Dubygalinskoe	Black and grey sandy sediment, homogenization	Soil, mixed sample out of 3 partial samples	Background sample, possible animal fecal pollution

3.4 Dubygalinskoe

Geographical coordinates – 50°03'51.27"N 81°47'27.58"E

Lake Dubygalinskoe (also known as Lake Okun'ki or Mitrofany) is located in the Ulansky district of East Kazakhstan Oblast. It is situated at the foot of the northern slopes of Mount Dubygaly. We have chosen this place for background sampling of soils and sediments, especially for comparison with samples from Eastern Kazakhstan part.

3.5 Ekibastuz – abandoned electrical power substation

Geographical coordinates – 51°48'59.10" N 75°18'46.00" E

The Ekibastuz electrical power substation was constructed for modifying alternating current (AC) to direct current (DC) using 15,000 capacitors placed in two outdoor areas. After the collapse of the Soviet Union the substation was left without an owner or guard. During the economic crisis, local residents illegally dismantled capacitors in order to remove copper scrap and this resulted in PCB leakage into the soil. During emergency clean-up works in 2002 the capacitors were dismantled and „sealed" with foam by the new owner of the substation. Part of the PCB contaminated soil was removed and packed in bags. Capacitors and contaminated soil were removed and placed in underground storage at the former Semipalatinsk nuclear testing site (technical test area Opytnoe Pole).

The substation is on the edge of Ekibastuz city in Pavlodar Oblast with a population of more than 125,000. In the vicinity of the site there are large areas of suburban gardens – "dachas" (minimum distance is 500 m, total area is about 3 km^2). In the guarded and fenced area of the facility (300 m from the object) resides a family whose job is to guard the site. The family grows and grazes their livestock on the site – cows, sheep and poultry.

TABLE 5: DESCRIPTION OF SAMPLES TAKEN IN THE EKIBASTUZ ELECTRICAL POWER SUBSTATION AND ITS SURROUNDINGS

Sample code	Date, time (if available)	GPS coordinates	Sampling spot	Sample material, preparation	Type of sample	Comment
			Soil			
EKI 2/1	16/8/2013 16:30	+51° 49' 01.4" +75° 18' 59.7"	30 m north of substation building	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	sandy soil with little stones, mixing, 2× quartation
EKI 2/2	16/8/2013 16:45	+51° 49' 02.8" +75° 19' 00.9"	North of substation building	Point soil sample	Point sample	Wires present, suspected place of contamination
EKI 2/3	16/8/2013 17:00	+51° 49' 03.6" +75° 19' 07.7"	Northeast of substation building, 80 m north from pillars	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples in a 10×10 m square, sampling depth 5 cm, each sampling point: 15 x 15 cm	Homogeneous sandy soil, mixing, 2× quartation
EKI 2/4	16/8/2013 17:15	+51° 49' 06.43" +75° 19' 05.47"	Northeast of substation building, behind concrete road, 10 m far from EKI 2/3 with panel road inbetween	Point soil sample	Point sample	Homogeneous sandy soil
EKI 2/5	16/8/2013 17:25	+51° 48' 56.5" +75° 19' 08.6"	South of the capacitor placing area	Mixed soil sample, homogenization	Mixed sample out of 5 subsamples in a 10×10 m square, sampling depth 5 cm, each sampling point: 15×15 cm, gentle depression at sampling site	
EKI 2/6	16/8/2013 17:40	+51° 48' 55.5" +75° 19' 03.6"	Southeast substation area	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	
EKI 2/7	16/8/2013 17:55	+51° 48' 53.7" +75° 19' 00.2"	South of the substation building	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	
EKI 2/8	16/8/2013	+51° 49' 00.1" +75° 19' 08.1"	Capacitor placing area	Point soil sample	Point sample	
EKI 2/9	16/8/2013	+51° 49' 00.1" +75° 19' 08.1"	vertical profile in capacitor placing area	Mixed soil sample, homogenization, quartation	Mixed sample out of 3 subsamples, sampling depth 20 cm	Visible potential contamination
EKI 2/10	16/8/2013	+51° 48' 59.9" +75° 19' 08.3"	Capacitor placing area	Point soil sample	Point sample, 5 cm sampling depth, under a broken stone layer	
EKI 2/11	16/8/2013 18:40	+51° 48' 59.5" +75° 19' 08.1"	Capacitor placing area	Mixed soil sample, homogenization, quartation	Mixed sample out of 4 subsamples in a 10×10 m square, sampling depth 5 cm (under a 20–30 thick broken stone layer)	

Sample code	Date, time (if available)	GPS coordinates	Sampling spot	Sample material, preparation	Type of sample	Comment
EKI 2/12	16/8/2013	+51° 49' 00.2" +75° 19' 10.6"	capacitor abutment	Point soil sample	Point sample	
EKI 2/13	16/8/2013	+51° 49' 00.2" +75° 19' 10.5"	between capacitors	Mixed soil sample, homogenization, quartation	Mixed sample out of 4 subsamples, sampling depth 5 cm	
EKI 2/14	16/8/2013	+51° 49' 0.03" +75° 18'59.15"	large building, soil on storey (ground floor) floor	Point soil sample	Point sample, 5 cm sampling depth	
EKI 2/15	16/8/2013	+51° 48' 59.38" +75° 18' 59.39"	large building, soil on the floor of building (ground floor)	Point soil sample	Point sample, 5 cm sampling depth	
EKI GR 1/II	17/8/2013 11:40	+51° 48' 14.15" +75° 18' 24.81"	garden bed	Mixed soil sample, homogenization	Mixed sample out of 6 subsamples	Homogenization
EKI GR 2/II	17/8/2013 12:45	+51° 47' 52.64" +75° 18' 35.74"	Cluster of summer houses, sampling behind building, where EKI EGG 2/II sample was taken	Mixed soil sample, homogenization	Mixed sample out of 5 subsamples	Homogenization
EKI GR 3/II	17/8/2013 14:20	+51° 49' 52.19" +75° 19' 29.48"	Meadow between dachas and the Irtysh-Karaganda canal, approximately 25 m from canal	Mixed soil sample, homogenization	Mixed sample out of 5 subsamples	Homogenization
EKI 1/S1	17/8/2013 12:30	+51° 51' 26.59" +75° 20' 31.10"	Lake Zhyngyldy shore, northeast of substation	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples. 3 samples on the shore line, 2 approx. 5 m far into the water of the lake	Black sediment, mixing. Reservoir for cooling water for nearby heat power plant. Suspected PCB contamination, no visible pollution
EKI 1/S2	17/8/2013 13:20	+51° 51' 25.47" +75° 18' 58.88"	Southern part of arid natural salty lake surrounded by salty wetlands with rich bird population. Seasonally wet. Western of lake Zhyngyldy	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples. 30 m along beach, sampled line approx. 15 - 20 m far from the current waterline	Clayey black sediment. Mixing.
S 1/II	16/8/2013 16:30	+51° 48' 59.25" +75° 18' 48.83"	columns A	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	Grass removed before sampling. Mixing, 2x quartation. Homogenous sandy soil. Sample may be contaminated with asbestos.
S 1.1/II	16/8/2013 17:00	+51° 48' 57.26" +75° 18' 45.97"	columns A	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	Grass removed before sampling. In case of 4 out of 5 subsamples: surface layer of bigger stones removed. Mixing, 2× quartation. Homogenous sandy soil. Sample may be contaminated with asbestos.

Sample code	Date, time (if available)	GPS coordinates	Sampling spot	Sample material, preparation	Type of sample	Comment
S 2/II	16/8/2013 17:45	+51° 49' 0.63" +75° 18' 54.58"	25 m in front of substation building, driving area	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	Capacitor fillings nearby. Homogeneous sandy soil. 2x quartation, sieving (3 mm fiction)
S 2.1/II	16/8/2013 18:00	+51° 49' 2.06" +75° 18' 52.16"	50 m aside substation building	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	Capacitor insulators nearby. Homogenous sandy soil. Grass removed before sampling.
S 2.2/II	16/8/2013 18:30	+51° 49' 2.2" +75° 18' 56.8"	50 m far from substation building	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	Homogenous sandy soil. 2× quartation, mixing. Visible contamination: foam pieces (maybe sample PS 2/II) and tarry paper
S 3/II	16/8/2013 19:00	+51° 48' 54.69" +75° 18' 56.41"	10 m far from substation building	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	Mixing, 2x quartation, sieving. Slightly heterogenous sandy soil.
S 3.1/II	16/8/2013 19:20	+51° 48' 89.37" +75° 18' 90.79"	50 m aside substation building to the west	Mixed soil sample, homogenization, quartation	Mixed sample out of 5 subsamples	Mixing, 2x quartation, sieving. Slightly heterogenous sandy soil.
Sediment						
EKI 1/S3	17/8/2013 14:08	+51° 47' 12.3" +75° 18' 07.5"	Nameless lake south of dachas	Sediment	Mixed sample out of 5 subsamples, 20×20 m square (3 times 30 m from shoreline, 2 times on shore beyond flooded zone), sampling depth 10 cm	Sample homogenization. Black sediment, yellow ochre colour in subsurface, alive algae on surface. Burnt cables on shore, burning area 10 m far from shore
EKI SED 4/II	17/8/2013 14:30	+51° 49' 51.09" +75° 19' 31.3"	Irtysh-Karaganda canal between substation and dachas	Sediment	Point sample	Light brown and fine sediment
EKI SED 5/II	17/8/2013 15:00	+51° 49' 9.16" +75° 19' 39.22"	wetland east ofsubstation, close to road	Sediment	Mixed sample out of 5 subsamples	Foul odour, homogenization
Other solid materials						
PS 2/II	16/8/2013 17:40	+51° 49' 0.93" +75° 18' 54.88"	30 m from substation building, 5 m far from S2 sampling point	Mineral wool	Point sample	Layered mineral wool, strange colouring, slight odour
PS 2.1/II	16/8/2013 18:20	+51° 49' 2.2" +75° 18' 52.25"	60 m from substation building edge	Part of dismantled capacitor	Point sample	A capacitor piece - the paper layer between plastic and aluminium foil of a dismantled capacitor was sampled.

Sample code	Date, time (if available)	GPS coordinates	Sampling spot	Sample material, preparation	Type of sample	Comment
			Eggs			
EKI EGG 1	17/8/2013 11:10	+51° 48' 40.87" +75° 18' 33.98"	Café Ataël, 500-700 m from substation	Free range chicken eggs	Mixed sample out of 4 subsamples	Open area, hens are fed with kitchen leavings
EKI EGG 2	17/8/2013 12:10	+51° 47' 53.34" +75° 18' 36.52"	Dacha in dacha area	Free range chicken eggs	Mixed sample out of 4 subsamples	
EKI-14-1-egg + EKI-27-egg	24/7/2014 15:30	+51° 48' 41.04" +75° 18' 34.70"	Café Ataël, 500-700 m from substation	Free range chicken eggs	Mixed sample out of 2 sub-samples + 4 subsamples taken two days later	Hens are fed with garden grass, bought cereals (wheat, barley) and kitchen leavings, freely roaming on a 100×50 m area. Coal ash mound behind house accessible for hens. Egg consumers – family (40, 30 and 24 year old women, 25 year old men, two children of 12 and 15 years) and café guests.
EKI-14-2-egg	24/7/2014 16:15	+51° 49' 57.45" +75° 18' 35.59"	Sojuz – dacha area north of substation	Free range chicken eggs	Mixed sample out of 6 or 8 subsamples.	Hens are fed with garden grass, bought cereals (wheat, barley). Hens are six months old, every year new hens are bought and the old consumed. Egg consumption – 10 eggs per week in whole family (a couple younger than 35 years and parents)
EKI-14-3-egg	24/7/2014 16:30	+51° 50' 03.41" +75°18'05.95"	Sojuz – dacha area north of substation. Dacha no. 1814.	Free range chicken eggs	Mixed sample out of 6 sub-samples.	Hens are fed with garden grass, bought cereals (wheat, barley). Hens are six months old, every year new hens are bought and the old consumed. Hens held in cages on soil ground. Egg consumption – 75–80 years old couple, eggs given also to children living elsewhere
			Fish			
EKI FISH 1/1	17/8/2013	+47° 55' 23.98" +62° 46' 59.98"	Middle of Zhyngyldy lake	Fish	Pikeperch, 2+ years old, 398/460 mm. Muscle meat and subcutaneous fat analyzed.	Reservoir for cooling water for nearby heat power plant, used cooling water is discharged back to lake. Inflow of water (if any during the year) from the substation area.
EKI FISH 1/2	17/8/2013	+47° 55' 23.98" +62° 46' 59.98"	Middle of Zhyngyldy lake	Fish	Pikeperch, 2+ years old, 415/475 mm. Muscle meat and subcutaneous fat analyzed.	Reservoir for cooling water for nearby heat power plant, used cooling water is discharged back to lake. Inflow of water (if any during the year) from the substation area.

3.6 Glubokoe

Geographical coordinates – 50°08'53.94" N 82°18'10.19" E

Glubokoe is a town in East Kazakhstan Oblast with almost 10,000 inhabitants. Five disposal sites of metallurgic slag from Itrysh Smelting Company (IMZ) belonging to Kazakhmys Corporation are located in the territory of Glubokoe. Over the years the district authorities have been trying to solve the environmental problems, namely, to establish processing of these wastes which are located in the immediate vicinity of the transboundary Irtysh River.

A master plan for Glubokoe has been developed, as well as a waste processing project based on new technologies. However, the problem has not been solved yet. The slag contains high levels of heavy metals, such as lead, zinc or copper.

The waste disposal sites № 1, 2 and 3 represent a particular threat, because they are located in the very vicinity of the Irtysh River, at a distance of 7–10 metres from the river bank. Although the dump is separated from the stream by a small dam, it leaks at a number of places and dangerous substances are getting into the water. Local people are afraid of what would happen in case of floods, if 8 tons of the slag got into the water stream.

So far, the local authorities have not conducted a debate with the citizens on the issue. The area of the waste dumps is not even fenced and there are no warning signs.

TABLE 6: DESCRIPTION OF SAMPLES TAKEN IN THE LOCALITY OF GLUBOKOE.

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Soil						
GLUB-P-1	26/7/2014 12:15	+50° 09' 37.9" +82° 16' 38.5"	The bottom of the heap at a distance 30–40 m	Soil, quartation, homogenization	Soil, mixed sample out of 8 partial samples.	
Sediments						
GLUB-SED-1	26/7/2014 11:15	+50° 9' 6.80", +82°16' 49.20"	Right bank of the river Irtysh below Glubokoe before slag landfill	Grey and brown, sandy and clayey sediment, homogenization	Sediment, mixed sample out of 3 partial samples, without 5 cm of top layer	
GLUB-SED-2	26/7/2014 12:15	+50° 09' 37.4" +82° 16' 37.3"	The pond under the slag heap	Black smelly muddy sediment, homogenization	Sediment, mixed sample out of 3 partial samples, sampling depth 5 cm	
GLUB-SED-3	26/7/2014 13:00	+50° 10' 14.8" +82° 16' 26.1"	Lagoon before discharging into the Irtysh river under the slag heap	Grey and black sediment with pieces of slag	Sediment, mixed sample out of 3 partial samples representing triangle 2 m, without 5 cm of top layer	
Other solid materials						
GLUB-ST-1	26/7/2014 12:15	+50°09' 38.0" +82°16' 37.6"	The bottom of the heap	Black slightly glassy slag - from copper production	Slag, point sample representing 20×20 cm	

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Fish						
GLUB-F-1	26/7/2014 13:00	+50°09' 33.48" +82° 16' 34.62"	Cut off meander of the river Irtysh – on the opposite site from the slag dump in Glubokoe	2 fish speicies samples; pike and perch; pool samples analyzed (see comments part)	3 pike fish samples: total length between 29.6 and 33.1 cm, age 1–2 years; 8 perch fish samples: total length 17.8 – 19.6, age 3 years	Pool samples marked as follows: GLUB-F-1/1-3 (pike) and GLUB-F-2/4-11 (perch)
GLUB-F-2	25–26/7/2014 night time	+50° 09' 54.02" +82°16' 26.24"	Cut off meander of the river Irtysh - downstream the river flow from slag dump in Glubokoe, without dumping site	Three different fish species; sample consists from 17 fish in total	7× roach fish: total length 17.3 – 19.0, age of 5 samples was 4 years, two remaining samples had age 3 and 5 year respectively; 2× carp „sazan" 1 and 2 years old 17 and 19 cm of total length; 8× perch: total length 16.9 – 18.5 cm, all in age of 3 years	Pool samples marked as follows GLUB-F-2/1-7 (roach), GLUB-F-2/8-9 (carp) and GLUB-F-2/10-17 (perch)
GLUB-F-3	25–26/7/2014 night time	+ 50° 15' 06.12" +81°45' 30.20"	Shilbinskoe dam on the river Irtysh nearest settlement is Ubinka	2 perch samples; analyzed as pool sample	2× perch: total length 21.1 – 24.0 cm, age 3 years	

3.7 Karaganda city

Geographical coordinates – 49°48'40.76" N 73°05'27.37" E

We only sampled eggs from a poultry farm in a supermarket in order to get an idea about background levels of POPs.

3.8 Nura (river)

Geographical coordinates – 50°07'45.82" N 72°50'27.62" E

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).

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 acethylene 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. 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. 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.

The project team took samples of soil, sediments, chicken eggs and fish in locations of the river Nura and settlements on this river, however evaluation of these samples is not part of this publication but other output of this project which is called "Contaminated sites and their management", apart free range chicken eggs samples which are listed below. Basic information about other samples can be found in Šír's report (Šír 2015).

TABLE 7: DESCRIPTION OF SAMPLE TAKEN IN THE CITY OF KARAGANDA

Sample code	Date, time (if available)	GPS coordinates	Sampling spot	Sample material, preparation	Type of sample	Comment
Eggs						
KAR-SUP	26/4/2015	+49°48' 40.76" +73° 5' 27.37"	Supermarket in the centre of Karaganda	Farm chicken eggs	Pooled sample out of 6 eggs	

TABLE 8: DESCRIPTION OF SAMPLES TAKEN IN THE AREA OF THE RIVER NURA DISCUSSED IN STUDIES PUBLISHED IN THIS BOOK

Sample code	Date, time (if available)	GPS coordinates	Sampling spot	Sample material, preparation	Type of sample	Comment
Eggs						
NUR EGG 1	19/8/2013 12:15	+50° 6.8295 +72° 48.5047	Private house in Samarkand	Free range chicken eggs, boiling	Pooled sample of 6 eggs, from various free range hens	Hens are fed with garden grass and food scraps (bread etc.)
NUR EGG DAM	19/8/2013	+50° 4' 35.77" +72° 55' 33.90"	Temirtau; Samarkand Reservoir, southwest bank near the old factory drain	Free range chicken eggs, boiling	Pooled sample of 6 eggs, from various free range hens	
NUR – EGG - 24/1	24/8/2013 11:45	+50° 02' 54.5" +72° 41' 38.0"	Dacha next to River Nura (Rostovka)	Free range chicken eggs, boiling	Pooled sample of 6 eggs, from various free range hens	
NUR – EGG - 24/2	24/8/2013 13:25	+50° 05' 56.1" +72° 52' 40.4"	Dacha near the drain (Chkalovo)	Free range chicken eggs, boiling	Pooled sample of 6 eggs, from various free range hens	
NUR-EGG-14/1	5/8/2014	+50° 02' 00.2" +72° 40' 10.3"	Rostovka village	Free range chicken eggs, boiling	Pooled sample of 6 eggs, from various free range hens	Hens are fed with grass, vegetables
NUR-EGG-14/2	5/8/2014	+50° 05' 17.1", +72° 52' 05.3"	Chkalovo village	Free range chicken eggs, boiling	Pooled sample of 6 eggs, from various free range hens	

3.9 Orta Deresin – former military base Tokrau

Geographical coordinates – 46°50‘44.06“ N 75°37‘23.19“ E

A military arsenal near the village of Tokrau was the largest ammunition storage of the Ministry of Defence of Kazakhstan. The concrete vaults of military unit No. 89533 contained more than 10,000 tons of weapons – shells, ammunition, mortars, rockets. Among other equipment, there were also uranium armour-piercing shells. Ammunition was stored in Tokrau by the Soviet army during the war in Afghanistan.

On August 8, 2001 the fire broke out on the territory of the arsenal warehouse, and soon turned into continuous explosions of ammunition. Because of these explosions, the fire brigades were not able to start extinguishing the fire for several days. In order to avoid human casualties of Tokrau population, the settlement was quickly evacuated, and a safety zone was established with a 10 kilometres radius. Fire and explosions did not stop for a whole week. It completely destroyed a five-story building and the soldiers‘ barracks, damaged railway, power lines, and the only water tower in the district. The accident caused volley emissions of significant quantities of chemical and radioactive substances into the environment.

Although more than ten years after the fire, the public still does not have any information on the state of the environment of Tokrau Arsenal and its surroundings. According to experts, fire and explosions could create hazardous chlorinated persistent organic pollutants (POPs) that stay in the environment, harm the health of humans and animals and cause toxic poisoning of a wide spectrum. Due to the fact that Tokrau Arsenal is located above the area of a groundwater reservoir and existing underground water stream of the river Tokrau, the former fire and explosions could threaten not only the residents of the nearby village of Orta Deresin (about 1,000 people), but also the entire population of Balkhash city (about 100,000 people.).

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TABLE 9: DESCRIPTION OF SAMPLES TAKEN IN THE LOCALITY ORTA DERESIN

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
			Soil			
ORTADER 1	23/8/2013 13:00	+46° 49' 59.5" +75°36' 02.2"	Former military base Orta Deresin, out of base		Soil, point sample	
ORTADER 2	23/8/2013 13:30	+46° 50' 56.8" +75°36' 29.5"	Former military base Orta Deresin, out of base	Sandy soil	Soil, point sample	
ORTADER 3	23/8/2013 13:50	+46° 51' 29.9" +75°36' 41.4"	Former military base Orta Deresin, out of base	Sandy soil	Soil, point sample	
ORTADER 4	23/8/2013 14:00	+46° 51' 28.4" +75°38' 04.5"	Former military base Orta Deresin, out of base	Sandy soil	Soil, point sample	
ORTADER 5	23/8/2013 14:20	+46° 51' 08.1" +75°38' 03.8"	Former military base Orta Deresin, out of base	Sandy soil	Soil, point sample	
ORTADER 6	23/8/2013 14:25	+46° 50' 45.6" +75°38' 04.7"	Former military base Orta Deresin, out of base	Sandy soil	Soil, point sample	

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
ORTADER 7	23/8/2013 14:35	+46° 50' 01.1" +75°38' 01.7"	Former military base Orta Deresin, out of base	Sandy soil	Soil, point sample	
ORTADER 8	23/8/2013 15:00	+46° 50' 01.1" +75°38' 01.7"	Former military base Orta Deresin, former transformator station	Sandy soil	Soil, mixed sample out of 3 partial samples	
Sediments						
ORTADER 9	23/8/2013 16:30	+46° 42' 24.8" +75°22' 46.2"	Orta Deresin, Balkhash lake shore	Black, sandy sediment, homogenization, quartation	Sediment, mixed sample out of 5 partial samples	Background sample

3.10 Shabanbai Bi

Geographical coordinates – 48°24‘13.76“ N 75°23‘42.65“ E

Shabanbai Bi is a village located in the southern part of the Karagandy Oblast. The village is situated at the foot of Aksoran, the highest peak of the Kyzylarai mountains (nature protected area – “zakaznik”), is one of the places in Central Kazakhstan where ecotourism is developed based on the local community. Tourists are encouraged to lodge in the houses of local inhabitants as an incomparable way of getting acquainted with the simple way of village life, and to sample the traditional Kazakh cuisine (visitkazahstan.kz 2014). We have chosen this site as a clean background locality, however the results of egg analysis have shown hidden problems, as described further in this publication.

TABLE 10: DESCRIPTION OF SAMPLES TAKEN IN THE LOCALITY SHABANBAI BI.

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Soil						
SHA-P-REF	31/7/2014 20:00	+48° 24' 31.06" +75° 22' 33.17"	Pasture near Shabanbai Bi	Dark grey and brown loamy soil, dry, homogenization, quartation	Soil, mixed sample out of 5 partial samples, 5×5 m square, sampling depth 6 cm, 1 cm of top layer removed	Background sample, without smell, possible animal fecal pollution
Eggs						
ARAI-EGG	23/9/2014	+48°24' 25.10" +75°23' 37.95"	Shabanbai-Bi, middle of village; country house used for recreational purposes, its older part is inhabited by local people who breed chickens	Free range chicken eggs	Chickens eat bread, grass, bought grain, kitchen leftovers, they may freely move around the village, each adult person consumes 2 eggs daily	10 chickens 2–3 years old + one cock

3.11 Stepnogorsk

Geographical coordinates – 52°21‘8.26“ N 71°53‘4.19“ E

Stepnogorsk is a town in Akmola Oblast. It was established in 1959, and has been a town since 1964. It is located about 200km North-East of Astana. The population reached almost 47,000 inhabitants according to the census in 2009 (Wikipedia 2015). It began as a secret town. Stepnogorsk was found when large resources of uranium were discovered and Stepnogorsk Virgin Mining and Chemical Corporation was established – operating the largest uranium processing plant in Kazakhstan and one of the largest in the world. The mine at the village of Shantobe and the dock in Atbasar district belong to the factory too. For decades, industrial waste water has been discharged into the three tailing ponds with an area of 800 ha. The technology guaranteed safety of the hazardous waste – but only under condition of continuous operation of the processing plant and continuous irrigation of the ponds. Nowadays, all 70 thousand inhabitants live under threat of 500 ha dusty radioactive beaches that are getting larger every year. Three villages – Aksu, Kvartsitka and Zavodskoy, located just in the vicinity of tailing ponds, are home to 8,000 people. The industrial zone of Stepnogorsk is placed in Zavodskoy too, and many commute from the town to work here. Others graze domestic animals in the steppe surrounding radioactive waste, and grow fruits and vegetables in the territory that is partly sold on the market. As a result, another 30,000 people might be threatened (Arnika - Toxics and Waste Programme 2015).

TABLE 11: DESCRIPTION OF SAMPLES TAKEN IN THE LOCALITY OF STEPNOGORSK.

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
STEP-001	22/07/2014	+52° 25’ 42.9” +72° 04’ 04.6”	Soil- waste pond , Point 61 border of sanitary zone, about 1km from the processing plant	Loamy and sandy soil, quartation, homogenization, quartation	Soil, mixed sample out of 5 partial samples, 5×5 m square, sampling depth 5 cm	
STEP-002	22/07/2014	+52° 29’ 19.1” +71°49’ 42.7”	Soil- waste pond , Point 62 border of sanitary zone, about 1km from the processing plant	Loamy and sandy soil, quartation, homogenization, quartation	Soil, mixed sample out of 5 partial samples, 5×5 m square, sampling depth 5 cm	Possible contamination with fecal matter
STEP-003-PG	22/07/2014	+52° 21’ 58.2” +71° 59’ 02.9”	City, Stepnogorsk, Zavodskoj-ulica Mira 12, children’s playground	Sandy and loamy soil with a share of small rocky fraction, dry	Soil, mixed sample out of 5 partial samples representing two square meters	
STEP-004-SED	22/07/2014	+52° 09’ 08.0” +72° 06’ 02.4	Aksu River-north of the city towards the processing plant	Sediment, homogenization	Sediment, mixed sample out of 5 partial samples, sampling depth 10 cm	Residues of plant materials, root binding
STEP-005-SED	22/07/2014	+52° 14’ 10.8” +71° 51’ 41.7”	Aksu River-north of the city towards the processing plant	Sediment, homogenization		About km of STEP-004-SED, river usually without water, river flows towards the STEP-004-SED

3.12 Temirtau

Geographical coordinates – 50°03‘5.77“ N 72°57‘58.58“ E

Temirtau city (170,000 inhabitants) and its surroundings (100,000–500,000 inhabitants) are dominated by industries including a coal-fired power station, chemical production plants, foundries, forges and large steelworks belonging to the ArcelorMittal group. The steel mill Arcelor Mittal Temirtau (AMT) is located a distance of 500 m from the nearest houses. According to the Kazakhstani NIP from 2009, there were 105 transformers filled with Sovtol (commercial PCB mixture marketed in the former USSR) and 1024 capacitors containing PCBs in use in AMT (Republic of Kazakhstan 2009). The situation was addressed under the UNDP project "Development and implementation of the comprehensive plan on the management of PCBs" in 2014, when the Sovtol liquid was relocated to France. However, EcoMuseum and CINEST Karaganda report some PCB containing electrical equipment to still be in use in AMT.

Industries unintentionally producing PCDD/Fs include coke and foundry productions, both taking place in AMT as the only such enterprise in Kazakhstan. The processes of unloading and coke extinction, when PCDD/Fs can be released, are taking place in open air without a gas trapping and cleaning device. Formation of PCDD/Fs is also possible during limestone burning in shaft kilns. In Kazakhstan, lime is produced in the Temirtau Chemical and Metallurgical Plant, Ltd (Republic of Kazakhstan 2009). The Bashkortastan Republican Scientific Ecological Center carried out the first sampling campaign focused on PCDD/Fs in Kazakhstan in 2005. The PCDD/Fs concentration in indoor air sampled at the AMT sinter machine no. 5 was 42.64 pg m^{-3} (3.77 pg WHO-TEQ m^{-3}), in the dust (wall scrapes) 5419.7 pg g^{-1} (607.7 pg WHO-TEQ g^{-1}). According to the Kazakhstani NIP (2009), wastes produced by these industries may be a source of environmental pollution.

TABLE 12: DESCRIPTION OF SAMPLES TAKEN IN TEMIRTAU CITY AND CHEMICAL TAILINGS POND.

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
			Soil			
Temirtau 1	21/7/2013	+50° 03' 35.6" +73° 00' 14.5"	Temirtau, Bayseytovoy street 3, 5 and 5/1; childrens playground in the yard	Soil, mixing, homogenization	Mixed sample. In the distance about 1 m around the sand-pit, square 6×6 m, sampling depth 5 cm, 10×10 cm squares sampled - in the corners of the square and in the middle of the square sides	
TER PG 1./II.	18/8/2013 11:15	+50° 3.4931 +73°0.1069	City, Temirtau, Prospekt Respubliki 7, children's playground in the courtyard	Loamy and sandy soil, mixing, quartation	Soil, mixed sample out of 8 partial samples	
TER PG 2./II	18/8/2013 12:00	+50° 3.0371 +72°59.7620	City, Temirtau, Karagandinskoye Shosse 46, children's playground in the courtyard	Loamy and sandy soil, mixing, quartation, sieving	Soil, mixed sample out of 8 partial samples	
TER PG 3./II	18/8/2013	+50° 3.6891 +73° 0.2410	City, Temirtau, Bayseytovoy 4/1, children's playground in the courtyard	Loamy and sandy soil, mixing, quartation, sieving	Soil, mixed sample out of 8 partial samples	Asphalt chippings were found in 1 partial sample

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
TER PG 4./II	18/8/2013 15:20	+50° 3.7087, +72° 57.2393	City, Temirtau, Bulvar Nezavisimosti 3/1 & 3, children's playground in the courtyard of Prospekt Respubliky 85	Sandy soil, quartation	Soil, mixed sample out of 8 partial samples	
TER PG 5./II.	18/8/2013 16:00	+50° 3.1439, +72° 56.4802	City, Temirtau, Temirtanskaya ulitsa 1, school playground, Middle school 16	Loamy and sandy soil, mixing, quartation, sieving	Soil, mixed sample out of 10 partial samples	Larger school playground area, a larger number of simple samples of the entire range
TER PG 6./II	18/8/2013 16:00	+50° 2.5629, +72° 56.4637	City, Temirtau, 8. mikrorayou, dom 54, children's playground between several block buildings	Loamy soil, homogenization, quartation, sieving	Soil, mixed sample out of 8 partial samples	Playground in several places covered by steel slag
Sediments						
Temirtau 3	21/7/2013	+50° 01'13.0" +72° 58'18.6"	Sediment from the wetland in the front of AMT smelter dump foot	Mixed sample out of 6 subsamples (2 x 3 samples in two 1.5 m long lines 1.5 m distant from each other). Sampling depth 2–5 cm, square 10×10 cm.	Upper muddy fraction	
TEM CHL 2	18/8/2013 11:30	+50° 04' 19.7", +72°51' 28.3"	Little pond at the base of the Karbid chemical factory wastepond	Mixed sample out of 5 subsamples, 15 cm depth, 20 m line along pond shore sampled	Sandy clayey dark brown-grey sediment. Homogenization and mixing.	
TEM – CHL 8	18/8/2013 16:00	+50° 04' 11.6", +72°50' 58.2"	Chemical tailings pond of Kardbid plant, western edge of the pond	Light brown clayey surface crust	Sediment, point sample, depth 5 cm	Light area 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 plant, 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 11	18/8/2013 17:25	+50° 04' 32.4", +72°51' 01.6"	Marsh in the drainage of the Karbid chemical factor wastepond, close to the road to Temirtau	Sediment, mixing, homogenization	Mixed sample out of 5 subsamples, sampling depth 10 cm, sampled along marsh shore in 0.5–1.5 m distance from shore	Black-grey loamy, muddy and occasionally sandy sediment; muddy smell.

Sample code	Date	GPS	Sampling spot	Sample material, preparation	Type of sample	Comment
Other solid materials						
Temirtau 2	21/7/2013	+50° 01' 20.72" +72°58' 28.31"	Foot of the AMT smelter waste dump	Residues from the metallurgical processes; mixing	Mixed sample out of 10 sub-samples. Line cca 1.5 m from the foot of the dump. Sampling every 1 m, 5 m in the middle skipped, 10 cm sampling depth.	Sandy, partly with pieces of slag; sandy part only was taken
Temirtau 4	21/7/2013	+50° 01' 20.72" +72° 58' 28.31"	Foot of AMT smelter dump	4 pieces of slag		
TEM – CHL 1	18/8/2013 11:15	+50° 04' 16.3", +72°51' 27.4"	Chemical tailings pond of Kardbid plant, middle of tailings pond, near dam	Dark gray 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 6	18/8/2013 12:45	+50° 04' 14.1", +72°51' 30.5"	Chemical tailings pond of Kardbid plant, 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 12	18/8/2013 17:25	+50° 04' 15.9" +72°51' 31.1"	Chemical tailings pond of Kardbid plant, 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	

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Results of environmental sampling in Kazakhstan:
heavy metals in sediments and soils (Final report)

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1. INTRODUCTION

This study is focused on the presentation and discussion of the data related to contamination of soils and sediments by heavy metals. Environmental samples were obtained during two field visits conducted in Kazakhstan in August 2013 and in July - August 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 Kazakhstani partners, the Karaganda Regional Ecological Museum (EcoMuseum) and the Center for Introduction of New Environmentally Safe Technologies (CINEST).

1.1 Sampling sites

Detailed descriptions of the sampled sites and information about samples taken are provided in the General Introduction part of this publication (Toxic Hot Spots in Kazakhstan).

1.2 Sampling procedures and analytical methods

For sampling description please see “General introduction” section of this publication (Toxic Hot Spots in Kazakhstan).

After the 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 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. Sample was boiled for the 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 AMA analyser (AMA254, Altec).

The content of metals was expressed in mg kg^{-1} of dry matter.

2. RESULTS

Results of analytical measurement of heavy metals and arsenic are presented in the following tables. The content of elements is given in mg / kg of dry matter. <LOD: analyte concentration was below limit of detection. NA: not analysed.

2.1 Balkhash

TABLE 1: RESULTS OF CHEMICAL ANALYSIS FOR BALKHASH CITY AND LAKE.

Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
BAL 1/1	81.9	0.8	104.8	5.1	46.2	<LOD	0.085
BAL 1/2	1,622	9.7	3,593	7.8	911.1	242.5	0.558
BAL 1/3	117.4	1.2	281.6	4.4	43.6	<LOD	0.190
BAL 1/4	2,217	15.3	4,866	11.0	1,226	232.2	0.458
BAL 1/5	4,182	22.9	3,394	35.9	3,089	354.0	0.901
BAL 1/6	481.0	3.2	700.6	2.2	243.9	<LOD	0.230
BAL 1/7	251.3	2.6	45.9	3.1	212.6	<LOD	0.139
BAL 1/8	218.5	1.4	454.4	3.0	153.1	<LOD	0.105
BAL 1/9	468.0	5.5	678.7	8.7	443.3	<LOD	0.202
BAL 1/10	420.2	3.0	1,283	13.0	259.1	<LOD	0.180
BAL 1/11	175.8	1.4	194.7	7.4	181.6	<LOD	0.084

Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
BAL 1/13	666.1	11.7	1127	14.6	1,012	<LOD	<LOD
BAL-GR-23/1	125.5	1.1	95.6	20.3	357.9	<LOD	0.042
BAL-GR-23/2	229.7	2.1	366.3	7.1	211.8	<LOD	0.060
BAL-HOT-GR-1	35.7	<LOD	453.4	5.9	20.0	<LOD	0.048
BAL-HOT-GR-2	6.2	2.4	10,500	2.2	316.3	<LOD	0.034
BAL-HOT-GR-3	199.2	6.8	50,030	5.7	749.2	<LOD	0.148
BAL-HOT-GR-4	99.7	6.8	13,880	24.6	484.5	<LOD	0.045
BAL-HOT-SED-1	191.6	0.7	55,820	14.7	238.8	<LOD	0.127
BAL-HOT-SED-2	141.7	<LOD	1,221	4.9	34.4	<LOD	0.072
BAL-SED-1	33.1	0.7	102.3	4.6	40.4	<LOD	0.263
BAL-SED-2	387.6	5.6	675.0	9.8	328.5	143.8	0.113
BAL-SED-3	421.4	6.4	690.9	2.6	284.1	199.9	0.143
BAL-SED-5	360.2	3.5	726.1	3.5	319.5	<LOD	0.094
BAL-SED-6	2,242	18.2	4,685	7.2	1,339	495.4	<LOD
POP-BAL	440.4	1.5	1,557	7.3	3,792	156.8	0.028
BAL-1-SED-REF	<LOD	<LOD	7.40	<LOD	19.83	<LOD	NA
BAL-2-SED-REF	<LOD	<LOD	3.79	<LOD	21.42	<LOD	NA
BAL-PG-30-1	341.9	4.19	631.6	<LOD	251.7	29.94	NA
BAL-PG-30-2	390.3	4.47	671.7	<LOD	295.0	39.47	NA
BAL-PG-30-3	65.35	<LOD	205.4	<LOD	106.0	8.81	NA
BAL-SED-14-1	317.2	7.26	1,828	<LOD	380.0	87.62	NA
BAL-SED-14-2	463.1	2.68	1,222	<LOD	335.6	61.88	NA
BAL-SED-14-2	141.7	<LOD	2633	<LOD	455.0	27.69	NA

2.2 Daryal

TABLE 2: RESULTS OF CHEMICAL ANALYSIS FOR THE LOCALITY OF DARYAL.

Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
DAR-SED-01	3.74	<LOD	18.88	<LOD	26.33	<LOD	NA
DAR-SED-02	11.35	<LOD	12.08	<LOD	26.52	<LOD	NA
DAR-SED-03	323.9	<LOD	27.28	<LOD	61.42	<LOD	NA
DAR-01	44.01	<LOD	43.82	<LOD	47.48	<LOD	NA
DAR-02	117.8	<LOD	37.72	<LOD	141.9	<LOD	NA
DAR-03	25.01	<LOD	40.76	<LOD	44.03	<LOD	NA

2.3 Orta Deresin

TABLE 3: RESULTS OF CHEMICAL ANALYSIS FOR THE LOCALITY OF ORTA DERESIN.*

Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
ORTADER 2	14.6	0.4	32.3	15.2	41.9	<LOD	0.206
ORTADER 9	7.9	<LOD	15.9	4.4	24.5	<LOD	<LOD

*Samples ORTADER 1, and 3-8 were not analyzed for heavy metals content.

2.4 Temirtau

TABLE 4: RESULTS OF CHEMICAL ANALYSIS FOR THE LOCALITY OF TEMIRTAU.

Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
TEM – CHL 1	2.56	0.16	9.32	<LOD	20.16	<LOD	0.040
TEM – CHL 2	8.2	<LOD	3.5	2.9	9.2	<LOD	0.196
TEM – CHL 3	7.21	0.55	22.15	<LOD	111.0	<LOD	0.116
TEM – CHL 4	0.52	0.41	14.21	7.28	23.22	<LOD	<LOD

Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
TEM – CHL 5	2.87	0.30	12.43	<LOD	64.15	<LOD	0.049
TEM – CHL 6	<LOD	<LOD	7.92	<LOD	94.65	<LOD	0.034
TEM – CHL 8	<LOD	<LOD	4.12	<LOD	6.71	<LOD	0.008
TEM – CHL 9	2.96	0.28	10.78	3.27	46.00	<LOD	0.037
TEM – CHL 10	8.48	<LOD	13.11	28.36	51.19	<LOD	<LOD
TEM – CHL 11	10.1	<LOD	10.6	14.9	38.3	<LOD	0.381
TEM – CHL 12	3.32	<LOD	8.99	<LOD	64.46	<LOD	<LOD
TER PG 1./II.	20.86	0.38	19.06	24.45	112.3	<LOD	0.087
TER PG 2./II	2,413	0.26	17.85	19.21	129.3	<LOD	0.052
TER PG 3./II	77.90	0.50	22.18	31.17	156.8	<LOD	0.137
TER PG 4./II	18.99	0.23	16.39	19.61	72.28	<LOD	0.056
TER PG 5./II.	27.24	0.25	17.64	21.01	95.42	<LOD	0.073
TER PG 6./II	13.93	0.00	13.85	21.05	60.18	<LOD	0.028

2.5 Stepnogorsk

TABLE 5: RESULTS OF CHEMICAL ANALYSIS FOR THE LOCALITY OF STEPNOGORSK.

Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
STEP-001	7.51	<LOD	24.46	37.43	45.30	<LOD	NA
STEP-002	8.31	<LOD	18.93	48.24	70.05	<LOD	NA
STEP-003-PG	20.65	<LOD	42.02	32.06	128.8	29.00	NA
STEP-004-SED	<LOD	<LOD	108.9	<LOD	175.5	<LOD	NA
STEP-005-SED	56.73	<LOD	51.52	75.10	244.1	<LOD	NA

2.6 Glubokoe

TABLE 6: RESULTS OF CHEMICAL ANALYSIS FOR THE LOCALITY OF GLUBOKOE.							
Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
GLUB-SED-1	174.1	13.60	278.3	24.62	674.6	<LOD	NA
GLUB-SED-2	1,230	21.06	2,279	45.58	1,566	46.31	NA
GLUB-P-1	3,519	20.57	4,837	88.29	5,691	493.8	NA
GLUB-ST-1	1,965	<LOD	1,407	105.62	22,020	34.01	NA
GLUB-SED-3	131.5	3.38	380.6	14.69	674.6	9.60	NA

2.7 Dubygalinskoe

TABLE 7: RESULTS OF CHEMICAL ANALYSIS FOR THE LOCALITY DUBYGALINSKOE.							
Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
DUB-SED-1	6.31	<LOD	4.40	<LOD	27.30	<LOD	NA
DUB-SOIL-1	13.83	<LOD	6.59	<LOD	64.55	<LOD	NA
DUB-SED-2	<LOD	<LOD	4.76	<LOD	31.87	<LOD	NA

2.8 Shabanbai Bi

TABLE 8: RESULTS OF CHEMICAL ANALYSIS FOR THE LOCALITY OF SHABANBAI BI.							
Sample code	Lead	Cadmium	Copper	Chromium	Zinc	Arsenic	Mercury
SHA-P-REF	15.76	<LOD	20.27	15.63	65.49	<LOD	NA

3. DISCUSSION

Various legal standards and auxiliary evalution criteria are presented in this chapter. The metals concentrations determined in samples from the investigated sites are then compared to respective legal standards. Finally, target samples with high content of metals were chosen for calculation of cancerogenic and non-carcinogenic risks associated with them.

3.1 Legal standards

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

First, the 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. 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 statement of compliance with norms of maximum allowable concentrations of harmful substances, harmful microorganisms and other biological contaminants in the soil established by the Ministry of Health and Ministry of Environment of Kazakhstan in 2004. Limits and norms stated in previous Regulations are based on Kazakhstani hygienic normatives for soil - Soil pollution standards (established in November 29, 1997).

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 chronical exposure. This exposure is based on the direct contact with target compounds. Regional screening levels were derived by US EPA (United States Environmental Protection Agency) for some compounds that have a CAS registration number. RSL are concentrations of chemical compounds in the environment (soils, sediments, water or 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 content of some substances as a result of geological conditions.

Concentrations of pollutants in samples from playgrounds were compared with hygienic limits set by Decree no. 238/2011 for playgrounds in the Czech Republic (MZD 2011).

3.2 Evaluation of pollutant levels

An extensive survey focused on heavy metals monitoring was conducted in the city **Balkhash** and its surroundings. There were 13 samples of sediments, 11 samples of soil, 6 samples of soil taken from children playgrounds and 2 background samples of sediment. In general, increased levels of lead in sediments and soils often exceeded

TABLE 9: LEGAL STANDARDS FOR SOILS. THE CONTENT OF ELEMENTS IS GIVEN IN mg kg^{-1} OF DRY MATTER.	Lead	Cadmium	Copper	Chromium (hexavalent)	Chromium (total)	Zinc	Arsenic	Mercury
Kazakhstani limits based on hygienic normatives for soils	32	0.5	3.0	0.05	6.0	23	2.0	2.1
Levels of pollution limits – industrial areas (based on USEPA)	800	800	41,000	5.6	-	310,000	2.4	43
Levels of pollution limits – other areas (based on USEPA)	400	70	3,100	0.29	-	23,000	0.61	10
Cz Decree – playgrounds	50	0.3	45	-	85	90	10	0.3

Kazakhstani Soil pollution standards by 5 – 20-times and levels of cadmium often exceeded pollution standards by 5 – 10-fold. The highest levels of heavy metals (mainly copper) were observed in sediments and soils under the tailing pond of BGMK close to the lake shore, which represents a significant threat to water quality of Balkhash. Very high levels of heavy metals were observed in samples of sand from several playgrounds in the city. Kazakhstani hygienic normative values were exceeded up to 70-times for lead (Czech limit for playgrounds up to 45-fold), up to 30-times for cadmium (Czech limit for playgrounds up to 50-fold) and up to 120-times for arsenic (Czech limit for playgrounds up to 25-fold). Similar levels of pollution were also measured for the sample of soil taken in the city suburbs near older family houses close to the BGMK. In general, concentrations of all measured heavy metals in almost all samples are significantly exceeded compared to background levels in samples from Balkhash lake showing the influence of the metallurgic plant BGMK (see graphs on Figures 1 and 2).

There were 3 samples of sediment and 3 samples of soil taken in the locality **Daryal**. Concentrations of lead exceeded Kazakhstani hygienic normative values in sediment taken from the flooded pit, which is possibly a former drainage channel. Increased levels of lead were also measured in a sample of soil from a heap next to the flooded pit. Heavy metal contamination in the locality of Daryal is not so significant compared to other studied localities.

There were 11 samples of sediment and ash taken from the chemical tailings pond of Karbid plant and 6 samples of soils from children's playgrounds in the locality **Temirtau**. The highest level of heavy metal (lead) was observed in loamy sand from a playground in the city. Limits set for playgrounds in the Czech Republic was exceeded by almost 50-times, Kazakhstani hygienic normative values were exceeded 75-times. Slightly increased mercury concentrations in comparison with the background was found in a few samples taken from chemical tailings pond of Karbid plant.

There were taken 8 samples of soil in the locality of **Orta Deresin**. Slightly increased mercury concentrations in comparison with the background were found in the analyzed samples.

Evalution of samples taken in **Stepnogorsk** and **Glubokoe** provides the following findings. There were 2 samples of soil, 1 sample of sand from a playground and 2 samples of sediments taken in Stepnogorsk. The most serious levels of heavy metals were measured in a sample from the playground for arsenic and zinc. The sample results were threefold higher than the Czech limit for playgrounds and Kazakhstani hygienic normative value was exceeded by almost 15-times. The Kazakhstani hygienic normative value was also exceeded for lead in sediment from Aksu River north of Stepnogorsk. In general, observed levels of heavy metals in Stepnogorsk are less serious than in Glubokoe surrounding the slag waste dump and levels of lead apart from samples of sediment and playground are comparable to those measured in background samples from Dubygalinskoe lake, where two samples of sediments and one soil sample were taken in order to get some idea about background levels of heavy metals in Eastern Kazakhstan. There were 3 samples of sediments, one soil sample and one slag sample taken in Glubokoe. The highest levels of heavy metals were observed in a soil sample taken next to the slag waste dump, where enormous levels of arsenic, copper and lead were found exceeding not only levels of hygienic normative set for Kazakhstan (for Pb and As) but also levels for remediation of sites for industrial or general use set in the Czech Republic. So this site should be remediated and cleaned up. The same applies for sediment samples from the lake below the slag waste dump. There were also increased levels of cadmium in both samples mentioned above, exceeding Kazakhstani hygienic normative by 40-fold. Relatively high levels of cadmium and lead were found also in sediment sample from Irtysh River downstream from Glubokoe town most likely due to the influence of the metallurgic plant in Glubokoe.

There were 7 **background samples** taken at different locations to get some idea about background levels of heavy metals in Kazakhstan. 3 samples of sediments from the Balkhash, 2 samples of sediments and 1 sample of soil in the locality of Dubygalinskoe and 1 sample of soil near Shabanbai Bi. On average, concentrations of lead, copper, chromium and zinc were distinctly lower in background samples than at sites affected by industrial activities and the differences can be several orders of magnitude. Cadmium and arsenic were not detected in background samples at all.

3.3 Auxiliary criteria

Content of metals can be compared with other auxiliary criteria set for the purpose of evaluating the potential need for remediation of contaminated sites in the Czech Republic at the end of the 1990s (MZP 1996). These criteria are not legally binding, however, 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. 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 does pose. 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.

TABLE 10: AUXILIARY CRITERIA FOR SOILS. THE CONTENT OF ELEMENTS IS GIVEN IN mg kg^{-1} OF DRY MATTER.

Criterion	Lead	Cadmium	Copper	Chromium (total)	Zinc	Arsenic	Mercury
A	80	0.5	70	130	150	30	0.4
B	250	10	500	450	1,500	65	2.5
C – residential area	300	20	600	500	2,500	70	10
C – recreation area	500	25	1,000	800	3,000	100	15
C – industrial area	800	30	1,500	1,000	5,000	140	20

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 and solution are necessary documents for the decision on the type of remedial measures.

3.4 Situation in Balkhash

A detailed study, which assesses the impact of industrial activities, was performed with samples from Balkhash City, where 11 samples of soils and sediments from residental areas near metallurgical works were collected. Concentrations of heavy metals in these samples were compared with background levels determined by the measurement of 7 samples of soils and sediments from different locations. Background levels represent the average metal content in the soil matrix in central Kazakhstan. The adverse impact of anthropogenic activities, which produces a significant amount of heavy metal pollution due to the use of outdated technologies is documented in the following graphs (see Figures 1 and 2). The situation in residential areas of Balkhash City is alarming. Modern technology (BAT – Best Available Techniques) to reduce emissions from the metallurgical plant should be implemented for metallurgical processes to avoid the continuous spread of contamination into the environment and to protect public health.

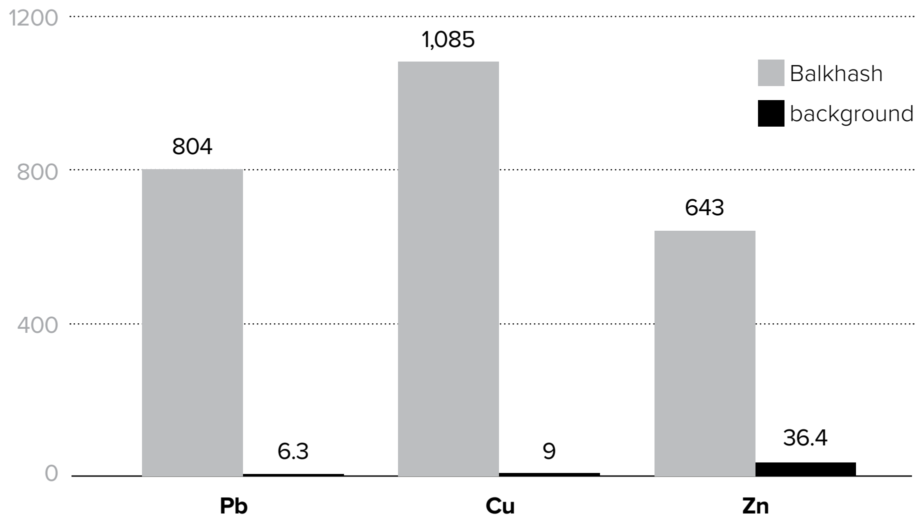

Figure 1: Comparison of average concentrations of lead, copper and zinc in samples of soils and sediments from the Balkhash City and background samples. Concentrations are in mg kg^{-1} of dry matter.

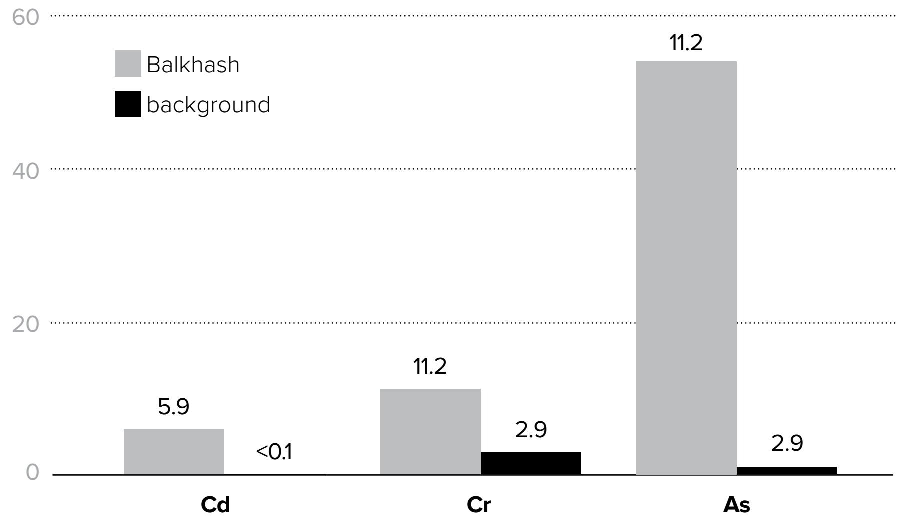

Figure 2: Comparison of average concentrations of cadmium, chromium and arsenic in samples of soils and sediments from the Balkhash City and background samples. Concentrations are in mg kg^{-1} of dry matter.

4. 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 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 the body repair processes which are able to successfully cope with exposure to a toxic substance, but only to a certain dose, then the effect is already apparent. A threshold value, known as the NOAEL (No Observed Adverse Effect Level), is the exposure level 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. 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 lifetime.

For the calculation of risk exposure to substances with non-carcinogenic effect a received and absorbed dose with acceptable toxicological intake of the substance is compared (ie. 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 effect uses parameter ELCR - Excess Lifetime Cancer Risk (dimensionless indicator corresponding to the probability of developing cancer with lifetime exposure, which can be described by the following equation:

$$ECLDR = CDI \times SF$$

$$ECLDR = LADD \times SF$$

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 11: AGENTS CLASSIFICATION 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) 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: arsenic and inorganic arsenic compounds as Group 1 – Carcinogenic to humans, lead as Group 2B – Possibly carcinogenic to humans, inorganic compounds of lead as Group 2A - Probably carcinogenic to humans and organic compounds of lead as Group 3 - Not classifiable as to its carcinogenicity to humans. On the basis of the toxicological data, risk assessment using RISC software was performed.

4.1 RISC model

Risk-Integrated Software for Cleanups (RISC) is a 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 that 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 12: RESULTS OF THE CALCULATION OF HUMAN HEALTH RISKS ASSOCIATED WITH POLLUTANTS IN SELECTED SAMPLES – CARCINOGENIC RISK.*

Contaminant	Locality	Sample	Concentration in soil (mg kg^{-1})	Exposition pathway			Total
				Ingestion of soil	Dermal contact of soil	Ingestion of vegetable	
Arsenic	Balkhash	BAL1/2	242.5	6.70E-05	3.90E-06	-	7.09E-05
		BAL1/4	232.2	6.40E-05	3.80E-06	-	6.78E-05
		BAL1/5	354.0	9.70E-05	5.70E-06	1.60E-04	2.60E-04
		BAL SED 2	143.8	4.00E-05	2.30E-06	-	4.23E-05

Contaminant	Locality	Sample	Concentration in soil (mg kg⁻¹)	Exposition pathway			Total
				Ingestion of soil	Dermal contact of soil	Ingestion of vegetable	
Arsenic	Balkhash	BAL SED 3	199.9	5.50E-05	3.20E-06	-	5.82E-05
		BAL SED 6	495.4	1.40E-04	8.00E-06	-	1.48E-04
		POP BAL	156.8	4.30E-05	2.50E-06	-	4.55E-05
		BAL - PG - 30 - 1	29.94	8.20E-06	4.80E-07	-	8.68E-06
		BAL - PG - 30 - 2	39.47	1.10E-05	6.40E-07	-	1.16E-05
		BAL - PG - 30 - 3	8.81	2.40E-06	1.40E-07	-	2.54E-06
		BAL - SED - 14 - 1	87.62	2.40E-05	1.40E-06	-	2.54E-05
		BAL - SED - 14 - 2	61.88	1.70E-05	1.00E-06	-	1.80E-05
		BAL - SED - 14 - 3	27.69	7.60E-06	4.70E-07	-	8.07E-06
	Glubokoe	GLUB - SED - 2	46.31	1.30E-05	7.50E-07	-	1.38E-05
		GLUB - P - 1	493.8	1.40E-04	8.00E-06	-	1.48E-04
		GLUB - ST - 1	34.01	9.30E-06	5.50E-07	-	9.85E-06
	Stepnogorsk	STEP - 3 - PG	29.00	8.60E-06	4.70E-07	-	9.07E-06

*Results are based on standard calculation coefficients defined in Risk-Integrated Software for Cleanups (RISC). Results are related to the average population.

TABLE 13: RESULTS OF THE CALCULATION OF HUMAN HEALTH RISKS ASSOCIATED WITH POLLUTANTS IN SELECTED SAMPLES – HAZARD QUOTIENTS (HQ).*

Contaminant	Locality	Sample	Concentration in soil (mg kg⁻¹)	Exposition pathway			Total
				Ingestion of soil	Dermal contact of soil	Ingestion of vegetable	
Arsenic	Balkhash	BAL1/2	242.5	1.70E+00	1.00E-01	-	1.80E+00
		BAL1/4	232.2	1.70E+00	9.70E-02	-	1.80E+00
		BAL1/5	354.0	2.50E+00	1.50E-01	4.00E+00	6.70E+00
		BAL SED 2	143.8	1.00E+00	6.00E-02	-	1.06E+00
		BAL SED 3	199.9	1.40E+00	8.40E-02	-	1.48E+00
		BAL SED 6	495.4	3.50E+00	2.10E-01	-	3.71E+00

Contaminant	Locality	Sample	Concentration in soil (mg kg^{-1})	Exposition pathway			Total
				Ingestion of soil	Dermal contact of soil	Ingestion of vegetable	
Arsenic	Balkhash	POP BAL	156.8	1.10E+00	6.60E-02	-	1.17E+00
		BAL - PG - 30 - 1	29.94	2.10E-01	1.30E-02	-	2.23E-01
		BAL - PG - 30 - 2	39.47	2.80E-01	1.70E-02	-	2.97E-01
		BAL - PG - 30 - 3	8.81	6.30E-02	3.70E-03	-	6.67E-02
		BAL - SED - 14 - 1	87.62	6.20E-01	3.70E-02	-	6.57E-01
		BAL - SED - 14 - 2	61.88	4.40E-01	2.60E-02	-	4.66E-01
		BAL - SED - 14 - 3	27.69	2.00E-01	1.20E-02	-	2.12E-01
	Glubokoe	GLUB - SED - 2	46.31	3.30E-01	1.90E-02	-	3.49E-01
		GLUB - P - 1	493.8	3.50E+00	2.10E-01	-	3.71E+00
		GLUB - ST - 1	34.01	2.40E-01	1.40E-02	-	2.54E-01
	Stepnogorsk	STEP - 3 - PG	29.00	2.10E-01	1.20E-02	-	2.22E-01
Lead	Balkhash	BAL1/2	1,621	9.60E-01	1.90E-02	-	9.79E-01
		BAL1/4	2,217	1.30E+00	2.60E-02	-	1.33E+00
		BAL1/5	4,182	2.50E+00	4.90E-02	0.00E+00	2.55E+00
		BAL1/12	666.1	4.00E-01	7.80E-03	-	4.08E-01
		BAL SED 6	2,242	1.30E+00	2.60E-02	-	1.33E+00
	Temirtau	TER PG 2/II	2,410	1.40E+00	2.80E-02	-	1.43E+00
	Glubokoe	GLUB - SED - 2	1,230	7.30E-01	1.40E-02	-	7.44E-01
		GLUB - P - 1	3,519	2.10E+00	4.10E-02	-	2.14E+00
		GLUB - ST - 1	1,965	1.20E+00	2.30E-02	-	1.22E+00

*Results are based on standard calculation coefficients defined in Risk-Integrated Software for Cleanups (RISC). Results are related to the average population.

5. CONCLUSIONS

This study focused on monitoring and evaluation of concentrations of heavy metals in soils and sediments at several locations in Kazakhstan. A series of samples were taken at contaminated sites as well as samples from the sites where contamination was not expected in order to generate comparable background levels.

There are several spots where enormous levels of arsenic and lead were found in soils and sediments. These levels of pollutants represent a significant threat to environment. The highest levels of heavy metals were observed in sediments and soils under the tailing pond in Balkhash close to the lake shore (copper) and in soil samples taken next to the slag waste dump in Glubokoe (lead and arsenic). Concentrations of heavy metals exceeded not only levels of hygienic normative set for Kazakhstan but also levels for remediation of sites for industrial or general use set in the Czech Republic. These sites should be remediated and cleaned up. It was also alarming that extremely high concentrations of heavy metals were found in samples from the children's playgrounds in the city of Balkhash (mainly lead, cadmium, copper and arsenic) and in the city of Temirtau (lead), which represent a threat to small children.

Concentrations of measured metals were distinctly lower in background samples taken at several locations than at sites affected by industrial activities; moreover cadmium and arsenic were not detected in background samples at all. The adverse impact of industrial activity is especially evident in the Balkhash City, where the average concentration of heavy metals in soils and sediment near metallurgical works is up to two orders of magnitude higher than in background samples.

Analysis using the Risk-Integrated Software for Cleanups (RISC) indicated the following results: Some samples polluted with arsenic showed unacceptable carcinogenic risk and several samples showed that adverse carcinogenic effects may occur in the long term. A series of samples polluted with arsenic and lead showed exceeded hazard quotient (HQ). A potential adverse health effects exist in this case. More research should be done in order to determine these toxic threats at the studied sites.

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‘Dangerous State of Play’

Heavy Metal Contamination of Kazakhstan’s Playgrounds

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1. INTRODUCTION

This is a report on sampling and analysis of soil samples from children's playgrounds at three different locations in Kazakhstan. Contamination by heavy metals is a particular concern and the levels found are compared with international standards.

These locations were chosen after discussion between the three partner organizations implementing the project: Arnika – Toxics and Waste Programme and EkoMuseum and CINEST in Kazakhstan. This report should be read together with the Arnika publication Environmental Monitoring in Central and Eastern Kazakhstan – Sampling Report which provides detailed data about the sampling methodology and sites (on CD attached to this report) together with a full list of the analytical results in the wider sampling programme in this publication.

Children's recreational facilities such as playgrounds represent a potentially hazardous environment for children in contaminated areas - particularly because of the potential interaction with contaminated surfaces and soils including, in some cases, significant ingestion of soil (Duggan et al., 1985; Mielke et al., 2011; Nielsen and Kristiansen, 2004).

There may be additional hazards associated with the original sources of pollution such as contamination in the air, dust or water. No analysis of air quality was undertaken as part of this project and this report does not address these issues.

2. METHODOLOGY OF SAMPLING AND SAMPLE ANALYSIS

2.1 Sampling

The sampling of soil playgrounds in Kazakhstan formed part of a wider sampling programme undertaken in 2013–2014 in which a number of samples were taken from six sites as shown on the map in the general introduction to this publication (Toxic Hot Spots in Kazakhstan).

A total of fifteen soil samples were taken from playgrounds in four of the eight sampling sites i.e. Balkhash, Temirtau, Stepnogorsk and Akchatau.

In general composite soil samples were taken which were formed by mixing several smaller samples[1] taken from around the sampling site. The mixed samples were stored in plastic sample containers (V = 500 ml) with screw lids. Samples were kept in dark cool boxed before analysis.

1 Composite samples were mixed from 5–10 smaller samples in order to get more representative samples for each of the playgrounds.

3. RESULTS

Full sampling data are included in the attached Monitoring Report (see attached CD) but a summary of composite table of results from the four sites is as follows (see Table 1.).

TABLE 1: RESULTS OF CHEMICAL ANALYSES OF COMPOSITE SOIL SAMPLES FROM PLAYGROUNDS IN FOUR LOCATIONS IN CENTRAL KAZAKHSTAN. Highlighted figures are those which exceed Czech guidelines for children's playgrounds (see Table 4).

Sample / Chemical	Temir 1	TER PG 1/ II	TER PG 2/ II	TER PG 3/ II	TER PG 4/ II	TER PG 5/ II	TER PG 6/ II	BAL 1/1	BAL 1/3	BAL 1/4	BAL PG 30-1	BAL PG 30-2	BAL PG 30-3	STEP-003-PG	AKCH I	Average
PCDD/F + dl-PCBs (pg g^{-1})	3.2	40	2.6	3.7	7.8	6.8	6.4	2.2	4.6	4.8	NA	NA	NA	NA	NA	8.21
Lead (mg kg^{-1})	54.5	20.9	**2,410**	**77.9**	19	27.2	13.9	**81.9**	**117.4**	**2,217**	**341.9**	**390.31**	**65.35**	20.65	29.3	**392.48**
Cadmium (mg kg^{-1})	0.4	0.4	0.3	0.5	0.2	0.2	0	**0.8**	**1.2**	**15.3**	**4.19**	**4.47**	0	0	0	**1.86**
Copper (mg kg^{-1})	42	19.1	17.9	22.2	16.4	17.6	13.9	**104.8**	**281.6**	**4,866.1**	**631.64**	**671.67**	**205.44**	42.02	31.4	**465.58**
Chromium - total (mg kg^{-1})	42.2	24.5	19.2	31.2	19.6	21	21	5.1	4.4	11	0	0	0	36.02	23.7	17.26
Zinc (mg kg^{-1})	**1,302**	112.3	129.3	**156.8**	72.3	95.4	60.2	46.2	43.6	**1,226.2**	**251.73**	**295.03**	106	128.83	125.3	**276.75**
Arsenic (mg kg^{-1})	0	0	0	0	0	0	0	0	0	**232.2**	**29.94**	**39.47**	8.81	**29**	0	**22.63**
Mercury - THg (mg kg^{-1})	0.071	0.087	0.052	0.137	0.056	0.073	0.028	0.085	0.190	**0.458**	NA	NA	NA	NA	NA	0.10

NA = not analyzed

3.1 Soil Guideline Values

Kazakhstan currently has no limit values for playgrounds or residential soils. Indeed there are few national standards for heavy metal and none for PCDD/F contamination. The values found can therefore be compared with regional and international Soil Guideline Values summarised in Tables 2 and 3.

There are now many international standards for soil contamination. Unfortunately only few countries have established specific values for particularly sensitive uses such as playgrounds. These are sometimes considered as special cases on a risk basis in which case normative values are not available for comparison. The Czech Republic has published limit values for metals relating specifically to playgrounds (MZD 2011) which are also useful for evaluation of the levels found in this review (see Table 4).

TABLE 2: REGIONAL STANDARDS ESTABLISHED BY THE RUSSIAN FEDERATION.

Contaminant	Approximately Allowed Concentration mg kg⁻¹ soil	Limit of Allowed Concentration mg kg⁻¹ soil	Soluble forms	Source
Mercury		2.10		1
Copper			3.00	1
Lead		32.00	6.00	1
Zinc			23.00	
Chromium+3			6.00	1
Chromium+6		0.05		3
Cadmium		0.50		1
Arsenic		2.00		1
Polychlorinated biphenyls (PCB sum)	0.06			2
Polychlorinated dibenzo-dioxins (PCDDs)+dibenzofurans (PCDF) TE sum	0.33 ng kg⁻¹			4

Sources:
1. USSR, Hygienic normatives (standards) chemicals in soil (PDK) GN 6229-91, ГН 6229-91, Перечень ПДК и ОДК хим. веществ в почве
2. Russian Federation, Order 16.12.2003г. №1322 Tatarstan Environment and Natural Resources Министерство экологии и природных ресурсов Респ.Татарстан, Приказ от 16.12.2003г. №1322
3. Russian Federation, GN 2.1.7.2041-06 Hygienic normatives (standards) chemicals in soil. This norms introduced instead of 6229-91
Гигиенические нормативы ГН 2.1.7.2041-06
4. Order of USSR Health Ministry 08.09.86 № 697 DSP, Приказ МЗ СССР от 08.09.86 г. № 697 ДСП

TABLE 3: COMPARATIVE INTERNATIONAL STANDARDS. Source: Brevik (2013).

	United States (US EPA 2009)		Australia (NEPM 1999)			New Zealand (NES 2011)		The Netherlands (VROM 2000)	Canada (SQG 2001)		United Kingdom (EA 2009)	
	EPA RSL Res	EPA RSL Ind	HIL (A)	HIL (D)	Eil	HD Res	10% Prod Res	SIV	SQH-HH	SQH-EH	SGV resid	SGV allmt
As	0.39	1.6	100	400	20	45	20	55	12	17	32	43
Cd	70	800	20	80	3	230	3	12	14	10	10	1.8
Cr(VI)	0.29	5.9	100	400	1	1,500	460	380	0.4			
Cr(III)	120,000	1,500,000	120,000	480,000	400	Nl	Nl					
Cr total									220	64		
Cu	3,100	41,000	1,000	4,000	100	Nl	Nl	190	1,100	63		
Hg inorg	10	43	15	60	1	1,000	310	10	6.6	12	170	80
Hg methyl	7.8	100	10	40							11	8
Pb	400	800	300	1,200	600	500	210	530	140	300		
Ni	3,700-3,800	44,000-47,000	600	2,400	60			210		50	130	230
Zn	23,000	310,000	7,000	28,000	200			720		200		

Notice:
United States: RSL Res, Residential Soil; RSL Ind, Industrial soil. Australia: HIL, health investigation levels; (A) high density residential; (D), recreational; EIL, ecological investigation level. New Zealand: HD RES, high-density residential; 10% Prod Res, 10% produce residential. The Netherlands: SIV, Soil intervention values for soil remediation. Canada: SQH, Soil Quality Health Guidelines; SQG-HH, human health; SQG-EH, environmental health; United Kingdom: SGV, soil guideline value; SGV Resid, residential; SGV Allmt, allotments (Urban gardens)

TABLE 4: LIMIT VALUES APPLIED IN THE CZECH REPUBLIC.

Limits	Levels of heavy metals (mg kg^{-1} dry matter)						
	As	Cd	Cr	Cu	Pb	Zn	Hg
Cz MoE – industrial areas	2.4	800	-	41,000	800	310,000	
Cz MoE – other (general use) areas	0.61	70	-	3,100	400	230,00	
CzR – playgrounds (MZD 2011)	10	0.5	100	100	60	150	0.3

3.2 Results by individual contaminants

Lead

Most of the samples exceeded the natural levels of lead which are reported in the range 13-16 mg kg^{-1} (Adriano 2001). Only two samples were above international soil guideline values, however. These were Termitau sample 2/II and Balkhash sample 1/4 which had exceptionally high levels of lead. Two others were either close or above some of international soil guideline values. These were the two samples from Balkhash 30-1 and 30-2 which had levels above 300 mg kg^{-1} of lead.

Cadmium

Most of the samples contained only very low levels (<1mg kg^{-1}) of cadmium[2]. The notable exceptions wereBAL 1/4, BAL 30-1 and BAL 30-2 which contained 9.7 and 15.3 and 4.2 and 4.5 mg kg^{-1} respectively. One sample (BAL 1/3) had level slightly above 1 mg kg^{-1}.

Copper

Most of the samples were found to contain low levels of copper – below even those lower levels of contamination which are of particular concern in relation to ecological protection in international standards and guidelines – although the Czech guidelines for playgrounds are exceeded at all the Balkhash sites. The most worrying levels were Balkhash samples 1/4, 30-1 and 30-2 which contained 4.8 and over 0.6 g kg^{-1}. These high levels certainly justify further investigation when compared with international standards and guidelines.

Chromium

Analysis was only undertaken for total chromium and so it is not possible to establish the likely hazards are these are driven mainly by the far more toxic chromium VI species. None of the levels were sufficiently high to be of obvious concern.

2 These levels are described as being typical of background levels in the United Kingdom by Kah et al – see table below.

Zinc

Zinc is mainly concern in relation to ecotoxicity rather than human health- particularly at the levels found in this study although the sites at Balkhash 1/4 and Temirtau 1 were high and, taken together with the other contamination zinc increases the health concerns about exposure at these two sites.

Arsenic

Only five samples, four from Balkhash and one from Stepnogorsk, contained levels of arsenic above the laboratory detection levels. One sample from Balkhash (1/4), contained very high levels arsenic compared with the natural background level, which varies between about 7 and 40 mg kg^{-1} (Brevik et al 2013) and it was also significantly higher than international soil guidelines levels.. Four samples (three from Balkhash and one from Stepnogorsk) were above the Czech guidelines for children's playgrounds (see Tables 1 and 4).

Mercury

Normal soils have Hg concentration of less than 0.01 mg kg^{-1} (Diawara et al 2006). None of the playground samples have levels of mercury which exceed international guidelines. Few guidelines have been established specifically for playgrounds, however, in spite of the special and higher risks associated with exposure of children. Furthermore there are no safe levels for mercury contamination of playgrounds and levels should be as close to the background soil levels as possible.

The Czech guideline levels for playgrounds was exceeded in sample BAL 1/4.

Dioxins and PCBs

The dioxin (PCDD/Fs) and dioxin like PCB levels are in the expected range for contamination of urban areas from the European perspective with the possible exception of Temirtau sample PG1/II (40 pg g^{-1}). This is a higher level than would normally be expected and whilst it would not, of itself, require remedial work to be undertaken it is recommended that additional samples are taken in this area and analysed by GCMS to establish whether the contamination is more widespread and, if so, at what levels.

It should also be noted that background level of dioxin (PCDD/F) in soil is pg I-TEQ g^{-1} according to the National Implementation Plan for the Stockholm Convention (Republic of Kazakhstan 2009)[3], and this is lower than for some EU countries. All samples from playgrounds above 2 pg bio-TEQ g^{-1} can be considered elevated compared with this background level

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3.3 Other Contaminated Playgrounds

There have been a number of studies relating to similar contamination issues in other countries. These demonstrate that the soil from the playgrounds in Balkhash is much more heavily contaminated by heavy metals such as copper, lead, cadmium and arsenic than has been reported in studies by De Miguel (2007) (Madrid, Spain), Wong (1997) (Hong Kong, China), Diawara (2006) (Pueblo, Colorado, USA), Figueiredo (2011) (São Paulo City, Brazil) or Mostert (2012)[4] (Queensland, Australia). These comparative values are in Table 5.

The level of lead in soil at playgrounds in Balkhash is an order of magnitude higher than these levels.

TABLE 5: LEVELS OF HEAVY METALS IN SOIL AT PLAYGROUNDS IN OTHER STUDIES.

PG	Madrid 2002 & 2003	Madrid; Min - Max	Hong Kong	SD	Pueblo	São Paulo
Copper			16.14	4.73		
Lead	38 & 22	6.1–106	89.94	52.6	87.7	
Cadmium	0.19 & 0.4	0.05–0.50	0.94	0.31	2.53	
Arsenic	7.3 & 6.9	3.7–16	16.5	4.57	12.6	1.2–24
Mercury						

3 „Obtained figures for soil taken 1–3 km from the Balkhash industrial zone show less than 1 pg g^{-1}.“ (Republic of Kazakhstan 2009)

4 Note that Mostert highlighted paints from playground equipment as being a contributor to the contamination. In that case about 8.4 % of the heavy metal contamination on the playground. This is obviously a particularly important issue if lead paint has been used.

4. DISCUSSION

4.1 Potential sources of contamination in Kazakhstan

The main sources of atmospheric pollution in Kazakhstan are listed by the UNECE as the heat-and-power industry, ferrous and non-ferrous metallurgy, oil-and-gas industry together with road and rail transport.

The UNECE reported the Priority list of cities of the Republic of Kazakhstan ranked by level of atmospheric air pollution (UNECE, 2003); see Table 6.

Akchatau

Akchatau (or Aqshatau) is the location of the first major tungsten deposit discovered in Central Kazakhstan (Laznicka, 2010).

Balkhash

Among the largest enterprises, the Balkhash Mining-and-Metallurgical Plant is considered to be the largest atmospheric polluter and contributes about 20% of all pollution in the republic (UNECE 2003) in spite of this the city only ranked 16th on the UNECE priority list.

Wikipedia confirms[5] that emissions due to mining and metallurgical processes are a key factor affecting the ecology of the Ili-Balkhash basin and that these emissions are mainly associated with pollution from the Balkhash Mining and Metallurgy Plant operated by Kazakhmys.

Kazakhmys is a UK-registered copper mining company and the largest producer of copper in Kazakhstan. The Balkhash smelter is estimated to be the 22nd largest in the world (Schlesinger, 2011) and is one of only three plants in the world which still use the stationary Vanyukov submerged-tuyere furnaces developed in the former Soviet Union (Schlesinger, 2011).

In the early 1990s, production levels were reported to be 280–320 thousand tonnes per year, depositing 76 tonnes of copper, 68 tonnes of zinc and 66 tonnes of lead on the surface of the lake. Since then, emission almost doubled[6].

At the 2005 International Environmental Forum devoted to Lake Balkhash, Kazakhmys announced that by 2006 it would restructure its processes, thereby reducing emissions by 80–90 %.

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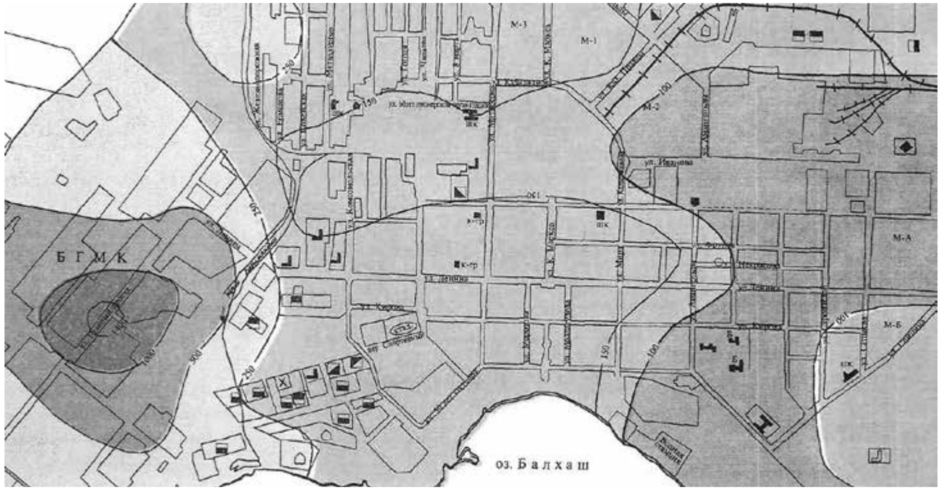
5 http://en.wikipedia.org/wiki/Lake_Balkhash

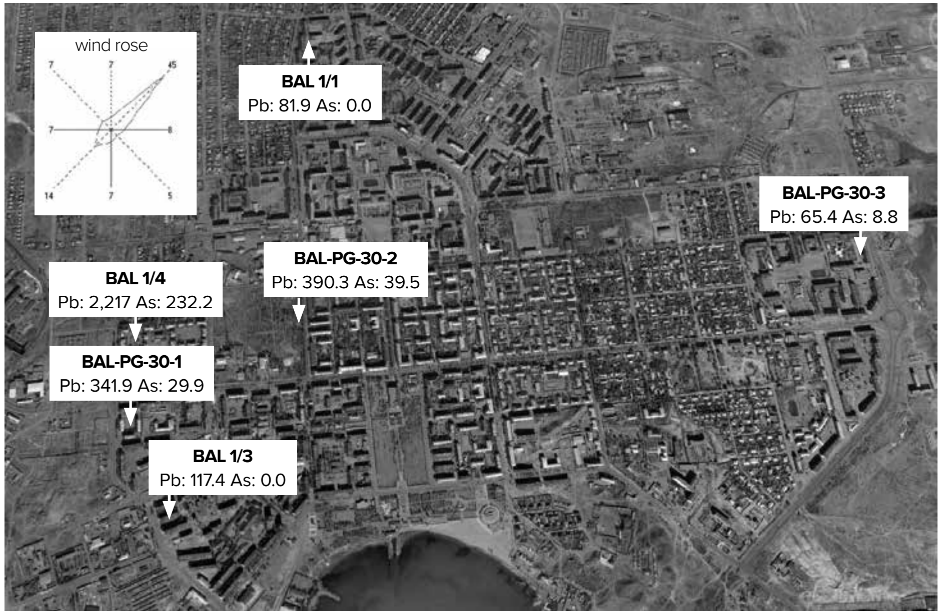
6 http://en.wikipedia.org/wiki/Lake_Balkhash

TABLE 6: PRIORITY LIST OF CITIES OF THE REPUBLIC OF KAZAKHSTAN RANKED BY LEVEL OF ATMOSPHERIC AIR POLLUTION.

City	API			Industry sectors having impact on air pollution
	2000	2001	2002	
1 Ust-Kamenogorsk	17.8	14.2	16.0	Non-ferrous metalurgy, energy
2 Almaty	9.9	13.1	11.7	Energy, urban transport
3 Glubokoe village	14.4	10.2	11.5	Non-ferrous metalurgy
4 Ridder	10.0	10.3	11.3	Non-ferrous metalurgy, energy
5 Aktobe	10.0	8.5	9.5	Ferrous metalurgy, Chemical industry
6 Shymkent	10.0	11.8	9.5	Non-ferrous metalurgy, chemical industry, Oil processing
7 Temirtau	6.9	7.8	8.8	Ferrous metalurgy, Chemical industry
8 Taraz	7.8	6.7	8.3	Chemical industry
9 Zhezkazgan	7.5	7.9	6.8	Non-ferrous metalurgy, energy
10 Karaganda	4.6	4.6	6.5	Energy, Coal mining, Urban transport
11 Aktau	4.6	4.4	4.8	Chemical industry
12 Kostanai	2.9	3.2	3.4	Energy
13 Petropavlovsk	6.8	5.1	3.4	Energy, Instrument-making industry
14 Astana	2.7	1.3	2.6	Energy, Urban transport
15 Semipalatinsk	4.0	3.3	2.6	Energy, Construction materials
16 Balkhash	3.3	2.2	2.4	Non-ferrous metalurgy, energy
17 Atyrau	2.5	1.8	2.0	Oil processing
18 Ekiastuz	1.7	1.4	1.9	Energy, Coal mining
19 Pavlodar	2.3	2.7	1.5	Oil processing, Energy
20 Uralsk	1.4	1.2	1.2	Energy
Average	6.56	6.09	6.24	



Picture 1: Map of overall soil contamination by heavy metals in Balkhash according research undertaken before 2005. Source Dyusembayeva, N. K. (2014) .



Picture 2: Map of the Balkhash city with marked samples from playgrounds and observed levels of lead (Pb) and arsenic (As) in mg kg^{-1}. Source of basic map Google Earth.

5. EXPOSURE AND HEALTH IMPACTS

Soil and dust ingestion can be important pathways of exposure to environmental agents, particularly for certain contaminants that tend to bind to soils (e.g., lead, dioxins, PCBs). Soil and dust can become contaminated as a result of direct or indirect discharges, atmospheric deposition of contaminants, runoff flow from contaminated areas, use of pesticides and fertilizers, and other processes.

Outdoor soil and dust may be tracked into indoor environments becoming a source of indoor dust. Ingestion of soil and dust is a potentially important route of exposure to environmental contaminants for children, because they may spend a significant amount of time playing on the floor indoors, on the ground outdoors, and have a tendency to place objects, including their fingers, in their mouths.

5.1 Pica and soil eating behaviour

Soil and dust that has adhered to the hands and objects can be transferred to the mouth and inadvertently ingested. For example, the main pathway for lead exposure in young children is ingestion of indoor surface dust, as a result of the hand-to-mouth behavior. Although some children ingest soil and dust unintentionally, others may engage in deliberative soil ingestion behaviors (i.e., soil pica). (Moya and Phillips, 2014)

Infants and children can have enhanced exposures to metals through the pathway of surface dust because (1) they crawl and play in close proximity to surface dust and (2) they often mouth their hands (e.g., finger sucking) and objects in their environment. This causes an intake of surface dust that is generally greater than that which is normally found in adults (Fairbrother 2007).

An obvious exposure route in playgrounds is from children inadvertently eating contaminated soil from their hands. Most children eat only relatively small quantities of soil or dust from hand to mouth behaviour but some groups of children face higher risks of exposure from this pathway.

This includes poorer children who face a number of challenges related to poisoning, including inadequate nutrition, which can lead to soil pica behaviour. This can also include higher rates of absorbtion of metals like due to iron deficiency anemia, and inadequate education and access to health care (Filippelli, 2010).

It is therefore important to consider soil ingestion and Pica (enhanced soil eating) behaviour as a possible pathway as this could easily be significant for children with access to contaminated materials.

USEPA outline the issues associated with soil eating in their Child Specific Exposure Factor Handbook (USEPA, 2008):

“The ingestion of soil and dust is a potential route of exposure to environmental chemicals. Children may ingest significant quantities of soil, due to their tendency to play on the floor indoors and on the ground outdoors and their tendency to mouth objects or their hands. Children may also ingest soil and dust through deliberate hand to mouth movements, or unintentionally by eating food that has dropped on the floor. Thus, understanding soil and dust ingestion patterns is an important part of estimating children's overall exposures to environmental chemicals."

USEPA recommend that for Pica levels of intakes are assumed to be 1 g/day.

Even these levels may not represent the highest exposures. Calabrese (1997) for example, reports that: "Several soil ingestion studies have indicated that some children ingest substantial amounts of soil on given days. Although the EPA has assumed that 95 % of children ingest 200 mg soil/day or less for exposure assessment purposes, some children have been observed to ingest up to 25–60 g soil during a single day".

Pica is not just a short-term exposure - over the first five years it is estimated that the average child affected by pica consumes about 8,000 g of soil although consumption is not equally spread over the period (Kimbrough, 1984).

Whilst Pica may be relatively uncommon USEPA cites Bruhn (Bruhn and Pangborn, 1971) who reported the incidence of pica for "dirt"[7] to be 18 percent in children.

A model-based prediction developed by (Calabrese, 1997) indicated that "the majority (62 %) of children will ingest >1 g soil on 1–2 days/year, while 42 % and 33 % of children were estimated to ingest >5 and >10 g soil on 1–2 days/year, respectively". It was concluded that these estimates were qualitatively significant "because they suggest that soil pica is not restricted to a very small percentage of the normal population of children, but may be expected to occur in a sizable proportion of children throughout

TABLE 7: RECOMMENDED VALUES FOR DAILY SOIL, DUST, AND SOIL + DUST INGESTION (mg/day) FROM EPA'S EXPOSURE FACTORS HANDBOOK: 2011 EDITION.

Age Group	Soil[8]				Dust[9]		Soil + Dust	
		High end						
	General Population Central Tendency[10]	General Population Upper Percentile[15]	Soil-Pica[16]	Geophagy[17]	General Population Central Tendency[11]	General Population Upper Percentile[12]	General Population Central Tendency[13]	General Population Upper Percentile[14]
6 weeks to <1 year	30				30		60	
1 to <6 years	50		1,000	50,000	60		100[18]	
3 to <6 years		200				100		200
6 to <21 years	50		1,000	50,000	60		100[18]	
Adult	20[19]			50,00	30		50	

7 "dirt" was not clearly defined however...
8 Includes soil and outdoor settled dust.
9 Includes indoor settled dust only.
10 Davis and Mirick (2006); Hogan et al. (1998); Davis et al. (1990); van Wijnen et al. (1990); Calabrese and Stanek (1995).
11 Hogan et al. (1998).
12 Özakaynak et al. (2011); rounded to one significant figure.
13 Özakaynak et al. (2011); Stanek and Calabrese (1995b); rounded to one significant figure.
14 Özakaynak et al. (2011); rounded to one significant figure.
15 Özakaynak et al. (2011); Stanek and Calabrese (1995b); rounded to one significant figure.
16 ATSDR (2001); Stanek et al. (1998); Calabrese et al. (1997b; 1997a; 1991; 1989); Calabrese and Stanek (1993); Barnes (1990); Wong (1988); Vermeer and Frate (1979).
17 Vermeer and Frate (1979).
18 Total soil and dust ingestion rate is 110mg/day; rounded to one significant figure it is 100mg/day.
19 Estimates of soil and dust were derived from soil + dust and assuming 45 % soil and 55% dust.

the course of the year". It was also concluded that "if soil pica is seen as an expected, although highly variable, activity in a normal population of young children, rather than an unusual activity in a small subset of the population, its implications for risk assessment become more significant."

A more recent review by Ozkaynak (2011) gave results for children 3 to <6 years old showed that mean and 95th percentile total ingestion of soil and dust values are 68 and 224 mg/day, respectively. Means from soil ingestion, hand-to-mouth dust ingestion, and object-to-mouth dust ingestion are 41 mg/day, 20 mg/day, and 7 mg/day, respectively. The levels used to reflect Pica may, however, significantly underestimate the real risk if there are children using the playgrounds with the more extreme forms of pica behaviour.

In summary, Moya (2014), in a recent and detailed meta-review of soil ingestion studies, comments that studies have reported soil ingestion rates for children ranging between 400 and 41,000 mg/day. We cannot, therefore, assume that the soil ingestion rates upon which existing standards are based are precautionary. Protection of the most exposed and vulnerable children needs significantly cleaner soil than has been required to date.

TABLE 8: HEALTH EFFECTS OBSERVED ACCORDING TO CONCENTRATION LEVELS OF CADMIUM IN SOILS AND RESIDENTS EXPOSED (KAH ET AL. 2012).

Study area	Urinary level of Cd in exposed population (µg g^{-1} creatinine)	Concentration in soil (mg kg^{-1})	Other concentrations	Type of effect observed	References
United Kingdom (Avonmouth)	0,2-0.3	n/a	n/a	Biomarkers of renal dysfunction (borderline significance)	Thomas et al. 2009
United Kingdom (Worcestershire)	0.3	7.6–78.7	n/a	None (blood/urine level similar to control)	Wood 1996
Germany	0.4; range: <0.1–4 (control: 0.51; range: <0.1–2.4)	13 (up to 49)	Up to 2.79 mg kg^{-1} in celery	None (similar blood/urine between exposed and control population of women 65-66 yr old)	Ewers et al. 1993
United Kingdom (Shipham)	0.7 (control: 0.6)	97 (2–360, garden soil)	5 up to 20 times above normal levels in vegetables	Small excesses of borderline significance for blood pressure, genitourinary disease, nephritis, cardiovascular disease. Any excess in mortality considered to be slight and of borderline significance	Strehlow and Barltrop 1988 Elliot et al. 2000
Sweden	0.7	n/a	n/a	Biomarkers of renal dysfunction	Jarup et al. 2000
Belgium	1.0 (control: 0.63) Nawrot et al., 2006	n/a 0.8–17 (garden soil)	n/a 0.1 to 4.0 mg kg^{-1} dry weight in vegetables	Biomarkers of renal dysfunction Fracture (post-menopausal women) Cancer (especially lung) Total and non-cardiovascular mortality	Jarup et al. 2000 Nawrot et al. 2006; 2008 Staessen et al. 1994; 1996; 1999; 2000
Japan (nonpolluted)	1.5-2.4	n/a	n/a	Biomarkers of renal dysfunction	Suwazono et al. 2000
Korea	2.9 (control: 1.5)	0.36 (control: 0.18)	0,049 mg kg^{-1} rice (control: 0.025)	None (biomarkers of renal/bone dysfunction)	Kim et al. 2008
Japan (Jinzu basin)	n/a	n/a	0.06–1.06 mg kg^{-1} rice (1971–1996)	Biomarkers of renal dysfunction Mortality	Mastuda et al. 2002 Watanabe et al. 2002

Study area	Urinary level of Cd in exposed population (µg g^{-1} creatinine)	Concentration in soil (mg kg^{-1})	Other concentrations	Type of effect observed	References
Japan (Kakehashi basin)	5.9 (0.3–57.5; 1981–82)	1 (paddy soil)	>0.4 mg kg^{-1} rice	Biomarkers of renal dysfunction Preterm delivery Mortality (due to kidney/urinary diseases and nephritis/ nephrosis)	Nishijo et al. 2002; 2004; 2006; Nakagawa et al. 2006
Japan (Nagasaki and Akita prefectures)	9.6 (2.0–50.8, 1982) 6.1 (0.3–53.8, 1992)	>1.0 (paddy soil)	>0.4 mg kg^{-1} rice 0.15 µg l^{-1} drinking water	Biomarkers of renal dysfunction Mortality (total and kidney/urinary diseases and nephritis/nephrosis; association between exposure and mortality weakening over time)	Arisawa et al. 2001; 2007 a; 2007 b
China (Dayu county)	11.27 (control: 3.03)	0.89–1.49	0.05 mg l^{-1} irrigation water	Biomarkers of renal dysfunction	Cai et al. 1990
China (Zhejiang)	11.18 (control: 1.83)	0.87 (control: 0.04)	2.4–3.7 mg kg^{-1} in rice (control: 0.072–0.05)	Biomarkers of renal dysfunction Low bone density, prevalence of fracture for >50 years old	Nordberg et al. 1997; Jin et al. 2002; Zhu et al. 2004; Chen et al. 2009; Wue et al. 2008; Liang et al. 2012
France	n/a. Significantly higher than control population	0.7–233	Blood concentration ≤0.52 and ≤0.86 µg l^{-1} in children and adults, respectively	No effect on levels of renal biomarkers	de Burbure et al. 2003
Jamaica	n/a	Maximum 931	Mean 0.4 mg kg^{-1} in vegetables (maximum 6.5 mg kg^{-1})	No clear evidence of cadmium-related human disorders	Barton et al. 2004; Lalor 2008

Note. As a reference, background concentrations in the United Kingdom for cadmium in soil are typically <1 mg kg^{-1}. n/a: No value is reported.

TABLE 9: THIS TABLE IS BASED ON DATA DERIVED FROM COMPARISONS OF THE CONCENTRATIONS OF TRACE METALS IN URBAN SOILS OF DIFFERENT CITIES IN CHINA (mg kg^{-1}). SOURCE: LUO ET AL. (2012).

Contents	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Range	6.86–32.8	0.13–6.9	3.55–58.9	17.8–197	16.2–1,226	0.12–0.77	4.08–910	26.7–110	69.1–301
Mean	15	0.88	25.4	76.8	99.2	0.35	99.6	61.3	133

6. RECOMMENDATIONS

The playgrounds in Balkhash, and especially around sample locations 1/2 and 1/4, are of particular concern due to the contamination by lead, copper, cadmium, zinc and arsenic.

Widespread contamination of playground soils ultimately requires a solution which breaks the pathway from the contamination to the child by removing surface soils from human contact. Remediation efforts for most of heavily contaminated sites have involved 'dig and dump' soil removal, disposal and replacement. This is normally an expensive option which requires suitable treatment or, more likely, landfill capacity and can be seen as simply shifting the problem elsewhere – albeit with reduced risks of immediate contamination.

Filippelli (2010) reported another approach, "which is much cheaper and appears to be as effective as soil removal", which is simply to cover the contaminated yard soils with about 15 cm of lead-free soil. This was tested by Howard Mielke in New Orleans using less contaminated soil from the nearby Mississippi levee (Mielke et al. 2006). This clean soil is simply graded over the old soil layer, hydroseeded (a slurry of seeds and moisture-retaining fill mixture sprayed onto the ground), and left to grow a lawn. This approach is far less expensive than soil removal and can "cap" the contaminated soils, removing them from contact by children. The result of initial work was a substantial reduction in the blood-lead levels of children living in the affected homes.

Whilst this may provide an affordable temporary solution there is significant uncertainty about the long-term appropriateness of such an approach for Balkhash because of the difficulty in maintaining a grass surface to bind the cover soil. Physical erosion in the playground, especially near heavily used equipment, together with the vulnerability of surface erosion by wind probably makes this unsuitable as a long-term solution in this case.

Furthermore Filippelli (2010) noted that "Mielke observed that over the course of several months after treatment, soil lead levels in the treated sites began increasing. This increase was due to the resuspension and deposition of soil dust from adjacent untreated areas that still had high soil lead concentrations". This indicates that diffuse soil lead is an important source of future contamination of adjacent land in urban areas and also indicates that a comprehensive area wide treatment approach is required to provide a long-term elimination of exposure. This may not be a realistic option to the problems currently faced in Kazakhstan and it is therefore important that long-term monitoring of the playgrounds is undertaken to ensure that whatever interim remediation is used future re-contamination is measured and appropriate action can then be taken before levels reach those which are likely to be harmful to human health.

No surface wipes of the playground equipment were taken. Also there was no measurement of the levels of contamination in the air as part of this project (although some data is available for POPs). It is likely, however, that atmospheric deposition from the adjacent copper smelter is continuing and is adding to the contamination burden.

One obvious approach is to clean the play equipment and to seal the ground by paving it or applying tarmac together with appropriate impact absorbing materials for safety.

The results from a recent study (Taylor et al 2015) are close to a smelter in Australia where a similar approach was adopted are clear. The authors report "Although washing reduces metal loading on playgrounds and hands after play, it does not resolve the problem of contemporary emissions and their deposition and accumulation on playground surfaces. Until the smelter reduces its emissions to the atmosphere...... washing of playgrounds can provide only limited protection from toxic dust deposition exposures". The authors specifically note that "Other locations experiencing ongoing atmospheric emissions and subsequent depositions are likely to face similar limitations from washing regimes that are designed to limit the hazard from metal environmental exposures".

Ultimately, therefore, the only long-term solution to reduce harm to exposed children is to address the original source of the contamination and to reduce the emissions from the Balkhash Mining and Metallurgy Plant.

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Persistent Organic Pollutants in Ekibastuz, Blalkhash and Temirtau

Final report on the results of environmental sampling conducted in Kazakhstan in 2013 and 2014 as a part of the project 'Empowering the civil society in Kazakhstan in improvement of chemical safety'

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Brno, April 2015

SUMMARY

The data presented and discussed in this report were obtained during two field visits and environmental sampling campaigns conducted in Kazakhstan in July and August 2013 and July, August and September 2014. Both sampling campaigns represent an important part of a joint project of the Czech not-for profit organization Arnika Association and two Kazakhstani partners, the Karaganda Regional Ecological Museum (EcoMuseum) and the Center for Introduction of New Environmentally Safe Technologies (CINEST). The main goal of the project is empowering of the civil society in Kazakhstan and the improvement of chemical safety.

Kazakhstan is a country struggling with very serious problems related to industrial chemical pollution and the use of hazardous materials by local communities. Contamination with polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) as well as mercury is of particular interest. There are a number of hot spots in Kazakhstan that are highly contaminated by these pollutants. The contamination is in particular a serious problem for people living around contaminated sites. Also, the access to environmental information is, in general, very low in Kazakhstan and the legislative framework for involvement of civil society in decision making is inadequate.

The field visit in July and August 2013 and July and August 2014 was conducted by members of the Arnika Association, independent scientists and members of EcoMuseum and CINEST, Karaganda. Sampling of sediments, soil and other solid matrices was conducted at several sites suspected to be polluted by persistent organic pollutants. In this report, results from sampling at a well-known PCB hot spot (Ekibastuz electrical power substation) and two cities and their surroundings affected by metallurgical industry (Balkhash and Temirtau) are presented and discussed.

It has to be taken into account, that the extent of the sampling campaign was limited by financial, temporal and personal resources. The comparison of reported pollutant concentrations with Russian, Soviet, Kazakhstani, Tatarstani and international legal limits was possible only to a limited extent, as some of these norms are outdated or in other ways less relevant. Therefore, in order to be able to evaluate the results of such field studies properly, a normative legal basis in the area of POP management including legal POP limits in Kazakhstan has to be developed together with methodological guidelines. Samples from the investigated areas also have to be compared to relevant background levels, which have to be obtained by well-designed sampling.

The actual spatial extension of the area seriously contaminated by PCBs in the Ekibastuz electrical power substation should be determined in a dedicated study and then disposed of in such a way that the PCB content is destroyed or irreversibly transformed or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option. Attention should be also paid to the AMT smelter waste dump in Temirtau and BGMK tailing pond in Balkhash as some samples taken there exhibited considerable PCB levels. A more thorough examination of the sites should be conducted in order to exclude PCB outflow spreading into the surrounding area. Spatial gradient sampling conducted at Temirtau children‘s playgrounds does not suggest PCDD/Fs pollution dispersion by wind from the AMT mill. Egg sampling in the Balkhash and Ekibastuz residential areas revealed a high PCDD/Fs contamination of eggs in some samples. However, the source of PCDD/Fs contamination in eggs from free ranging hens is not easy to interpret. The lifetime exposure, and where appropriate, the acute exposure of consumers to PCDD/Fs and DL PCBs especially via eggs in the residential areas, should be evaluated and the consumers informed about the results. Also, various possible sources for PCDD/Fs food contamination including waste and biomass burning should be explained to these residents.

1. INTRODUCTION

The data presented and discussed in this report were obtained during two field visits and environmental sampling campaigns conducted in Kazakhstan in July and August 2013 and July, August and September 2014. Both sampling campaigns represent an important part of the project „Empowering the civil society in Kazakhstan in improvement of chemical safety“. This is a joint project of the Czech not-for profit organization Arnika Association and two Kazakhstani partners, the Karaganda Regional Ecological Museum (EcoMuseum) and the Center for Introduction of New Environmentally Safe Technologies (CINEST). The main goal of the project is to reduce the level of poverty in Kazakhstan (mainly in poor local communities) by focusing on its environmental and chemical safety factors. Specific project objectives comprise (a) the strengthening of cooperation and building of capacities of environmental civil society organizations to support their involvement in decision making, (b) increasing public access to information and raising awareness on chemical safety issues and (c) initiating legislative changes related to chemical safety and developing replicable model examples. The project also aims to help Kazakhstan to implement the Stockholm Convention on Persistent Organic Pollutants and the UNECE Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters usually known as the Aarhus Convention.

The Stockholm Convention on Persistent Organic Pollutants (POPs) was ratified by the Republic of Kazakhstan on May 23, 2001. In accordance with the main provisions of the SC, each country that is a party to the Convention prohibits and/or takes legal and administrative actions required for the elimination and/or restriction of production and use of chemicals listed in Annexes A and B to the Convention, as well as on reduction or elimination of POPs releases resulting from intended or unintended production, as well as releases related to stocks and wastes containing POPs. The SC regulates the following pesticides: chlordecone, α-hexachlorocyclohexane, β-hexachlorocyclohexane, lindane (γ-hexachlorocyclohexane), pentachlorobenzene, DDT, aldrin, chlordane, dieldrin, endosulfan, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene. Further, it regulates these industrial chemicals: polychlorinated biphenyls, hexachlorobenzene, hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, pentachlorobenzene, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether and pentabromodiphenyl ether. It also regulates unintentional by-products: polychlorinated dibenzo-p-furans, polychlorinated dibenzo-p-dioxins, α-hexachlorocyclohexane, β-hexachlorocyclohexane, pentachlorobenzene, hexachlorobenzene and polychlorinated biphenyls (SC, 2014).

The main sources of contamination by POPs in Kazakhstan are obsolete pesticides and PCBs, industrial technologies resulting in the unintentional release of POPs and POPs containing equipment (Republic of Kazakhstan, 2009). Kazakhstan is a country struggling with very serious problems related to industrial chemical pollution and to the use of hazardous materials by local communities. This is a problem common to the most of post-Soviet countries.

Contamination with polychlorinated biphenyls (PCBs) is of special interest. There are a number of hot spots in Kazakhstan that are highly contaminated by PCBs, such as the Ust-Kamenogorsk storage pond, Ust-Kamenogorsk capacitor plant and Ablaketka village, Ekibastuz power sub-station, JSC "Pavlodar chemical plant" or Daryal-U former military base. There are 116 pure PCB transformers, 50 000 PCB capacitors and 225 000 tons of waste highly contaminated with PCBs in Kazakhstan (NIP, 2009). Significant problems with mercury and dioxin pollution and radioactive contamination were also recorded. The contamination is in particular a serious problem for people living around contaminated sites. However, due to the persistent and "mobile" character of these substances, pollution can also be transported over long distances and have a negative impact on areas very distant from pollution sources.

The UNECE Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters (Aarhus Convention) was ratified by the Republic of Kazakhstan on January 11, 2001. In order to contribute to the protection of the right of every person of present and future generations to live in an environment adequate to his or her health and well-being, each Party shall guarantee the rights of access to information, public participation in decision-making, and access to justice in environmental matters in accordance with the provisions of this Convention (AC, 1998). Unfortunately, there are serious problems of implementation of the Aarhus Convention in Kazakhstan. The access to environmental information is in general very low and the legislative framework for involvement of civil society in decision making is inadequate.

Although there were 8 sites contaminated with PCBs identified in Kazakhstan (Republic of Kazakhstan, 2009) and other sites contaminated with heavy metals, only some of them were chosen for investigation due to limited temporal, personal and financial resources. The field visit in Kazakhstan in July and August, 2013 and July and August 2014 was conducted by the following persons:

Jindřich Petrlík – Arnika Association, coordinator of survey
Viktorie Lupačová - Arnika Association, survey coordinator assistant
Jan Nezhyba – Arnika Association, he took part in certified Forsapi training courses on water, sediment and waste sampling
Matěj Man – Arnika Association, student of biology at the Charles University in Prague
Martin Skalský – Arnika Association, coordinator of the project in Kazakhstan
Martin Bystrianský – postgraduate student at the University of Chemistry and Technology, Prague
Marek Šír – postgraduate student aat the University of Chemistry and Technology, Prague
Dmitry Kalmykov – EcoMuseum Karaganda
Alena Pankova – CINEST Karaganda
Dana Yermolyonok – CINEST Karaganda
Irina Kolchina – EcoMuseum Karaganda
Ondřej Petrlík – photographer

The survey in Kazakhstan was conducted in close cooperation with local partners, EcoMuseum and CINEST in the Karaganda region, which also conducted additional egg sampling of free range chicken eggs in September 2014.

2. SAMPLING CAMPAIGN

The majority of sampling was conducted in July 20–21, 2013 and August 18 – 23, 2013. The weather was warm (22–30 °C), with a clear or partly covered sky, weak to moderate wind and dry. The trip in July 2013 served for inspection of the Balkhash city and lake and pilot samples were taken, too. The results of the analyses served for selecting additional sampling sites. When choosing sampling sites, information from previous studies and the Kazakhstani NIP were used as well. An important source of information was the hot-spot profiles elaborated by Dmitry Kalmykov (EkoMuseum Karaganda) and Dana Yermolyonok (CINEST). The sampling plan was designed in cooperation with Marek Šír, Martin Bystrianský and Jan Nezhyba. A second sampling campaign followed in July, August and September 2014 and was focused on obtaining additional samples as suggested by the analysis and preliminary interpretation of the samples taken in 2013.

2.1 Sampling sites

A detailed spatial and interactive depiction of sampling sites and spots is given in a special CD annex of this report.

2.1.1 Ekibastuz electrical power substation

The Ekibastuz electrical power substation was constructed for modifying alternating current (AC) to direct current (DC) using 15 000 capacitors placed in two outdoor areas. After the collapse of the Soviet Union the substation was left without an owner or guard. During the economic crisis, local residents illegally dismantled capacitors in order to remove copper scrap and this resulted in PCB leakage to the soil. During emergency clean-up works in 2002 the capacitors were dismantled and "sealed" with foam by the new owner of the substation. Part of the PCB contaminated soil was removed and packed in bags. Capacitors and contaminated soil were removed and placed in underground storage at the former Semipalatinsk nuclear testing site (technical test area Opytnoe Pole). The soil under the docks on which the capacitors were installed was not removed. PCB contamination under the dock poles was reported to reach 26 200 mg kg^{-1} (Ishankulov, 2008; Republic of Kazakhstan, 2009).

The volume of contaminated soil in the Ekibastuz electrical power substation area was calculated in a project dealing with localization and removal of PCBs and obsolete pesticides that was conducted by SNC-Lavalin International Inc. (SLII, 2011). It is compared to the amount of contaminated soils calculated in a previous study conducted by FCG International Inc. in 2010 (Tab. 1). According to the report of FCG International Incorporated from 2010 (which unfortunately is not available to the author of this study and only cited by EcoMuseum and CINEST Karaganda staff), there are four areas of contamination on the Ekibastuz site. Two of those are in the locations of poles for PCB-capacitors (65,000 m^2 and 62,000 m^2). The third area (about 45,000 m^2) is 200 m to the north, outside of the substation. The fourth area (about 90,000 m^2) is 700 meters west of the main area. Results of the SNC-Lavalin International Inc. study do not confirm a significant contamination of soils as stated by FCG.

TABLE 1 CALCULATED AREA AND VOLUME OF THE CONTAMINATED SOIL IN THE EKIBASTUZ ELECTRICAL POWER SUBSTATION (SLII, 2011)

	Calculated data for the entire area		Data reported by FCG, 2010 Volume (m^3)	
	Area (m^2)	Volume (m^3)	Min	Max
Hazardous waste	3,700	2,800	6,000	24,000
Heavily contaminated soil	7,000	5,200	60,000	180,000
Weakly contaminated soil	16,000	12,500	36,000	110,000

Close to the Ekibastuz substation, a dacha area with at least 5,000 inhabitants is located. Local agricultural products are also sold in the Ekibastuz city and consumed by approximately 10,000 – 30,000 people. Therefore, the dacha owners as well as the Ekibastuz city population are suspected to be threatened by the pollution from the substation. Further, the Irtysh-Karaganda canal providing drinking water is located close to the substation.

Sampling of soil and solid material was conducted in the power substation area as well as in its surroundings. Sediment was sampled in nearby lakes. Biota samples consisted of eggs from freely roaming hens from nearby households. Further, fish samples were taken by a local fisherman from the middle of the Zhyngyldy lake. Tables in section "General introduction" of this publication (Toxic Hot Spots in Kazakhstan) provide a detailed description of samples (sampling date and time, matrix, sampling spot description and coordinates, type of sample and eventual comments.

2.1.2 Balkhash

The Balkhash city (76,000 inhabitants) and its surroundings (30,000–50,000 inhabitants) is dominated by mining and nonferrous metallurgical enterprises. The major enterprise is Balkhashtsvetmet (the earlier Russian Balkhash Gorno-Metallurgical Combinat, BGMK). Further, the Balkhash Non-Ferrous Metals Processing Plant (Russian Zavod Obrabotki Tsvetnych Metallov, ZOCM) is part of the Kazakhmys Corporation LLC. Chemicals unintentionally produced in these industrial processes, that are subject to Annex C of the SC (PCDD/Fs, PCBs and HCB) are reported to be one of major subjects of health concerns in the Balkhash city. The annual release of PCDD/Fs from production of ferrous and nonferrous metals in the whole of Kazakhstan is estimated to be 3.324 gTE $year^{-1}$ (Republic of Kazakhstan, 2009.

The Bashkortastan Republican Scientific Ecological Center carried out the first sampling campaign focused on PCDD/Fs in Kazakhstan in 2005. The PCDD/Fs concentration in indoor air sampled in the BGMK copper smelting shop was 51.33 pg m^{-3} (4.08 pg WHO-TEQ m^{-3}) and in dust (wall scrapes) 5,377 pg g^{-1} (263 pg WHO-TEQ g^{-1}). In soils sampled within 1-3 km distance from the industrial zone the PCDD/Fs content was less than 1 pg g^{-1}. According to the NIP of Kazakhstan, this indicates the absence of active transport of pollutants from the industrial chimneys. However, PCDD/Fs concentrations of more than 6 pg g^{-1} in the Balkhash city Central Park soils indicate the presence of local combustion sources, e.g. biomass burning (Republic of Kazakhstan, 2009).

The NIP of Kazakhstan discusses the possible threat of POPs on human health. Balkhash city was selected as one of two model areas. In 1999-2003 the birth rate of infants with defects was 2.7 times higher in Balkhash compared to whole Republic of Kazakhstan. The level of androgenic birth hormonal development defects in Balkhash

TABLE 2 ABUNDANCE OF HORMONAL TYPES OF CANCERS (PER 100 THOUSAND FEMALES AND MALES), COMPARISON OF THE REPUBLIC OF KAZAKHSTAN AND BALKHASH CITY (ISHANKULOV, 2008)

	Tumours of female genital sphere	Breast cancer	Prostate cancer	Urinary bladder cancer	Thyroid carcinoma
Republic of Kazakhstan	344.9	170.1	35.3	19.1	14.0
Balkhash city	431.5	205.7	31.8	33.6	30.9

(14.4 %) is twice as high compared to whole Republic of Kazakhstan (6.5 %) (Republic of Kazakhstan, 2009). Tab. 2 compares the abundance of hormonal types of cancer between the whole Republic of Kazakhstan and Balkhash city (Ishankulov, 2008).

Sampling of soil and fly ash was conducted in the metallurgical factory surroundings. Sediment was sampled predominantly on lake shores. Biota samples consisted of eggs from hens from households located near metallurgical enterprises and an electrical power station. Further, fish samples were taken by a local fisherman from the Balkhash lake. Tables in section "General introduction" of this publication (Toxic Hot Spots in Kazakhstan) provide a detailed description of samples (sampling date and time, matrix, sampling spot description and coordinates, type of sample and eventual comments).

2.1.3 Temirtau

Temirtau city (170,000 inhabitants) and its surroundings (100,000 – 500,000 inhabitants) are dominated by industries including a coal-fired power station, chemical production plants, foundries, forges and large steelworks belonging to the ArcelorMittal group. The steel mill Arcelor Mittal Temirtau (AMT) is located a distance of 500 m to the nearest houses. According to the Kazakhstani NIP from 2009, there were 105 transformers filled with Sovtol (commercial PCB mixture marketed in the former USSR) and 1024 capacitors containing PCBs in use in AMT. The situation was addressed under the UNDP project „Development and implementation of the comprehensive plan on the management of PCBs" in 2014, when the Sovtol liquid was relocated to France. However, EcoMuseum and CINEST Karaganda report some PCB containing electrical equipment to still be in use in AMT.

Industries unintentionally producing PCDD/Fs include coke and foundry productions, both taking place in AMT as the only such enterprise in Kazakhstan. The processes of unloading and coke extinction, when PCDD/Fs can be released, are taking place in open air without a gas trapping and cleaning device. Formation of PCDD/Fs is also possible during limestone burning in shaft kilns. In Kazakhstan, lime is produced in the Temirtau Chemical and Metallurgical Plant, Ltd (Republic of Kazakhstan, 2009). The Bashkortastan Republican Scientific Ecological Center carried out the first sampling campaign focused on PCDD/Fs in Kazakhstan in 2005. The PCDD/Fs concentration in indoor air sampled at the AMT sinter machine no. 5 was 42.64 pg m^{-3} (3.77 pg WHO-TEQ m^{-3}), in the dust (wall scrapes) 5,419.7 pg g^{-1} (607.7 pg WHO-TEQ g^{-1}). According to the Kazakhstani NIP (2009), wastes produced by these industries may be a source of environmental pollution.

Sampling of soil was conducted at several children's and pupils playgrounds in the Temirtau city in different distances from the AMT and other industries. Sediment and slag was sampled in industry (AMT, Karbid chemical factory) waste ponds. Tables in section "General introduction" of this publication (Toxic Hot Spots in Kazakhstan) provide a detailed description of samples (sampling date and time, matrix, sampling spot description and coordinates, type of sample and eventual comments).

2.2 Sampling and analytical methods

For sampling description please see "General introduction" section of this publication (Toxic Hot Spots in Kazakhstan).

Samples determined for the analysis of PCDD/Fs and dioxin-like PCBs using the DR CALUX method were sent to a Dutch certified laboratory (BioDetection Systems B.V., Amsterdam). The method used is extraction with organic solvents; the extracts are cleaned on an acid silica column. The cleaned extracts are dissolved in DMSO (dimethyl sulfoxide). The DR CALUX activity is determined (24h exposure) and benchmarked against 2,3,7,8-TCDD. For the method DR CALUX and the parameter PCDD/Fs and DL PCBs (total BEQ) the used method is to shake extraction with organic solvents (hexane); the extracts are cleaned on an acid silica column. The cleaned extracts are dissolved in DMSO. The DR CALUX activity is determined (24h exposure). The response of the sample is corrected for the background and subsequently corrected for the apparent bioassay recovery with a reference sample at the level of interest. The evaluation was done on the maximum level for PCDD/Fs, from which a cut off value has been established to determine if a sample is compliant or suspect. As a maximum level the level of the matrix is used. After the evaluation an estimation is given of the sample in the form of a BEQ outcome. All DR CALUX analysis results comply with EU requirements as indicated in the Commission Regulation (EC) No 252/2012 (laying down the sampling methods and the methods of analysis for the official control of PCDD/Fs and the determination of DL PCBs in foodstuffs).

Soil, sediment and other solid material samples were analyzed for the content of OCPs and PCBs in the University of Chemistry and Technology, Prague. 2.5 g of the sample were sonic extracted with hexane for 20 minutes. The extract was analyzed by gas chromatography coupled with an electron capture detector.

Sediment samples were analyzed for HCB content in a Czech certified laboratory (University of Chemistry and Technology, Department of Food Chemistry and Analysis). The analytes were extracted by dichloromethane in a Soxhlet apparatus. The extracts were concentrated on a vacuum rotary evaporator, converted into a cyclohexane:ethylacetate (1:1) mixture and cleaned by means of gel permeation chromatography (GPC). The extract was again concentrated and then dissolved in isooctane. The identification and quantification of the analyte was conducted by gas chromatography coupled with mass spectrometry detection.

Egg and fish samples were analyzed on the content of non-dioxin-like PCBs and OCPs in a Czech certified laboratory (University of Chemistry and Technology, Department of Food Chemistry and Analysis). The analytes were extracted by a mixture of organic solvents hexane:dichloromethane (1:1). The extracts were cleaned by means of gel permeation chromatography (GPC). The identification and quantification of the analyte was conducted by gas chromatography coupled with tandem mass spectrometry detection in electron ionization mode.

Selected samples were analyzed for content of individual PCDD/Fs and an extended list of PCB congeners by HRGC-HRMS at the accredited laboratory of the State Veterinary Institute in Prague, Czech Republic.

3. RESULTS

The results of chemical analyses on non-DL PCB congeners, selected OCPs and PCDD/Fs + DL PCBs (CALUX bioassay results) are presented in tables 3, 4, 6, 7 and 9. A few selected samples were also analyzed on the content of individual PCDD/Fs and an extended list of PCB congeners by HRGC-HRMS (Tab. 5 and 8).

3.1 Ekibastuz

TABLE 3 RESULTS OF CHEMICAL ANALYSES FOR THE EKIBASTUZ SITE.

< LOD: analyte concentration was below limit of detection. NA: not analyzed. PCBs and OCPs are given in ng g^{-1}. PCDD/Fs and DL PCBs for non-food samples are given in pg PCDD/Fs DL PCB TEQ g^{-1} dry weight. Results for egg samples are presented in pg BEQ g^{-1} fat, for fish samples in pg BEQ g^{-1} product. All egg samples had a content of fat higher than 10%.

Sample code	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	Total measured PCBs	ΣPCBs*
EKI 2/1	0.21	2.51	0.26	< LOD	< LOD	< LOD	< LOD	3.0	14.9
EKI 2/2	41.10	71.07	39.06	< LOD	14.78	10.01	11.35	187.4	936.9
EKI 2/3	0.30	5.89	0.02	< LOD	< LOD	< LOD	< LOD	6.2	31.0
EKI 2/4	0.13	1.88	0.06	< LOD	< LOD	< LOD	< LOD	2.1	10.3
EKI 2/5	0.31	4.13	0.28	< LOD	< LOD	< LOD	< LOD	4.7	23.6
EKI 2/6	0.25	2.93	0.07	< LOD	< LOD	< LOD	< LOD	3.2	16.2
EKI 2/7	0.51	3.54	0.15	< LOD	< LOD	< LOD	< LOD	4.2	21.0

Sample code	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	Total measured PCBs	ΣPCBs*
EKI 2/8	2,310	894.84	148.61	70.15	14.92	16.62	5.63	3,461	16,953
EKI 2/9	412.09	115.79	17.17	< LOD	5.96	0.80	0.52	552.3	2,761
EKI 2/10	4,714	2,654	751.23	534.59	105.11	130.73	38.93	8930	41,974
EKI 2/11	27.91	28.13	11.36	< LOD	7.90	1.99	1.54	78.8	394.2
EKI 2/12	139,815	39,387	6,377	3,708	561.52	655.21	162.97	190,668	934,779
EKI 2/13	127,330	28,353	3,436	1,836	248.37	259.63	71.71	161,537	798,502
EKI 2/14	1.04	6.60	1.96	< LOD	< LOD	< LOD	< LOD	9.6	48.0
EKI 2/15	1.07	4.70	0.08	< LOD	< LOD	< LOD	< LOD	5.9	29.3
EKI 14-1 egg + EKI-27-egg	0.48	< LOD	< LOD	0.52	0.82	0.85	0.70	3.37	2.85
EKI 14-2 egg	0.49	< LOD	0.05	0.91	0.87	0.90	0.23	3.45	2.34
EKI 14-3 egg	0.33	< LOD	< LOD	0.44	0.42	0.45	0.19	1.83	1.39
EKI GR 1/II	0.05	2.29	0.36	< LOD	< LOD	< LOD	< LOD	2.7	13.3
EKI GR 2/II	0.09	0.53	0.19	< LOD	< LOD	< LOD	< LOD	0.7	3.6
EKI GR 3/II	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
EKI 1/S1	0.15	4.12	0.26	< LOD	< LOD	< LOD	< LOD	4.52	22.6
EKI 1/S2	27.91	28.13	11.36	< LOD	7.9	1.99	1.54	78.83	394.2
EKI 1/S3	0.14	0.83	0.30	< LOD	< LOD	< LOD	< LOD	1.28	6.38
EKI SED 4/II	0.13	0.74	0.26	< LOD	< LOD	< LOD	< LOD	1.1	5.7
EKI SED 5/II	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PS 2/II	0.19	13.99	0.30	< LOD	< LOD	< LOD	< LOD	14.5	72.3
PS 2.1/II	293.73	228.52	21.22	< LOD	7.54	2.37	2.15	555.5	2777
S 1/II	300.90	80.24	11.89	< LOD	< LOD	< LOD	< LOD	92.1	460.6
S 1.1/II	20,871	5177	612.40	261.55	38.83	46.61	12.51	27,021	133,797
S 2/II	0.30	3.07	3.59	< LOD	2.36	1.51	1.62	12.5	62.3

Sample code	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	Total measured PCBs	ΣPCBs*
S 2.1/II	0.27	7.32	< LOD	< LOD	< LOD	< LOD	< LOD	7.6	38.0
S 2.2/II	0.17	8.21	5.16	< LOD	2.70	2.57	2.94	21.7	108.7
S 3/II	0.18	4.37	0.63	< LOD	< LOD	< LOD	< LOD	5.2	25.9
S 3.1/II	1,532	508.59	97.31	< LOD	< LOD	< LOD	< LOD	2138	10,691

Samples EGG 1, EGG 2 EKI FISH 1/1, and EKI FISH 1/2 were not analyzed for PCB congeners.
*soils, sediments: recalculated for the sum of all PCB congeners by multiplying the sum of six selected PCB congeners (28, 52, 101, 138, 153, 180) with 5 according to the recommendations in the Czech norm ČSN EN 12766-2 and Czech order 384/2001 Sb.
*fish, eggs and milk: sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180

Sample code	α-HCH	β-HCH	γ-HCH	δ-HCH	HCB	PCDD/Fs + DL PCBs (CALUX)
EKI 2/5	NA	NA	NA	NA	NA	2.2
EKI 2/8	NA	NA	NA	NA	NA	108
EKI 2/9	NA	NA	NA	NA	NA	64
EGG 1	NA	NA	NA	NA	NA	6.4!
EGG 2	NA	NA	NA	NA	NA	4.8!
EKI 14-1 egg + EKI-27-egg	0.07	1.30	< LOD	NA	0.67	NA
EKI 14-2 egg	0.16	0.94	0.45	NA	0.15	NA
EKI 14-3 egg	0.75	3.33	0.41	NA	0.21	3.8!
EKI 1/S1	< LOD	< LOD	< LOD	614.2	< LOD	NA
EKI 1/S2	< LOD	108.1	< LOD	844.0	< LOD	NA
EKI 1/S3	< LOD	< LOD	< LOD	< LOD	< LOD	NA
EKI SED 5/II	NA	NA	NA	NA	NA	2.1
S 2/II	NA	NA	NA	NA	NA	2.1
S 2.1/II	NA	NA	NA	NA	NA	2.7
S 2.2/II	NA	NA	NA	NA	NA	10
S 3.1/II	< LOD	< LOD	< LOD	< LOD	< LOD	NA

Sample code	α-HCH	β-HCH	γ-HCH	δ-HCH	HCB	PCDD/Fs + DL PCBs (CALUX)
EKI FISH 1/1+	NA	NA	NA	NA	NA	(0.08)**
EKI FISH 1/2++	NA	NA	NA	NA	NA	0.12

Following samples were not analyzed for OCPs or PCDD/Fs + dl PCBs: EKI 2/1, EKI 2/2, EKI 2/3, EKI 2/4, EKI 2/6, EKI 2/7, EKI 2/9, EKI 2/10, EKI 2/11, EKI 2/12, EKI 2/13, EKI 2/14, EKI 2/15, EKI GR 1/II, EKI GR 2/II, EKI GR 3/II, EKI SED 4/II, PS 2/II, PS 2.1/II, S 1/II, S 1.1/II, and S 3/II
**result below LOQ, estimate given in parentheses
+fat content 0.22 %
++fat content 0.32 %
!suspected to be non-compliant

TABLE 4 RESULTS FOR CHEMICAL ANALYSIS OF SELECTED EGGS FROM EKIBASTUZ FOR CONTENT OF DDTs GIVEN IN ng g^{-1} SAMPLE.

Sample code	o,p´-DDE	p,p´-DDE	o,p´-DDD	p,p´-DDD	o,p-DDT	p,p´-DDT
EKI 14-1 egg + EKI-27-egg	< LOD	1.01	< LOD	< LOD	0.10	0.69
EKI 14-2 egg	< LOD	7.34	0.06	0.39	1.35	10.6
EKI 14-3 egg	< LOD	8.02	< LOD	0.15	1.00	7.60

TABLE 5 PCDD/Fs AND DL PCBs CONGENER SPECIFIC ANALYSIS OF SELECTED EKIBASTUZ SAMPLES GIVEN IN pg g^{-1} FOR ONE SOIL AND pg g^{-1} FAT FOR TWO EGG SAMPLES.

Uncertainties are obtained by multiplying the measurement standard uncertainty with the amplification coefficient k=2. All egg samples had a content of fat higher than 10%.

Sample code	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF
EKI 2/8	<0.061	<0.074	<0.079	<0.066	<0.059	0.653 ±40 %	<4.52	8.88 ±40 %	0.529 ±40 %	1.89 ±40 %
EKI 14-1 egg + EKI-27-egg	0.237 ±40 %	1.14 ±40 %	0.886 ±40 %	3.27 ±40 %	0.859 ±40 %	3.4 ±40 %	2.88 ±40 %	2.56 ±40 %	3.21 ±40 %	6.87 ±40 %
EKI 14-2 egg	0.292 ±40 %	0.618 ±40 %	<0.306	0.901 ±40 %	0.181 ±40 %	0.816 ±40 %	4.54 ±40 %	1.89 ±40 %	0.558 ±40 %	0.696 ±40 %

Sample code	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	WHO-PCDD/F-TEQ
EKI 2/8	0.178 ±40 %	0.093 ±40 %	<0.057	<0.068	<0.078	<0.064	<0.183	1.68 ±40 %
EKI 14-1 egg + EKI-27-egg	4.32 ±40 %	3.2 ±40 %	<0.127	6.09 ±40 %	3.25 ±40 %	<0.125	<0.758	5.73±30 %
EKI 14-2 egg	0.743 ±40 %	<0.501	<0.127	<0.395	<0.234	<0.125	0.786 ±40 %	1.65±30 %

Sample code	PCB 81	PCB 77	PCB 123	PCB 118	PCB 114	PCB 105	PCB 126	PCB 167	PCB 156
EKI 2/8	2840 ±30 %	58800 ±30 %	1170 ±30%	47600 ±30 %	2790 ±30 %	33200 ±30 %	192 ±30 %	266 ±30 %	582 ±30 %
EKI 14-1 egg + EKI-27-egg	21.8±30 %	144±30 %	71±30%	4490±30 %	147±30 %	2010±30 %	59.3±30 %	310±30 %	663±30 %
EKI 14-2 egg	27.9±30 %	481±30 %	132±30%	7110±30 %	264±30 %	3380±30 %	24.2±30 %	338±30 %	743±30 %

Sample code	PCB 157	PCB 169	PCB 189	WHO-PCDD/F-PCB-TEQ
EKI 2/8	120 ±30 %	0.874 ±30 %	53.7 ±30 %	30.2 ±35 %
EKI 14-1 egg + EKI-27-egg	155±30 %	8.68±30 %	81±30 %	12.2±30 %
EKI 14-2 egg	186±30 %	1.64±30 %	34.6±30 %	4.55±30 %

3.2 Balkhash

TABLE 6 RESULTS OF CHEMICAL ANALYSES FOR THE BALKHASH CITY AND LAKE.

< LOD: analyte concentration was below limit of detection. NA: not analyzed. PCBs and OCPs are given in ng g^{-1}. PCDD/Fs and DL PCBs for non-food samples are given in pg PCDD/Fs-DL PCB TEQ g^{-1} dry weight. Results for egg samples are presented in pg BEQ g^{-1} fat, for fish samples in pg BEQ g^{-1} product. All egg samples had a content of fat higher than 10 % except BAL-EGG-14-2 (9.95 %).

Sample code	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	total measured PCBs	ΣPCBs*
BAL1/1	0.51	3.54	0.15	< LOD	< LOD	< LOD	< LOD	4.20	21
BAL1/3	0.25	2.93	0.07	< LOD	< LOD	< LOD	< LOD	3.25	16.2
BAL1/7	293.73	228.52	21.22	< LOD	7.54	2.37	2.15	555.53	2,778
bal-EGG-14-1	0.37	< LOD	< LOD	5.90	6.98	7.01	3.11	23.37	17.47
bal-EGG-14-2	< LOD	< LOD	< LOD	1.42	2.90	3.71	3.51	11.54	10.12
bal-EGG-14-3	2.28	< LOD	8.34	17.8	20.8	20.5	6.92	76.64	58.84
bal-EGG-14-4	0.31	< LOD	3.67	9.45	14.6	16.3	7.86	52.19	42.74
bal-FISH-14-1´	0.06	0.07	0.38	0.48	0.99	0.99	0.37	3.34	2.86
bal-FISH-14-2´´	0.02	0.06	0.36	0.65	1.10	1.10	0.41	3.70	3.05
bal-FISH-14-3´´´	< LOD	< LOD	0.02	0.03	0.05	0.05	< LOD	0.15	0.12
bal-FISH-14-4×	< LOD	< LOD	0.02	0.02	0.05	0.04	< LOD	0.13	0.11
bal-FISH-14-5××	0.02	0.04	0.12	0.26	0.27	0.27	0.06	1.04	0.78
BAL SED 1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BAL SED 2	300.9	80.24	11.89	< LOD	< LOD	< LOD	< LOD	393.03	1,965
BAL SED 3	7,262	1,227	207.44	< LOD	76.11	10.26	11.11	8,794	43,976
BAL SED 5	41.1	71.1	39.1	< LOD	14.78	10.00	11.35	187.43	937

Following samples were not analyzed for PCB congeners: BAL1/4, BAL1/5, BAL1/6, BAL1/8, BAL1/9, BAL1/11, B-1, B-2, B-3, B-4, B-5, BAL FISH 1a, BAL FISH 1b, balchas ryby, BAL HOT GR-1, BAL HOT SED1, BAL HOT SED2, BAL-M, BAL SED 6, POP BAL

*soils, sediments: recalculated for the sum of all PCB congeners by multiplying the sum of six selected PCB congeners (28, 52, 101, 138, 153, 180) with 5 according to the recommendations in the Czech norm ČSN EN 12766-2 and Czech order 384/2001 Sb.

*fish, eggs and milk: sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180

Sample code	α-HCH	β-HCH (μg/g)	γ-HCH (Lindan)	δ-HCH	HCB	PCDD/F + DL PCBs (CALUX)
BAL1/1	< LOD	< LOD	< LOD	< LOD	< LOD	2.2
BAL1/3	< LOD	< LOD	< LOD	< LOD	< LOD	4.6
BAL1/4	NA	NA	NA	NA	NA	4.8
BAL1/5	NA	NA	NA	NA	NA	13
BAL1/6	NA	NA	NA	NA	NA	3.6
BAL1/7	NA	NA	NA	NA	NA	0.98
BAL1/8	< LOD	< LOD	< LOD	331.4	< LOD	NA
BAL1/11	< LOD	< LOD	< LOD	< LOD	< LOD	NA
B-1	NA	NA	NA	NA	NA	24!
B-2	NA	NA	NA	NA	NA	12!
B-3	NA	NA	NA	NA	NA	15!
B-4	NA	NA	NA	NA	NA	101!
B-5	NA	NA	NA	NA	NA	33!
bal-EGG-14-1	1.05	5.79	< LOD	NA	1.68	NA
bal-EGG-14-2	13.1	93.9	7.14	NA	2.62	NA
bal-EGG-14-3	2.60	15.4	2.71	NA	4.39	NA
bal-EGG-14-4	7.02	22.9	4.48	NA	2.13	NA
BAL FISH 1a+	NA	NA	NA	NA	NA	0.51
BAL FISH 1b++	NA	NA	NA	NA	NA	(0.080)**
balchas ryby+++	NA	NA	NA	NA	NA	0.14
bal-FISH-14-1´	0.09	0.29	0.10	NA	0.33	0.48
bal-FISH-14-2´´	0.07	0.15	< LOD	NA	0.31	NA
bal-FISH-14-3´´´	< LOD	0.04	0.02	NA	0.04	NA
bal-FISH-14-4×	< LOD	0.02	0.06	NA	0.03	NA

bal-FISH-14-5××	0.03	0.04	0.06	NA	0.05	NA
BAL HOT GR-1	< LOD	< LOD	< LOD	< LOD	< LOD	NA
BAL HOT SED1	NA	NA	NA	NA	0.12	NA
BAL HOT SED2	NA	NA	NA	NA	NA	0.41
BAL-M	NA	NA	NA	NA	NA	0.077!
BAL SED 1	< LOD	< LOD	< LOD	382.8	0.40	NA
BAL SED 2	< LOD	< LOD	< LOD	< LOD	< LOD	NA
BAL SED 3	< LOD	< LOD	< LOD	< LOD	< LOD	NA
BAL SED 5	< LOD	< LOD	< LOD	< LOD	0.57	NA
BAL SED 6	< LOD	< LOD	< LOD	183.8	< LOD	NA
POP BAL	NA	NA	NA	NA	NA	0.22

Sample BAL 1/9 was not analyzed for OCPs or PCDD/Fs + dl PCBs.
**result below LOQ, estimate given in parentheses
+ fat content 2.93% ++ fat content 0.52% +++ fat content 0.85% ´ fat content 3.0% ˝ fat content 9.0% ˝´ fat content 0.5% × fat content 0.3% ×× fat content 1.1 %
! suspected to be non-compliant

TABLE 7 RESULTS FOR CHEMICAL ANALYSIS OF SELECTED EGGS AND FISH FROM BALKHASH FOR CONTENT OF DDTs GIVEN IN ng g^{-1} OF FAT FOR EGGS RESPECTIVE IN ng g^{-1} WET WEIGHT FOR FISH SAMPLES.

Sample code	o,p´-DDE	p,p´-DDE	o,p´-DDD	p,p´-DDD	o,p-DDT	p,p´-DDT	Sum DDT
bal-EGG-14-1	< LOD	10.1	< LOD	< LOD	< LOD	< LOD	10,1
bal-EGG-14-2	< LOD	26.6	< LOD	< LOD	1.32	6.13	34.05
bal-EGG-14-3	0.18	172	0.42	1.47	20.8	124	318.87
bal-EGG-14-4	0.39	550	1.61	12.5	52.3	441	1,057.80
bal-FISH-14-1	< LOD	2.93	< LOD	0.05	0.38	0.07	3.43
bal-FISH-14-2	< LOD	2.45	< LOD	0.06	0.20	0.06	2.77
bal-FISH-14-3	< LOD	0.26	< LOD	< LOD	0.02	< LOD	0.28
bal-FISH-14-4	< LOD	0.08	< LOD	< LOD	< LOD	< LOD	0.08
bal-FISH-14-5	< LOD	0.39	0.03	< LOD	0.16	0.11	0.69

TABLE 8 PCDD/Fs AND DL PCBs CONGENER SPECIFIC ANALYSIS OF SELECTED BALKHASH EGG SAMPLES GIVEN IN pg g^{-1} FAT.

Uncertainties are obtained by multiplying the measurement standard uncertainty with the amplification coefficient k=2. All egg samples had a content of fat higher than 10% except BAL-EGG-14-2 (9.95 %).

Sample code	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF
bal-EGG-14-1	0.587±40 %	2.05±40 %	1.25±40 %	1.95±40 %	0.719±40 %	3.18±40 %	2.61±40 %	6.77±40 %	4.8±40 %	7.0±40 %
bal-EGG-14-2	0.333±40 %	2.31±40 %	1.58±40 %	5.45±40 %	1.18±40 %	10.6±40 %	9.33±40 %	3.29±40 %	4.04±40 %	8.64±40 %
bal-EGG-14-3	0.771±40 %	2.19±40 %	1.28±40 %	1.68±40 %	0.695±40 %	2.48±40 %	11.0±40 %	8.78±40 %	5.11±40 %	7.35±40 %
bal-EGG-14-4	0.405±40 %	1.1±40 %	0.597±40 %	0.727±40 %	0.349±40 %	1.14±40 %	3.1±40 %	4.68±40 %	3.29±40 %	4.27±40 %

Sample code	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	WHO-PCDD/F-TEQ
bal-EGG-14-1	5.31±40 %	4.83±40 %	0.186±40 %	5.2±40 %	5.62±40 %	0.292±40 %	0.331±40 %	7.59±30 %
bal-EGG-14-2	9.81±40 %	7.4±40 %	<0.127	14.4±40 %	14.3±40 %	1.19	2.71±40 %	9.94±30 %
bal-EGG-14-3	4.23±40 %	3.15±40 %	<0.127	3.74±40 %	3.04±40 %	<0.338	0.698±40 %	7.75±30 %
bal-EGG-14-4	2.53±40 %	2.04±40 %	<0.127	2.34±40 %	2.3±40 %	0.19 ±40 %	0.648±40 %	4.26±30 %

Sample code	PCB 81	PCB 77	PCB 123	PCB 118	PCB 114	PCB 105	PCB 126	PCB 167	PCB 156
bal-EGG-14-1	13.6±30 %	163±30 %	156±30 %	8150±30 %	267±30 %	3720±30 %	69.5±30 %	487±30 %	1120±30 %
bal-EGG-14-2	5.51±30 %	32.6±30 %	35.5±30 %	2070±30 %	66.1±30 %	874±30 %	25.7±30 %	201±30 %	435±30 %
bal-EGG-14-3	46.8±30 %	303±30 %	535±30 %	26800±30 %	787±30 %	10500±30 %	202±30 %	1310±30 %	2730±30 %
bal-EGG-14-4	17.1±30 %	118±30 %	207±30 %	13100±30 %	381±30 %	5210±30 %	125±30 %	893±30 %	1850±30 %

Sample code	PCB 157	PCB 169	PCB 189	WHO-PCDD/F-PCB-TEQ
bal-EGG-14-1	263±30 %	8.83±30 %	67.2±30 %	15.3±30 %
bal-EGG-14-2	71.9±30 %	6.35±30 %	97.7±30 %	12.8±30 %
bal-EGG-14-3	657±30 %	25.9±30 %	178±30 %	30.1±30 %
bal-EGG-14-4	423±30 %	17.3±30 %	184±30 %	18.0±30 %

3.3 Temirtau

TABLE 9 RESULTS OF CHEMICAL ANALYSES FOR THE TEMIRTAU SITE.

< LOD: analyte concentration was below limit of detection. NA: not analyzed. PCBs and OCPs are given in ng g-1 for all samples. PCDD/Fs and DL PCBs are given in pg PCDD/Fs-DL PCB TEQ g^{-1} dry weight.

Sample code	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	Total measured PCBs	ΣPCBs*
Temirtau 1	NA	NA	NA	NA	NA	NA	NA	NA	NA
TER PG 1/II	NA	NA	NA	NA	NA	NA	NA	NA	NA
TER PG 2/II	NA	NA	NA	NA	NA	NA	NA	NA	NA
TER PG 3/II	NA	NA	NA	NA	NA	NA	NA	NA	NA
TER PG 4/II	NA	NA	NA	NA	NA	NA	NA	NA	NA
TER PG 5/II	NA	NA	NA	NA	NA	NA	NA	NA	NA
TER PG 6/II	NA	NA	NA	NA	NA	NA	NA	NA	NA
Temirtau 3	< LOD	11.00	< LOD	< LOD	< LOD	< LOD	< LOD	11.0	55.0
TEM CHL 2	0.05	2.29	0.36	< LOD	< LOD	< LOD	< LOD	2.7	13.5
TEM CHL 11	0.09	0.53	0.19	< LOD	< LOD	< LOD	< LOD	0.81	4.05
Temirtau 2	< LOD	12.30	< LOD	< LOD	< LOD	< LOD	< LOD	12.30	61.5
Temirtau 4	NA	NA	NA	NA	NA	NA	NA	NA	NA

Following samples were not analyzed for PCB congeners: Temirtau 1, TER PG 1/II, TER PG 2/II, TER PG 3/II, TER PG 4/II, TER PG 5/II, TER PG 6/II, and Temirtau 4.
*recalculated for the sum of all PCB congeners by multiplying the sum of six selected PCB congeners (28, 52, 101, 138, 153, 180) with 5 according to the recommendations in the Czech norm ČSN EN 12766-2 and Czech order 384/2001 Sb.

Sample code	α-HCH	β-HCH	γ-HCH	δ-HCH	HCB	PCDD/Fs + DL PCBs (CALUX)
Temirtau 1	< LOD	< LOD	< LOD	< LOD	0.6	3.2
TER PG 1/II	NA	NA	NA	NA	NA	40
TER PG 2/II	NA	NA	NA	NA	NA	2.6
TER PG 3/II	NA	NA	NA	NA	NA	3.7
TER PG 4/II	NA	NA	NA	NA	NA	7.8
TER PG 5/II	NA	NA	NA	NA	NA	6.8
TER PG 6/II	NA	NA	NA	NA	NA	6.4
Temirtau 3	NA	NA	NA	NA	NA	3.3
TEM CHL 2	5.3	18.7	3.9	46.3	4.5	NA
TEM CHL 11	< LOD	< LOD	< LOD	177.5	< LOD	40
Temirtau 2	NA	NA	NA	NA	NA	0.56
Temirtau 4	NA	NA	NA	NA	NA	0.58

4. DISCUSSION

In this chapter, various legal standards are presented first. Then, background levels of studied pollutants are presented. Finally, the pollutant concentrations determined in samples from the investigated sites are compared both to respective legal standards and background levels.

4.1 Legal standards

The pollutant concentrations determined in the samples from all sites have to be compared to maximum or approximate allowed concentrations of these pollutants as defined in various national and international norms, decrees and laws (Tab. 10, 11 and 12). There is no specific POP legislation in Kazakhstan (Republic of Kazakhstan, 2009) except for certain technical, environmental and health quality standards for PCBs (UNDP and GoK, 2010). Current legal limits from Russia and past Soviet Union are mentioned. It has to be mentioned that many of these legal limits might be outdated. No POP maximum level are defined for soil in the EU legal standards. Therefore, Czech and German standards were used to discuss pollutant levels found in soils.

TABLE 10 RUSSIAN, SOVIET AND TATARSTAN LIMIT CONCENTRATION VALUES FOR PCBS AND OCPS IN SOIL EXPRESSED IN mg kg^{-1} DRY WEIGHT, PCDD/FS TEQ IN pg g^{-1}.

	Residential and agricultural soils, areas nearby water sources				
	Russian MAC	**Soviet MAC**	**Soviet AAC**	**Tatarstan MAC**	**Soviet AAC**
PCBs[1]				0.06	
α, β-HCH individual	0.1[2]				
γ-HCH individual		0.1[3]			
Hexachlorobenzene			0.08[4]		
PCDD/Fs[1] TEQ					0.33[5]

1 List of congeners in the sum not known. Order 16.12.2003г. N°1322 Tatarstan Environment and Natural Resources (Министерство экологии и природных ресурсов Респ.Татарстан, Приказ от 16.12.2003г. N°1322).
2 Russian Hygienic normatives (standards) of pesticide's concentration in environment's media. Гигиенические нормативы содержания пестицидов в объектах окружающей среды (перечень) ГН 1.2.2701 -10 Российская Федерация
3 USSR (PDK) chemicals in soil 30.10.80г. N°2264-80 (ПДК хим.в-в в почве от 30.10.80г. N°2264-80)
4 USSR Hygienic normatives (standards) chemicals in soil (PDK) GN 6229-91, ГН 6229-91, Перечень ПДК и ОДК хим. веществ в почве. AAC is a temporary hygienic norm based on data of uncompleted researches. AAC were planned to be replaced by MACs in three years but AAL are the only limits for some pollutants.
5 Order of USSR Health Ministry 08.09.86 N° 697 DSP, Приказ МЗ СССР от 08.09.86 г. N° 697 ДСП

TABLE 11 INTERNATIONAL LIMIT CONCENTRATION VALUES FOR PCBS, OCPS AND PCDD/FS IN VARIOUS TYPES OF SOILS EXPRESSED IN mg kg^{-1} DRY WEIGHT.

	agricultural soils			residential	industrial + commercial	children playgrounds	all soils except agricultural soils			
	Czech risk based MAC[3]	Czech MAC[4]	Czech preventive value[5]	Germany	Germany	Germany	Czech criterion A[2]	Czech criterion B[2]	Czech criterion C-residential[2]	Czech criterion C-industrial[2]
PCB sum[1]		0.01					0.02	2.5	5.0	30
PCB individual				0.8[5]	40[5]					
OCPs individual		0.01					0.05	2	2.5	10
OCPs sum		0.1								
α, β, γ-HCH individual	1									
α, β, γ-HCH sum			0.01							
HCH-mix or β-HCH				10[6]	400[6]					
Hexachlorobenzene	1		0.02	8[6]						
PCDD/Fs I-TEQ (ng kg^{-1})	100		0.001	1000[7]	10,000[7]	100[7]	1	100	500	10,000

1 Sum of congeners PCB 28, 52, 101, 118, 138, 153, 180

2 Soil, ground water and soil air pollution criteria according to the methodological guidelines of the Czech Ministry of Environment of 31 July 1996. These criteria are not legally binding, however, 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. 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 does pose. 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.

3 Maximum acceptable concentrations of pollutants in the arable or mould layer of agricultural soils determined according to risk levels. Proposal of the amendment to the decree 13/1994 Sb. When exceeded, these MACs indicate a direct risk to humans and animals when present at the site. These criteria did not went into force up to now.

4 Maximum acceptable concentrations of pollutants in agricultural soils according to decree 13/1994 Sb. These are often exceeded also in the Czech Republic.

5 Upper limit of natural or diffuse anthropogenic background. Criteria decisive for the protection of soil against risk inputs. Inputs should be monitored, a risk analysis is not necessary. Proposal of the ammendatory act of decree 13/1994 Sb.

6 Trigger values pursuant to § 8 paragraph 1 sentence 2 No. 1 Federal Soil Protection Law for the direct intake of pollutants at playgrounds, in residential areas, parks and recreational facilities, and industrial and commercial real properties

7 Action values pursuant to § 8 paragraph 1 sentence 2 No. 2 Federal Soil Protection Law for the direct intake of dioxins/furanes at playgrounds, in residential areas, parks and recreational facilities, and industrial and commercial real properties. In the event of dioxin-containing lye-residues from copper slate, the action values shall, due to the low resorption in the human organism, be applied not directly to protect human health but rather to ward off danger for a long time.

TABLE 12 LIMIT CONCENTRATION VALUES FOR OCPS, PCBS AND PCDD/FS TEQS IN VARIOUS FOOD ITEMS

	Hen eggs				Cow milk		Freshwater fish			
	Russian MAC[1]	Russian MAC[4]	EU ML[2]	EU MRL[3]	Russian MAC[1]	EU ML[2]	Russian MAC[1]	Russian MAC[4]	Kazakhstan MAC[5]	EU ML[2]
Unit	pg g^{-1} fat	ng g^{-1} *	pg g^{-1} fat	ng g^{-1}	pg g^{-1} fat	pg g^{-1} fat	pg g^{-1*}	ng g^{-1} fat	ng g^{-1} w.w.	pg g^{-1} w.w.
WHO-PCDD/Fs TEQ	3.0		2.5		3.0	2.5	4.0			3.5
WHO-PCDD/Fs-DL PCB TEQ			5.0			5.5				6.5
PCBs[6]									2,000	
PCBs[7]			40			40				125
DDT total[7]				50						
p,p´-DDT		100						200		
γ-HCH (lindane)				10				100		
α-, β-HCH		100		20, 10**				100		
HCB				20						

1 Current Russian СанПиН 2.3.2. 2401-08 Hygienic safety and nutrition value requirements for food. Sanitary-epidemiologic rule and normatives (СанПиН 2.3.2. 2401-08 Гигиенические требования безопасности и пищевой ценности пищевых продуктов Санитарно-эпидемиологические правила и нормативы)
2 EU Regulation (EC) N°1259/2011
3 Regulation (EC) N°149/2008. Maximum residue level (MRL) means the upper legal level of a concentration for a pesticide residue in or on food or feed set in accordance with the Regulation, based on good agricultural practice and the lowest consumer exposure necessary to protect vulnerable consumers.
4 Russian Federation GN 1.2.2701-10 Hygienic normativs (standards) pesticides concentration in environmental media (ГН 1.2.2701-10 "Гигиенические нормативы содержания пестицидов в объектах окружающей среды")
5 Kazakhstan SanPin Hygienic safety requirement and nutrition value for food 06.08.2010 N° 611от (СанПиН РК от 6 августа 2010 года N° 611 "Гигиенические требования к безопасности и пищевой ценности пищевых продуктов")
6 sum of not specified congeners
7 sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180
8 sum of p,p´-DDT, o,p´-DDT, p,p´-DDE and p,p´-DDD
*not clear whether calculated for fat content or not
**for each congener is MRL set separately

Russian, Kazakhstani and EU standards were used to discuss pollutant levels in food (table 15). When PCDD/Fs levels determined by the DR CALUX method are discussed, the following has to be considered. This cell based reporter gene assay is a validated method for screening for PCDD/Fs, and DL PCBs contents in food according to EU Commission Regulation EC/252/2012. Screening methodologies are usually used to exempt those samples that are below the maximum permitted limit (i.e. are compliant with the limit) and that can, therefore, be released to the market. In addition, one needs to select those samples that require confirmation (i.e. are suspected to be non-compliant) of their PCDD/Fs TEQ level. When bioassays are used as screening tools, the interpretation of the obtained results should consider the higher variability and uncertainty associated with them (van Overmeire et al., 2004).

The content of POPs in samples of solid matrices was also compared to the provisional low POPs content for wastes defined under the Basel Convention on the control of transboundary movements of hazardous wastes and their disposal: 50 mg kg^{-1} for HCB and PCBs and 15 µg TEQ for PCDD/Fs kg^{-1}. According to the Convention, wastes consisting of, containing or contaminated with POPs above the low POP content should be disposed of in such a way that the POP content is destroyed or irreversibly transformed or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option (BC, 2008). Unfortunately, the particular PCB congeners covered in the sum of PCBs are not defined in BC (2008). Therefore, this threshold value is compared to both the sum of 7 analyzed PCB congeners and the calculated sum of all PCB congeners (see footnotes in Tab. 5 and 7) in the following discussion.

4.2 Ekibastuz

The highest concentration of PCBs among the samples taken at the Ekibastuz electrical power substation and its surroundings were observed in soil samples EKI 2/12 (the sum of 7 measured PCB congeners was 191 mg kg^{-1}, the calculated sum of all PCB congeners was 935 mg kg^{-1}) and EKI 2/13 (the sum of 7 measured PCB congeners was 162 mg kg^{-1}, the calculated sum of all PCB congeners was 799 mg kg^{-1}). These by far exceeded the provisional low POP content for wastes defined under the Basel Convention and any legal limits for PCB sums in soil. Both samples were taken in the capacitor placing area east from the substation building. Sample EKI 2/12 was taken as a point sample at capacitors abatment and might be considered non-representative. However, sample EKI 2/13 (mixed sample out of 4 sub-samples) was taken nearby between capacitors and exhibited similar highly elevated levels.

Soil samples EKI 2/8, EKI 2/9 and EKI 2/10 also taken at the capacitor placing area, had high concentrations of PCBs (between 0.55 and 8.9 mg kg^{-1} sum of 7 analyzed PCB congeners).. Sample EKI 2/10 had a calculated total concentration of all PCB congeners of almost 42 mg kg^{-1}, which is close to the defined low POP content for wastes. However, the sum of 7 measured PCB congeners (8.93 mg kg^{-1}) in this sample was below the Czech criterion C for industrial areas (tab. 9). It has to be stressed, that this sample was a point sample and not representative. All samples taken at the capacitor placing area exceed the Tatarstan MAC of 0.06 mg kg^{-1} for residential and agricultural soils (Tab. 8) by several orders of magnitude except sample EKI 2/11, which was only slightly above this legal limit. However, the sampled area could be characterized as industrial soil, no residential and agricultural use is assumed, although there were signs of grazing animals in the area such as excrements.

Two soil samples were taken from the column area west of the substation building. Sample S 1.1/II had a calculated content of the sum of all PCB congeners exceeding the low POP content for wastes by almost three times. When considering the sum of 7 analyzed PCB congeners, the sample PCB contamination reach approximately half of the low POP content for wastes. However, it was close to the Czech criterion C for industrial areas. The exceedance of this criterion represents a contamination which may pose a significant risk to human health and environmental compartments. Both samples taken at the column area exceed the Tatarstan MAC of 0.06 mg kg^{-1} (Tab. 8) for residential and agricultural soils. However, these soils are also considered industrial soils.

Soil samples EKI 2/1 – 2/7 and S 2/II, S 2.1/II, S 2.2/II and S 3/II were all taken in the vicinity of the capacitor placing area and substation building. Except sample EKI 2/2, all samples had PCB concentrations well below the Tatarstan and other legal limit. Sample EKI 2/2 is characterized by the sum of 7 analyzed PCBs of 0.19 mg kg^{-1} and exceeds this limit by three times. However, this sample is a point sample and not representative. Soil sample S 3.1/II taken 50 m aside the substation‘s big building had a PCB concentration exceeding the Tatarstan legal limit for residential and agricultural soils by two orders of magnitude, however, it did not exceed any relevant international legal limit. Sweepings samples EKI 2/14 and EKI 2/15 from inside the substation‘s big building had a PCB content not exceeding any legal limit. A sample of layered mineral wool taken 30 m far from the substation (PS 2/II) and a capacitor piece (PS 2.1/II) contained detectable concentrations of PCBs, although orders of magnitude lower than the low POP content for wastes.

Three soil samples were taken in the residential dacha areas north and south of the power substation and showed concentrations well below the Tatarstan legal limit and international limits for residential areas. Sediment samples taken in the area surrounding of the Ekibastuz electrical power substation in the vicinity of lakes and the Irtysh-Karaganda canal had a low PCB content.

Selected soil and sediment samples were analyzed by DR CALUX for PCDD/Fs and DL PCB content. However, the results of this method cannot be compared directly to legal standards, as these are expressed in PCDD/Fs-DL PCB I-TEQ. However, it can be stated that the results indicate a low contamination by these POPs, except the point soil sample EKI 2/8 taken in the capacitor placing area of the Ekibastuz electrical power substation. This sample was analyzed also by HRGC-HRMS and the reported 1.68 pg WHO-PCDD/Fs TEQ g^{-1} is far below the defined low POP content for wastes, however, five times higher than the Soviet legal limits for agricultural and residential soils. Adding DL PCBs, the WHO- PCDD/Fs-DL PCBs TEQ is 30.2 pg g^{-1}. It can be stated, that the dioxin-like activity of this sample is dominated by DL PCBs.

Two mixed egg samples were taken in residential areas, one closer to the substation area (700 m distance, at café Atael, EKI EGG 1), one farther (dacha area to the south, EKI EGG 2). Both were analyzed by the DR CALUX bioassay on the content of PCDD/Fs and DL PCBs. DR CALUX BEQ results for food samples cannot be compared directly to legal standards, as these are expressed in WHO-PCDD/Fs-DL PCB TEQ. However, DR CALUX results suggest that both egg samples are suspected to be non-compliant with EU regulations. Therefore a new egg sample (EKI-egg-14-1 + EGI-egg-27) at café Atael which is 700 m from the substation was taken later. The HRGC-HRMS analysis showed, that both WHO-PCDD/Fs TEQ and WHO-PCDD/Fs-DL PCB TEQ levels are about two times higher than the Russian MAC and EU ML. The source of the reported contamination is not easy to interpret. Both households may burn their waste or biomass in the yards and in the case of café Atael samples, an ash mound is located behind the house, which chickens have access to. Therefore, the Ekibastuz electrical power substation cannot be suspected as the only major source for the possible and confirmed PCDD/Fs and DL PCBs contamination of these eggs. One more egg sample (EKI-egg-14-2) was taken in the dacha area north of substation and the HRGC-HRMS analysis results are below both Russian MAC and EU ML. Two fish samples from lake Zhyngyldy were compliant with EU regulations. However, these two point samples are not representative.

4.3 Balkhash

Two soil samples from Balkhash children‘s playgrounds were analyzed for PCB concentrations. The reported concentrations are one order of magnitude lower than the Tatarstan legal limit for agricultural and residential soils (Tab. 8). Legal limits for PCB levels for children playgrounds are not available.

The highest concentration of PCBs among the sediment samples taken in Balkhash were found in sample BAL SED 3 taken at a beach of the lake bay close to the BGMK tailing ponds. The calculated total concentration of all PCB congeners in this sample of almost 44 mg kg^{-1} is close to the defined low POP content for wastes. However, the sum of 7 measured PCB congeners (8.8 mg kg^{-1}) is well below the low POP content for wastes, but still considerable. In the nearby sediment sample BAL SED 2 a concentration of PCBs (almost 0.4 mg kg^{-1}, sum of 7 analyzed congeners) one order of magnitude lower was found. Sample BAL SED 5 taken north of the previous two samples had a PCB content similar to BAL SED 2 (almost 0.2 mg kg^{-1}, sum of 7 analyzed congeners). All samples were mixed samples, sample BAL SED 3 was taken from a lower depth than the other two samples. On the other hand, the sample BAL- SED 1 taken to the south of the previous samples had PCB concentrations under the limit of detection. The sediment sample BAL 1/7 taken at another lake bay (close to the Balkhash city) had PCB concentrations at the same order of magnitude as samples BAL SED 2 and BAL SED 5. Legal limits for PCB concentrations in sediments are not available for comparison.

Selected soil and sediment samples were analyzed by DR CALUX for PCDD/Fs and DL PCB content. The sampled sites are rural and residential areas, part of them children‘s playgrounds. The reported DR CALUX TEQs are one to two orders of magnitude higher than the Soviet AAC for agricultural and residential soils, which is, however, expressed in TEQs not obtained by the DR CALUX bioassay (therefore not directly comparable) and also an outdated legal limit. The DR CALUX TEQ found in two children‘s playground samples were two orders of magnitude lower than the German legal limit for children‘s playgrounds.

Five mixed egg samples taken out of 4 to 10 sub-samples each were taken in various residential areas, some close to the BGMK enterprise and electrical power plant. All the samples were analyzed by the DR CALUX bioassay for content of PCDD/Fs and DL PCBs. DR CALUX BEQ results for food samples cannot be compared directly to

Russian and international standards, as these are expressed in WHO-PCDD/Fs-DL PCB TEQ. However, DR CALUX results suggest that all egg samples are suspected to be non-compliant with EU regulations. Later, four mixed egg samples were taken at partly the same spots and analyzed by HRGC-HRMS. In all these samples the PCDD/Fs and DL PCBs content expressed in WHO TEQ exceeded the Russian MAC and EU ML. The source of the found contamination is not easy to interpret. All households may burn their waste or biomass in the yards, which chickens have access to. Therefore, the Balhkash metallurgical industry cannot be suspected as the only major source for the possible dioxin-like contamination of these eggs.

Eight fish samples (some of them pooled samples) from lake Balkhash were compliant with EU regulations according to DR CALUX. However, these rather point samples are not representative for a large lake. The DR CALUX testing results of a milk sample (BAL-M) taken in the southern city rural suburbs (same sampling place as for egg sample B-5) suggest this sample to be non-compliant with EU regulations. However, this sample was a point sample and thus not representative. The source of the possible contamination is complicated to interpret as is the case of the egg samples.

Selected samples were also analyzed on the content of hexachlorocyclohexane isomers and HCB. There exist no legal limits on POP content in sediments. If compared to soil legal limits, the HCB content in three mixed samples is far beyond the Soviet AAL. These samples were also analyzed on four hexachlorocyclohexane isomers. The only detected isomer was δ-hexachlorocyclohexane, for which no legal limit is available.

4.4 Temirtau

Mixed soil samples taken at 7 playgrounds in Temirtau were analyzed by DR CALUX on the PCDD/Fs and DL PCB content. The results of this method cannot be compared directly to German standards for playgrounds, as these are expressed in WHO-PCDD/Fs-DL PCB TEQ. Although it can be stated that none of the samples is suspected to be non-compliant with EU regulations, some attention should be payed to sample TER PG 1/II. This sample exhibited the highest PCDD/Fs concentration among the playground samples (40 ng PCDD/Fs-DL PCB CALUX TEQ kg^{-1} dry weight). The German action value for children playgrounds is 100 ng PCDD/Fs-DL PCB I-TEQ kg^{-1} dry weight. As results obtained by bioassays such as CALUX are subject to higher variability and uncertainty (van Overmeire et al., 2004), this particular sample should be analyzed by HRGC-HRMS for PCDD/Fs content in order to exclude pollutant levels close to the action value for children‘s playgrounds.

The soil samples were taken from playgrounds placed in various distances in a western direction from the AMT mill. Sample TER PG 1/II with the highest found PCDD/Fs content was taken from one of the playgrounds located the closest to the AMT (approximately 1.5 km). However, samples Temirtau 1, TEM PG 2/II and TEM PG 3/II were also taken from playgrounds located approximately the same distance as sample TER PG 1/II and exhibit PCDD/Fs concentrations one order of magnitude lower and very similar to the rest of playground samples taken in a distance approximately 4 km from the AMT mill. No concentration spatial gradient that would suggest a pollution dispersion by wind from the AMT mill is therefore observed.

The calculated total concentration of all PCB congeners in the mixed sediment sample Temirtau 3 taken in a wetland in front of the AMT smelter dump foot was 55 mg kg^{-1}. This is slightly higher than the defined low POP content for wastes. However, the sum of 7 measured PCB congeners (11 mg kg^{-1}) is well below the low POP content for wastes, but still considerable. A mixed slag sample (Temirtau 2) taken close to the same dump exhibited similar concentrations, i.e. 61.5 mg kg^{-1} for the sum of all PCB congeners and 12.3 mg kg^{-1} for the sum of 7 measured PCB congeners. Legal limits for PCB concentrations in sediments are not available for comparison. Both samples and a third mixed slag sample (Temirtau 4) exhibited DR CALUX PCDD/Fs TEQs compliant with EU regulations.

Two mixed sediment samples taken from the tailing pond of the Karbid chemical factory exhibit PCB levels well below the low POP content for waste and are also suggested to be compliant with EU regulations for PCDD/Fs content.

5. CONCLUSIONS

Samples from the investigated areas have to be compared to relevant background levels, which have to be obtained by well-designed sampling. The author of this study recommends to select clearly non-polluted background sites for soil and sediment sampling and conduct „background“ sampling of food samples by buying and analyzing relevant food samples from commercial industrialized producers. The development of a normative legal basis in the area of POP management including legal POP limits in Kazakhstan together with methodological guidelines is highly recommended, as otherwise the results of field studies such as the one presented here cannot be properly evaluated.

5.1 Ekibastuz

Two soil samples taken at the Ekibastuz electrical power substation, particularly in the capacitor placing area east to the station building, exceeded the low POP content for wastes defined under the Basel Convention several times. This reflects the fact stated by Ishankulov (2008) and the Kazakhstani NIP (Republic of Kazakhstan, 2009), that part of the soil under the docks on which the capacitors were installed was not removed. Also other soil samples taken in the capacitor placing area had high concentrations of PCBs, however, some of them were point samples. Therefore, the actual spatial extension of the area seriously contaminated by PCBs should be determined in a dedicated study and then disposed of in such a way that the PCB content is destroyed or irreversibly transformed or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option (BC, 2008).

One mixed soil sample taken at the column area east of the electrical power substation building had PCB levels close to the Czech criterion C for industrial areas. When exceeded, this criterion represents a contamination which may pose a significant risk to human health and environmental compartments. Thus, further sampling in this column area is recommended to verify whether this criterion is exceeded or not. If yes, the risk level should be determined 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 are necessary documents for the decision on the type of remedial measures.

One point soil sample taken north of the substation building at a place of suspected contamination (wires present) revealed PCB concentrations approximately three times higher than the Tatarstan legal limit. This particular place might be considered for more spatially extensive re-sampling although the comparison with the Tatarstan legal limits for residential and agricultural soils is of limited suitability. A mixed soil sample further from the substation building (50 m) had elevated levels of PCBs approaching Czech criterion B. This criterion is 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 does pose. Criteria B are 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, according to the investigation results, a decision on further investigation and the start of a monitoring campaign. Although the B criterion was actually not exceeded, it would be recommendable to sample the wider area of the electrical power substation in order to exclude a major spread of PCB contamination around the substation building and column area. It is also necessary to remove the rest of capacitor pieces and other material possibly containing PCBs, that is spread around the substation area. PCB contamination in the soils of the residential dacha area farther north and south to the Ekibastuz electrical power substation and the Irtysh-Karaganda canal was not proven in this study.

Selected soil and sediment samples had a low contamination by PCDD/Fs and DL PCBs. The PCDD/Fs content of one point soil sample was far below the defined low POP content for wastes. The dioxin-like activity of this sample is dominated by DL PCBs.

DR CALUX bioassay results suggest that two mixed egg samples taken in households nearby the Ekibastuz electrical power substation are suspected to be non-compliant with EU regulations. A repeated sampling at one of these sites (café Atael 700 m from the substation) was conducted and the sample was analyzed by HRGC-HRMS for confirmation (Vromman et al. 2012, EU Commission Regulation (EC) No 252/2012). This sample had PCDD/Fs and DL PCB levels above legal limits and the suspected contamination source might be an ash mound behind the house which chickens have access to. The chicken owners should be informed about this problem and appropriate measures should be taken. A health risk analysis should be conducted. Fish samples from a nearby lake analyzed by DR CALUX were compliant with EU regulations. However, these two point samples are not representative.

5.2 Balkhash

One mixed sediment sample taken close to the BGMK tailing pond exhibited considerable PCB concentrations, other samples taken nearby had concentration levels one order of magnitude lower. As there are no legal limits for PCBs in sediments available, a more thorough examination of the BGMK tailing pond should be conducted in order to exclude the risk of pollution spreading into the Balkhash lake. Regarding city soils, the Kazakhstani NIP (2009) suggests local combustion to be the source of PCDD/Fs.

DR CALUX bioassay results suggest that all mixed egg samples and one milk point sample taken in households in residential areas of Balkhash are suspected to be non-compliant with EU regulations, therefore it was necessary to conduct repeated sampling at these sites and analyse the samples by HRGC-HRMS for confirmation (Vromman et al. 2012, EU Commission Regulation (EC) No 252/2012). Repeated sampling that took place at partly the same spots as the previous sampling reveled PCDD/Fs and DL PCB levels expressed in WHO TEQ to be well above Russian and EU legal limits. The source of the likely contamination of these hen eggs and cow milk is not easy to interpret. A health risk analysis should be conducted and residents informed about possible local PCDD/Fs sources as waste and biomass burning. Fish samples from Balkhash lake analyzed by DR CALUX were compliant with EU regulations. However, these two point samples are not representative and because fish from the lake is sold in the whole country, representative sampling should be conducted.

5.3 Temirtau

The PCDD/Fs levels of the sampled Temirtau playground soils are considered to be compliant with EU regulations. One sample exhibited a PCDD/Fs level one order of magnitude higher than the other samples and was taken from a playground quite close to the AMT mill. However, the other 3 soil playground samples were taken from playgrounds located in approximately the same distance and these exhibit PCDD/Fs concentrations very similar to the rest of playground samples further away. It can be concluded, that no spatial gradient with respect to the distance to the AMT mill is observed that would suggest pollution dispersion from the AMT mill by wind. The sample with the highest PCDD/Fs CALUX levels is recommended to be analyzed by HRGC-HRMS on the PCDD/Fs content. In case it would be close to the German action value for children's playgrounds, a risk analysis is recommended to be conducted.

A mixed sediment and mixed slag sample from the AMT smelter waste dump suggest total PCB concentrations around the low POP content for waste defined under the Basel Convention. As there are no legal limits for sediment PCB content available, a more thorough examination of the AMT smelter waste dump should be conducted in order to exclude the risk of pollution spread.

5.4 Limitations of the study

The major limitations of the study are the limited financial, temporal and personal resources. Therefore, only an estimation of the current contamination level and character at the visited sites based on an insufficient number of samples could be derived. Still, an impression of the situation including the identification of several contaminated spots was obtained. However, future investigations in this field are still necessary. The results presented here cannot be considered exhaustive, rather expressing the need for an extended investigation in future.

The comparison of pollutant concentration levels found in the samples with legal standards has also its limitations. Each of the legal standards is defined in a different way and for a different purpose. In addition, there are no existing legal standards for some of the pollutants and matrices sampled and some legal limits might be outdated (especially Soviet limits). The estimation of a potential risk to humans and the environment cannot be conducted by consulting legal standards only, an extensive risk analysis based on a sufficient number of samples and detailed description of the state of the area and the potential risk receivers is crucial.

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Persistent Organic Pollutants (POPs) in free range chicken eggs from hot spots in Central Kazakhstan

Final report on the results of environmental sampling conducted in Kazakhstan in 2013–2015 as a part of the project "Empowering the civil society in Kazakhstan in improvement of chemical safety"

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1. INTRODUCTION

Free range chicken eggs were used for monitoring levels of contamination by POPs at certain places in many previous studies (AAslan, Kemal Korucu et al. 2010, Pless-Mulloli, Schilling et al. 2001, Pirard, Focant et al. 2004, DiGangi and Petrlik 2005, Shelepchikov, Revich et al. 2006, Arkenbout 2014). Eggs have been found to be sensitive indicators of POP contamination in soils or dust and are an important exposure pathway from soil pollution to humans, and eggs from contaminated areas which can readily lead to exposures with exceeding thresholds for the protection of human health (Van Eijkeren, Zeilmaker et al. 2006, Hoogenboom, ten Dam et al. 2014, Piskorska-Pliszczynska, Mikolajczyk et al. 2014). Chickens and eggs might therefore be ideal "active samplers" and indicator species for evaluation of the level of contamination of sampled areas by POPs, particularly by dioxins (PCDD/Fs) and PCBs. Based on this assumption, we have chosen sampling of free range chicken eggs and their analyses for selected POPs as one of the monitoring tools within the project "Empowering the civil society in Kazakhstan in improvement of chemical safety".

The data and analyses of free range chicken eggs discussed in this report were obtained during a two and half year long joint project of Kazakhstani and Czech NGOs. They were obtained during two field visits in 2013 and 2014 by majority, as in the cases of the reports by Dvorská (2015) or Šír (2015). Also, the sampled localities are the same or similar as in those reports. A general description of samples and sampled localities can be found in the General Introduction part of this publication (Toxic Hot Spots in Kazakhstan).

2. SAMPLING AND ANALYTICAL METHODS

Samples of free range chicken eggs were collected at seven localities in Kazakhstan from which one was expected to be clean and another one was a sample from a supermarket in the city of Karaganda, considered as a background sample as suggested by Dvorská (2015). Shabanbai Bi village in Kyzyl Arai nature protected zone (zakaznik) was originally chosen as a potentially clean background site, while five others were expected to be contaminated by POPs to a certain level. The cities of Balkhash and Temirtau were expected to be polluted by POPs as cities with large metallurgical plants. This assumption was also based on data from the Kazakhstani National Implementation Plan for the Stockholm Convention (Republic of Kazakhstan 2009). The villages of Rostovka and Chkalovo are located on the river Nura River, downstream from abandoned chemical facility in Karbid (production of acetaldehyde) as it is also a part of the city of Temirtau. This facility polluted the river Nura with mercury. The same chemical plant can also be a source of pollution by POPs (e.g. PCBs). The neighbourhood of an electricity substation was sampled in the city of Ekibastuz. This abandoned facility is assumed to be a potential source of contamination by PCBs and partially also by PCDD/Fs as impurities in PCB oils (see also Dvorská (2015). More information about selected sites is in the General Introduction part of this publication.

Pooled samples of more individual egg samples were collected at each of the selected sampling sites in order to get more representative samples. Table 1 summarizes the basic data about size of samples and measured levels of fat content in each of the pool samples. Twenty pool samples of free range chicken eggs were taken in total plus a last sample was taken in 2015 in Karaganda, where we bought chicken eggs in a supermarket as suggested by Dvorská (2015). The last sample is used to exhibit background levels of POPs because a remote location in Shabanbai Bi didn´t prove to be clean, as explained further. Eleven samples were taken in 2013 and ten in following year 2014.

TABLE 1: OVERVIEW OF FREE RANGE CHICKEN EGG SAMPLES FROM SELECTED SITES IN KAZAKHSTAN.

No	Sample	Locality	Year of sampling	Number of eggs in pooled samples	Fat content in %
1	BAL-EGG-14-1	Balkhash – southwest	2014	6	12.45
2	BAL-EGG-14-2	Balkhash – southwest	2014	6	9.95
3	BAL-EGG-14-3	Balkhash – Rembaza	2014	6	10.15
4	BAL-EGG-14-4	Balkhash – Rembaza	2014	4	11.35
5	B 1	Balkhash – Rembaza	2013	6	13.2
6	B 2	Balkhash – Rembaza	2013	6	16.4
7	B 3	Balkhash – southwest	2013	6	18.6
8	B 4	Balkhash – north	2013	4	13.5
9	B 5	Balkhash – southwest	2013	10	14.9
10	EKI egg 1	Eikbastuz – substation	2013	4	10.5
11	EKI egg 2	Eikbastuz – Soyuz	2013	4	16.4
12	EKI-14-1-egg and EKI-27-egg	Ekibastuz – substation	2014	6	12.4
13	EKI-14-2-egg	Ekibastuz – Soyuz	2014	6	11.7
14	EKI-14-3-EGG	Ekibastuz – Soyuz	2014	6	13.3
15	NUR-EGG-14/2	Chkalovo; Nura	2014	6	13.7
16	NUR egg 24-2	Chkalovo; Nura	2013	6	12.5
17	KAR-SU	Karaganda - supermarket	2015	6	14.0
18	NUR-EGG-14/1	Rostovka; Nura	2014	6	15.0
19	NUR egg 24-1	Rostovka; Nura	2013	6	16.2
20	NUR egg 1	Samarkand village; Nura	2013	6	18.0
21	ARAI EGG	Shabanbai Bi	2014	6	10.15
22	NUR egg dam	Temirtau; Samarkand dam	2013	6	24.1

Free range chicken eggs from the first field visit 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 (BioDetection Systems B.V., Amsterdam). The procedure for the BDS DR CALUX® bioassay has previously been described in detail (Besselink H 2004). Briefly, rat liver H4IIE cells stably transfected with an AhR-controlled luciferase reporter gene construct were cultured in α-MEM culture medium supplemented with 10 % (v/v) FCS under standard conditions (37 ºC, 5 % CO_2, 100 % humidity). Cells were exposed in triplicate on 96-well microtiter plates containing the standard 2,3,7,8-TCDD calibration range, a reference egg sample (analysed by GC-HRMS; for the bioassay apparent recovery), a procedure blank, a DMSO blank and the sample extracts in DMSO. Following a 24 hour incubation period, cells were lysed. A luciferin containing solution was added and the luminescence was measured using a luminometer (Berthold Centro XS3).

The DR CALUX bioassay method is proven for screening analyses which can give a good picture about the level of pollution[1]; however, for confirmation it is necessary to go for more specific PCDD/Fs and DL PCBs congener analyses, which also allows examination of finger prints of dioxins (PCDD/F congener patterns), specific for different sources of pollution. Most of the samples from the second sampling period (July–September 2014) were analyzed for content of individual PCDD/Fs and an extended list of PCB congeners by HRGC-HRMS at the accredited laboratory of the State Veterinary Institute in Prague, Czech Republic. Some of the samples were from at least the same area as those from the first field sampling.

Egg samples were also analyzed for content of non-dioxin-like PCBs and OCPs in a Czech certified laboratory (University of Chemistry and Technology, Department of Food Chemistry and Analysis). The analytes were extracted by a mixture of organic solvents hexane : dichloromethane (1:1). The extracts were cleaned by means of gel permeation chromatography (GPC). The identification and quantification of the analyte was conducted by gas chromatography coupled with tandem mass spectrometry detection in electron ionization mode.

The mercury content in the samples was analyzed with atomic absorption spectrometry in an Advanced Mercury Analyser (AMA 254,Altec) using standard operating procedure SOP 70.4 (AAS-AMA) at the State Veterinary Institute, Prague.

1 "Bioanalytical methods" means methods based on the use of biological principles like cell-based assays, receptorassays or immunoassays. They do not give results at the congener level but merely an indication of the TEQ level, expressed in Bioanalytical Equivalents (BEQ) to acknowledge the fact that not all compounds present in a sample extract that produce a response in the test may obey all requirements of the TEQ-principle. European Commission (2012). Commission Regulation (EU) No 252/2012 of 21 March 2012 laying down methods of sampling and analysis for the official control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EC) No 1883/2006 Text with EEA relevance European Commission. Official Journal of the European Communities: L 84, 23.83.2012, p. 2011–2022.

3. THE KAZAKHSTANI, EU, AND OTHER LIMITS FOR POPs IN EGGS

Chicken eggs are a quite common part of the diet in Kazakhstan and it is also common that people in Kazakhstan raise their own chicken and partly sell left over chicken eggs at markets as raw eggs or as food in cafes. One should expect that for such a common food there would be limits for the content of certain contaminants; however, we didn´t find any limit values set up for chicken eggs in Kazakhstani legislation for any POPs. We had to compare the results of analyses for POPs with other than Kazakhstani national legislation limit values for contaminants in food. Those we used for free range chicken eggs are summarized in Table 2. There is a Kazakhstani limit value for the content of mercury in chicken eggs (see Table 2).

TABLE 2: LIMIT CONCENTRATION VALUES FOR OCPs, MERCURY, PCBs AND PCDD/Fs TEQS IN CHICKEN EGGS

Unit	Hen eggs				
	Kazakhstani MAC[7] ng g^{-1} *	Russian MAC[1] pg g^{-1} fat	Russian MAC[4] ng g^{-1} *	EU ML[2] pg g^{-1} fat	EU MRL[3] ng g^{-1} fat
WHO-PCDD/Fs TEQ		3.0		2.5	
WHO-PCDD/Fs-dl-PCB TEQ				5.0	
PCBs[5]				40	
DDT total[6]					50
p,p´-DDT			100		
γ-HCH (lindane)			100		10
α-, β-HCH			100		20, 10**
HCB					20
Mercury	20				

[1]Current Russian СанПиН 2.3.2. 2401-08 Hygienic safety and nutrition value requirements for food. Sanitary-epidemiologic rule and normatives (СанПиН 2.3.2. 2401-08 Гигиенические требования безопасности и пищевой ценности пищевых продуктов Санитарно-эпидемиологические правила и нормативы)
[2]EU Regulation (EC) N°1259/2011
[3]Regulation (EC) N°149/2008. Maximum residue level (MRL) means the upper legal level of a concentration for a pesticide residue in or on food or feed set in accordance with the Regulation, based on good agricultural practice and the lowest consumer exposure necessary to protect vulnerable consumers.
[4]Russian Federation GN 1.2.2701-10 Hygienic normatives (standards) pesticides concentration in environmental media (ГН 1.2.2701-10 "Гигиенические нормативы содержания пестицидов в объектах окружающей среды")
[5]sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180
[6]sum of p,p´-DDT, o,p´-DDT, p,p´-DDE and p,p´-DDD
[7]Kazakhstan SanPin Hygienic safety requirement and nutrition value for food from 11th June2003
*not clear whether calculated for fat content or not
**for each congener is MRL set separately

4. RESULTS

The results of the analyses by using DR CALUX are summarized in Table 3 and the graph in Figure 1. The results of the analyses for other POPs and congener analyses by using HRGC-HRMS are summarized in Table 4. There are also few results for analyses of mercury content in selected samples of eggs in Table 4. The graph in Figure 2 compares the results of the analyses for 6 PCB indicator congeners. The graph also shows a comparison with EU limit value for PCBs content in chicken eggs. Free range chicken eggs from China and Belarus were also analyzed by using the same methods. So we can compare data from Kazakhstani hot spots with similar locations in other countries as well. The results for samples from China and Belarus are presented in Tables 3 and 4 together with the results for samples from Kazakhstan.

The results for OCPs on fresh weight basis are summarized in Table 5 and compared with respective EU limit values.

4.1 Dioxins (PCDD/Fs) and dioxin-like PCBs measured by DR CALUX

All samples of chicken eggs collected at Kazakhstani hot spots during a field visit in 2013 were screened for dioxins and dioxin-like PCBs by using the DR CALUX method in BDS laboratory, Amsterdam. Two samples from a second sampling period in 2014 were also analyzed there. The results are summarized in Table 3 together with selected results for the eggs from China and Belarus.

TABLE 3: RESULTS OF DR CALUX BIOASSAY ANALYSES FOR BOTH PCDD/Fs AND DL PCBs FOR SAMPLES FROM KAZAKHSTAN, CHINA AND BELARUS. DATA ARE IN pg BEQ g^{-1} FAT.

Sample	Locality	Country	PCDD/Fs and DL PCBs (DR CALUX)	PCDD/Fs (DR CALUX)
EKI-14-3-EGG	Ekibastuz – Soyuz	Kazakhstan	3.8	1.3
eki egg 2	Eikbastuz – dachas South	Kazakhstan	4.8	NA
eki egg 1	Eikbastuz – substation	Kazakhstan	6.4	NA
NUR egg 1	Samarkand village; Nura	Kazakhstan	9.2	NA
NUR egg 24-1	Rostovka; Nura	Kazakhstan	9.4	NA
B 2	Balkhash – Rembaza	Kazakhstan	12	NA
B 3	Balkhash – southwest	Kazakhstan	15	NA
ARAI EGG	Shabanbai Bi	Kazakhstan	16	7.6
NUR egg 24-2	Chkalovo; Nura	Kazakhstan	18	NA
B 1	Balkhash – Rembaza	Kazakhstan	24	NA
NUR egg dam	Temirtau; Samarkand dam	Kazakhstan	28	NA
B 5	Balkhash – southwest	Kazakhstan	33	NA
B 4	Balkhash – north	Kazakhstan	101	NA
LN 321/14	Beijing – supermarket	China	1.2	NA
LN 272/14	Gatovo	Belarus	8.1	5.2
Beihai 3 and 4	Beihai II	China	8.9	7.4
Likeng	Likeng	China	17	
Beihai 5 and 6	Beihai III	China	24	20
Beihai 1 and 2	Beihai I	China	37	30
LN 273/14	Wuhan 1	China	35	31

When PCDD/Fs levels determined by the DR CALUX method are discussed, the following has to be considered. This cell based reporter gene assay is a validated method for screening for PCDD/Fs and DL PCBs contents in food according to EU Commission Regulation EC/252/2012 (European Commission 2012). Screening methodologies are usually used to exempt those samples that are below the maximum permitted limit (i.e. are compliant with the limit) and that can, therefore, be released to the market. In addition, one needs to select those samples that require confirmation (i.e. are suspected to be non-compliant) of their PCDD/Fs TEQ level. When bioassays are used as screening tools, the interpretation of the obtained results should consider that also other dioxin-like POPs (such as mixed-halogenated dioxins/PCBs, N-dioxins) are covered by such effect-based bioanalysis tools (van Overmeire, van Loco et al. 2004, Gasparini M 2011).

Thirteen pool egg samples were analyzed using the DR CALUX method for determination of dioxin activity in total. Among those only two samples from Ekibastuz were below limits set up by the EU also used for consideration of results obtained by DR CALUX analyses. All other eleven samples were above 5 pg BEQ g^{-1} fat level for total PCDD/Fs and DL PCBs content, as it is shown by the graph in Figure 1. The highest level of 101 pg BEQ g^{-1} fat was measured in chicken eggs from Balkhash city, north from the metallurgical plant. The sample was taken in 2013 at the site where we were not able to repeat sampling in 2014. All other samples from Balkash city were also high, between 12 and 33 pg BEQ g^{-1} fat. These levels are comparable to those obtained for free range chicken eggs from Beihai, a similar hot spot with a metallurgical plant in China (8.9–37 pg BEQ g^{-1} fat). Samples for Temirtau broader area show slightly lower levels, between 9.2 and 28 pg BEQ g^{-1} fat, however not significantly lower than those from Balkhash. The sample from Shabanbai Bi which was considered to be a clean area (and sampled as such in 2014) has shown high contents of dioxins/DL PCBs at a total level of 16 pg BEQ g^{-1} fat, although the results suggest higher levels of DL PCBs rather than PCDD/Fs, which is the complete opposite compared to the locality of, for example, a waste incinerator in Wuhan, China and/or metallurgical site of Beihai, China (see results for PCDD/Fs share on total BEQ in Table 3). The sample from Shabanbai Bi was also analyzed by GC-HRMS for specific congeners and results have shown an even higher total TEQ content of PCDD/Fs plus DL PCBs and confirmed that the PCB share is higher than PCDD/Fs.

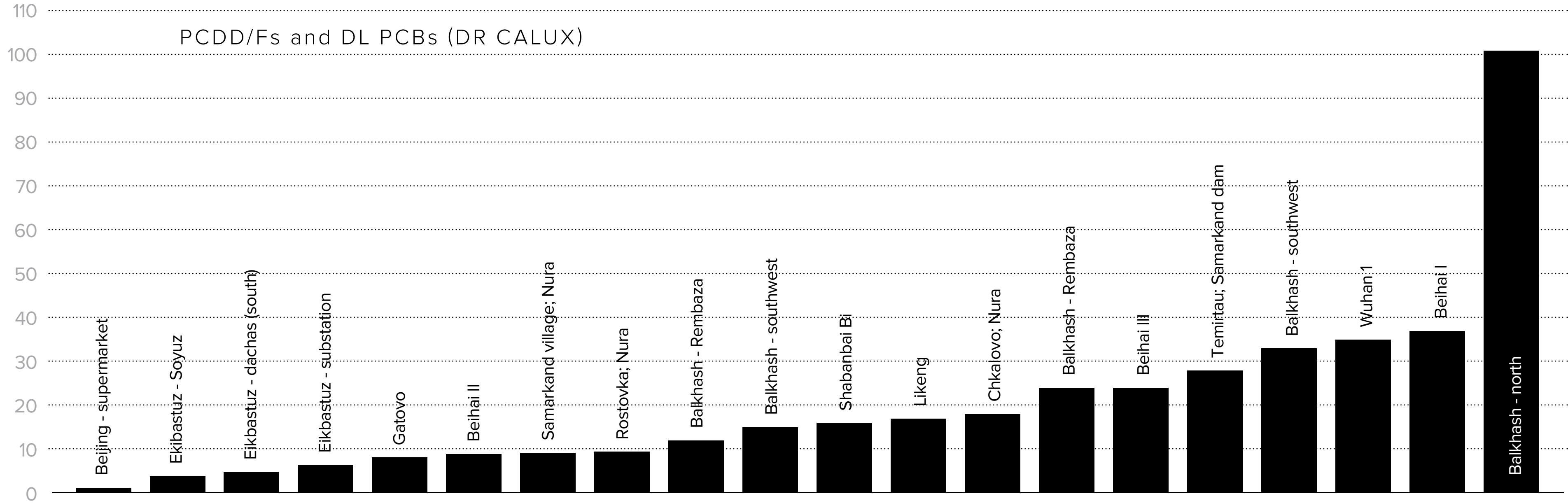


Figure 1: Graph showing comparison of total PCDD/Fs and DL PCBs in pg BEQ g^{-1} fat for different pooled chicken eggs samples from Kazakhstan, China and Belarus (full set of results is in Table 3).

4.2 Dioxins (PCDD/Fs), PCBs and other POPs measured by gas chromatography methods

GC-HRMS analyses were chosen for confirmation of contamination by dioxins and dioxin-like PCBs of chicken eggs at the same localities where they have been shown to be suspected for potentially high levels of these POPs after the first year of sampling. The same samples were also analyzed for other POPs, group of OCPs: hexachlorobenzene (HCB), hexychlorocyclohexanes (HCHs) and DDT and its metabolites. HCB is also considered to be an unintentionally produced POP (U-POP) in the same processes as dioxins and DL PCBs (Stockholm Convention on POPs 2008), although it is commonly measured together with other OCPs. Ten pooled samples of eggs were analyzed for PCDD/Fs and DL PCBs in total and eleven samples for other POPs. A few samples were also measured for mercury content. The results are summarized in Table 4.

TABLE 4: SUMMARIZED RESULTS OF ANALYSES FOR POPS AND MERCURY FOR TEN POOLED FREE RANGE CHICKEN EGGS SAMPLES FROM THE SECOND YEAR OF SAMPLING (2014), PLUS A BACKGROUND SAMPLE FROM A SUPERMARKET IN KARAGANDA SAMPLED IN 2015. THERE ARE ALSO RESULTS FOR SELECTED SAMPLES FROM CHINA AND BELARUS, AND EU LIMIT VALUES FOR COMPARISON.

Locality	Balkhash - southwest	Balkhash - southwest	Balkhash - Rembaza	Balkhash - Rembaza	Ekibastuz - substation	Ekibastuz - Soyuz	Ekibastuz - Soyuz	Rostovka	Chkalovo	Shabanbai Bi	Karaganda - superm.
Sample	BAL-EGG-14-1	BAL-EGG-14-2	BAL-EGG-14-3	BAL-EGG-14-4	EKI 14-1-EGG/EKI-27-EGG	EKI-14-2-EGG	EKI-14-3-EGG	NUR-EGG-14-1	NUR-EGG-14-2	ARAI-EGG	KAR-SUP
Fat content	12.45	9.95	10.15	11.35	12.4	11.7	13.3	15	13.7	10.15	14.0
PCDD/Fs (pg WHO TEQ g^{-1} fat)	7.69	9.81	7.73	4.25	5.73	1.57	NA	2.79	1.82	9.26	0.90*
DL PCBs (pg WHO TEQ g^{-1} fat)	7.66	2.88	22.33	13.70	6.45	2.89	NA	26.51	25.94	28.62	0.00*
Total PCDD/Fs + DL PCBs (pg WHO TEQ g^{-1} fat)	15.35	12.70	30.06	17.96	12.18	4.46	NA	29.30	27.76	37.88	0.90
PCDD/Fs and DL PCB (DR CALUX); (pg BEQ g^{-1} fat)	NA	NA	NA	NA	NA	NA	3.8	NA	NA	16	NA
PCDD/Fs (DR CALUX); (pg BEQ g^{-1} fat)	NA	NA	NA	NA	NA	NA	1.3	NA	NA	7.6	NA
HCB (ng g^{-1} fat)	1.68	2.62	4.39	2.13	5.40	1.28	1.58	2.33	5.04	6.25	1.09
7 PCB (ng g^{-1} fat)	23.37	11.54	76.64	52.19	27.18	29.49	13.76	319.40	395.18	2001.87	0.99
6 PCB (ng g^{-1} fat)	17.47	10.12	58.84	42.74	22.98	21.71	10.45	275.47	360.44	1975.97	0.99
sum HCH (ng g^{-1} fat)	6.84	114.14	20.71	34.40	11.05	13.25	33.76	45.67	15.33	860.80	0.36
sum DDT (ng g^{-1} fat)	10.10	34.05	318.87	1057.80	14.52	168.72	126.09	136.40	111.24	287.03	1.03
Hg (ng g^{-1})	NA	NA	NA	NA	NA	NA	NA	10.00	NA	1.00	NA

Locality	Beijing -supermarket	Wuhan	Wuhan	Gatovo	EU stand.
Sample	**LN 321/14**	**LN 324/14**	**LN 273/14**	**LN 272/14**	
Fat content	10.14	12.46	15.5	15.4	
PCDD/Fs (pg WHO TEQ g^{-1} fat)	0.20	8.59	12.17	4.25	2.50
DL PCBs (pg WHO TEQ g^{-1} fat)	0.28	4.70	3.79	11.33	
Total PCDD/Fs + DL PCBs (pg WHO TEQ g^{-1} fat)	0.48	13.29	15.96	15.58	5.00
PCDD/Fs and DL PCB (DR CALUX); (pg bio-TEQ g^{-1} fat)	1.2	8.8	35	8.1	5.00
PCDD/Fs (DR CALUX); (pg bio-TEQ g^{-1} fat)	NA	5.8	31	5.2	2.50
HCB (ng g^{-1} fat)	3.52	28.90	480.65	2.86	20.00
7 PCB (ng g^{-1} fat)	2.10	5.29	1.03	66.36	-
6 PCB (ng g^{-1} fat)	2.10	5.29	1.03	52.92	40.00
suma HCH (ng g^{-1} fat)	1.34	5.23	2.32	4.94	-
suma DDT (ng g^{-1} fat)	0.21	26.25	33.23	230.65	-
Hg (ng g^{-1})	NA	NA	NA	2.00	-

* more precise results are as follows: PCDD/Fs 0,89812 pg WHO-TEQ g^{-1} and DL PCBs 0,000263 pg WHO-TEQ g^{-1}

4.2.1 Dioxins (PCDD/Fs) and dioxin-like PCBs (DL PCBs)

Dioxins belong to a group of 75 polychlorinated dibenzo-p-dioxin (PCDD) congeners and 135 polychlorinated dibenzofuran (PCDF) congeners, of which 17 are of toxicological concern. Polychlorinated biphenyls (PCBs) are a group of 209 different congeners which can be divided into two groups according to their toxicological properties: 12 congeners exhibit toxicological properties similar to dioxins and are therefore often referred to as 'dioxin-like PCBs' (DL PCBs). The other PCBs do not exhibit dioxin-like toxicity but have a different toxicological profile and are referred to as 'non dioxin-like PCB' (NDL PCBs) (European Commission 2011). Levels of PCDD/Fs and DL PCBs are expressed in total WHO-TEQ calculated according toxic equivalency factors (TEFs) set by WHO experts panel in 2005 (Van den Berg, Birnbaum et al. 2006). These new TEFs were used to evaluate dioxin-like toxicity in ten pooled samples of chicken eggs from Kazakhstan.

Seven out of ten and six out of ten samples from Kazakhstan exceeded EU and Russian MAC levels of PCDD/Fs congeners in chicken eggs, respectively (compare Tables 4 and 2) and eight out of total ten samples exceeded EU limit value for both PCDD/Fs and DL PCBs in chicken eggs (European Commission 2011). The background levels for PCDD/Fs and DL PCBs measured in chicken eggs from a supermarket in Karaganda were 0.89812 and 0.00026 pg WHO-TEQ g^{-1} fat, respectively (see also discussion about background levels further in text). The highest level of dioxins (9.81 pg WHO-TEQ g^{-1} fat) was measured in eggs from Balkhash – southwest (BAL-EGG-14-2) and almost the same level was measured in the sample from Shabanbai Bi, which had highest level of total WHO-TEQ (37.88 pg WHO-TEQ g^{-1} fat), and toxicity of DL PCBs has prevailed in that sample (see graph in Figure 3). Most of the egg samples showing high levels of total WHO-TEQ had a prevalence of DL PCBs share over PCDD/Fs on total WHO-TEQ, as shown by the graph in Figure 3. It shows how big the impact is of potential PCBs sources of pollution or their creation in industrial processes such as metallurgical plants. Only in two egg samples from Balkhash – southwest PCDD/Fs were clearly dominating over DL PCBs in the sum of the total WHO-TEQ.

Total WHO-TEQ levels of PCDD/Fs and DL PCBs in samples from Kazakhstani hot spots are higher than in selected samples from Chinese and Belorussian hot spots; however, higher levels of PCDD/Fs were observed in eggs from the surroundings of the Wuhan waste incinerator in China. Samples from Shabanbai Bi, Rostovka, Chkalovo and Balkhash – Rembaza would belong to those with rather high levels of dioxins and DL PCBs, also in comparison with collection of samples from IPEN´s The Egg Report from 2005, and comparable with samples from Dandora, Kenya (mixed waste dumpsite), Lucknow, India (medical waste incinerator site) or Mbeubeuss, Senegal (mixed waste dumpsite) (DiGangi and Petrlik 2005, IPEN Dioxin PCBs and Waste Working Group, Envilead et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Pesticide Action Network (PAN) Africa et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Toxics Link et al. 2005). Putative sources of dioxin and dioxin-like PCBs contamination at selected Kazakhstani hot spots are considered in the discussion part below.

4.2.2 Polychlorinated biphenyls (PCBs)

Five out of a total of ten free range chicken eggs samples from Kazakhstani hot spots exceeded the EU limit for 6 PCB indicator congeners in hen eggs. An extremely high level of 1976 ng g^{-1} fat was observed in eggs from Shabanbai Bi and exceeded the EU

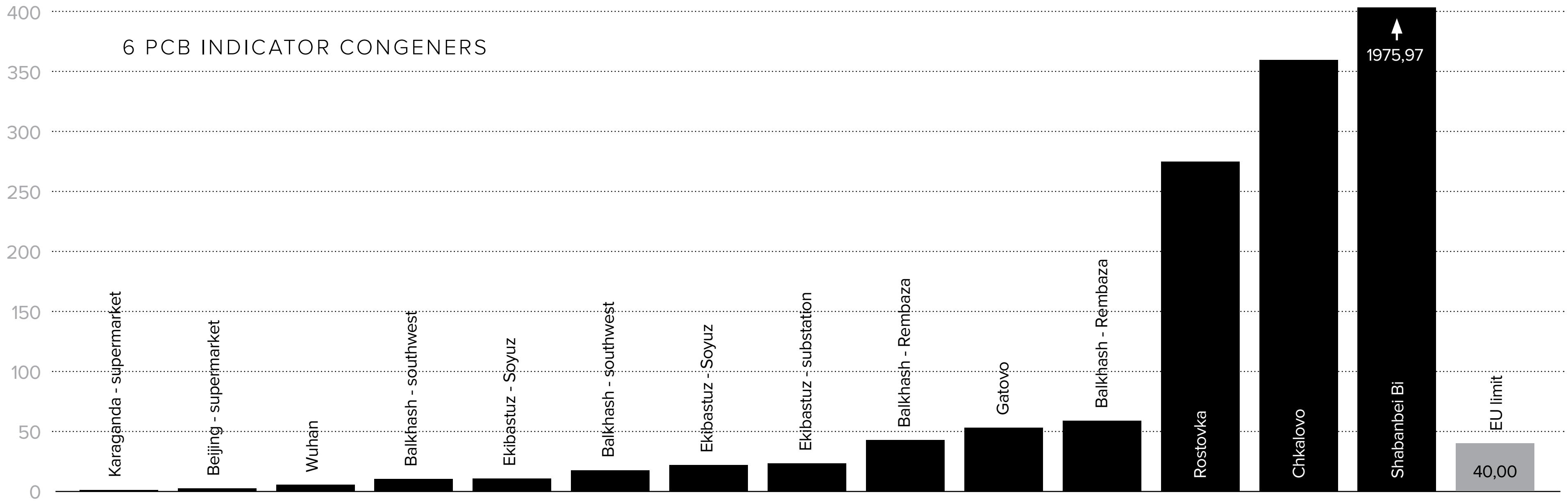


Figure 2: Graph comparing 6 PCB congener levels in different pooled chicken eggs samples from Kazakhstan, China and Belarus (full set of results is in Table 3).

limit by almost 50 fold. Six PCB congener levels in the samples from Rostovka and Chkalovo on river Nura exceeded the EU limit by seven and nine fold, respectively. All these three samples can be considered as highly contaminated by PCBs and potential sources of contamination should be found. Also, dioxin-like PCBs were high in all these three samples and were major contributors to the overall WHO-TEQ level in these pooled egg samples (see the graph in Figure 3).

Two samples from Balkhash – Rembaza also exceeded the EU limit value for 6 PCB congeners, although not so significantly. Also in this case DL PCBs were major contributors to total TEQ in eggs (see graph at Figure 3). Prevalence of PCBs upon PCDD/Fs in total TEQ was also measured in samples from Ekibastuz, where an electricity substation contaminated by PCBs is a putative source of egg contamination by U-POPs.

4.2.3 Organochlorinated pesticides (OCPs)

EU limits for pesticide residues, including OCPs in chicken eggs, are set per fresh weight of egg. A comparison of OCPs in eleven samples of chicken eggs from Kazakhstan is in Table 5. EU limits were exceeded only in two samples: the limit for the sum of DDT was exceeded in eggs from Balkhash – Rembaza (BAL-EGG-14-4) by more than two fold, and the limit for β-HCH was exceeded in the sample from Shabanbai Bi by more than six fold. Levels of p,p'-DDT were 124 and 441 ng g^{-1} fat respectively in two samples from Balkhash – Rembaza, which is over MAC according Russian legislation (see Table 2).

All free range chicken egg samples exceeded the background level of DDT in the eggs bought in the supermarket. Significantly higher levels of DDT were in the second sample from Balkhash – Rembaza (BAL-EGG-14-3), Shabanbai Bi, two samples from Ekibastuz – Soyuz, Rostovka, and Chkalovo. A comparable level of DDT was also found in free range chicken eggs from Gatovo. High levels of HCHs were only observed in the sample from Shabanbai Bi, and an elevated level of β-HCH near to the EU limit value was also found in eggs from Balkhash – southwest (BAL-EGG-14-2).

4.2.4 Mercury

Mercury levels in the two analyzed pooled samples of eggs were below the Kazakhstani limit. The level in eggs from Rostovka on the river Nura was 10-times higher than in the sample from Shabanbai Bi.

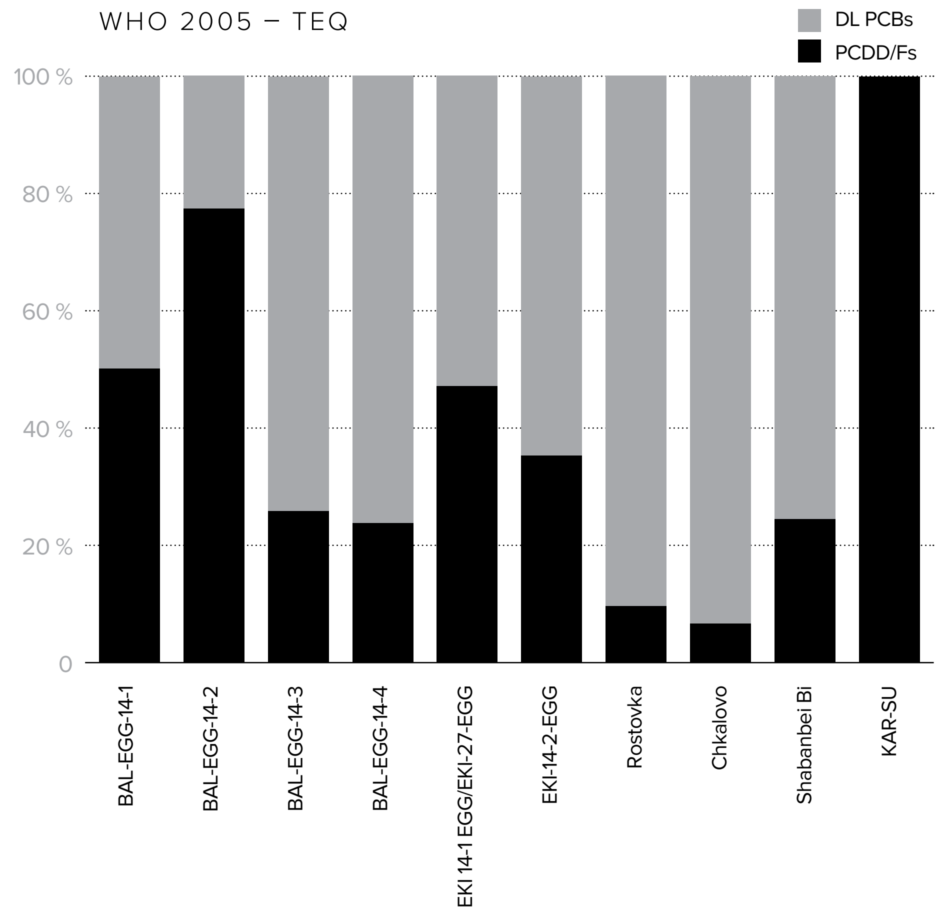


Figure 3: Balance between PCDD/Fs and DL PCBs on total WHO-TEQ levels in chicken egg samples from Kazakhstan.

TABLE 5: SUMMARIZED RESULTS OF ANALYSES FOR OCPs FOR TEN POOLED FREE RANGE CHICKEN EGG SAMPLES FROM THE SECOND YEAR OF SAMPLING (2014) PLUS A BACKGROUND SAMPLE FROM A SUPERMARKET IN KARAGANDA SAMPLED IN 2015. THERE ARE ALSO EU LIMIT VALUES FOR COMPARISON. THESE RESULTS ARE EXPRESSED IN ng g^{-1} FRESH WEIGHT BECAUSE EU LIMITS ARE SET FOR FRESH WEIGHT FOR OCPs.

Locality	Balkhash - southwest	Balkhash - southwest	Balkhash - Rembaza	Balkhash – Rembaza	Shabanbai Bi	Ekibastuz - substation	Ekibastuz - Soyuz	Ekibastuz - Soyuz	Rostovka	Chkalovo	Karaganda – superm.	EU stand.
Sample	BAL-EGG-14-1	BAL-EGG-14-2	BAL-EGG-14-3	BAL-EGG-14-4	ARAI-EGG	EKI-14-1-EGG; EKI-27-EGG	EKI-14-2-EGG	EKI-14-3-EGG	NUR-EGG-14-1	NUR-EGG-14-2	KAR-SUP	
HCB	0.21	0.26	0.45	0.24	0.63	0.67	0.15	0.21	0.35	0.69	0.15	20.00
α-HCH	0.13	1.30	0.26	0.80	18.47	0.07	0.16	0.75	0.48	0.14	0.01	20.00
γ-HCH	0.00	0.71	0.28	0.51	2.52	0.01	0.45	0.41	0.34	0.16	0.05	10.00
β-HCH	0.72	9.34	1.56	2.60	66.38	1.30	0.94	3.33	6.03	1.80	0.01	10.00
suma-4DDT (EU)	1.28	3.39	32.30	119.83	29.02	1.82	19.68	16.77	20.46	15.24	0.17	50.00

5. DISCUSSION

5.1 Background levels of POPs in eggs

The locality of Shabanbai Bi as a remote area in Kazakhstan has shown high levels of certain POPs in free range chicken eggs and therefore cannot be considered as a background locality for POPs. As this was discovered at a very late stage in our research; we sampled chicken eggs from a supermarket in Karaganda from chickens raised in a large farm without access to open air space in April 2015 in order to obtain information about background levels of POPs in chicken eggs from Kazakhstan. The results of the analyses for this sample are in Tables 4 and 5. The levels of POPs in this sample were similar for PCDD/Fs and DL PCBs (DiGangi and Petrlik 2005) or lower, e.g. for HCB, non-ortho PCBs or DDT (DiGangi and Petrlik 2005, IPEN Pesticides Working Group 2009), compared to those observed in the background samples from other studies of POPs in chicken eggs .

5.2 Dioxin congener patterns and putative sources

We can compare dioxin congener patterns in free range chicken eggs with their typical patterns for certain types of pollution sources in order to get closer to discovery of their sources at the studied sites. The graph in Figure 4 shows the balance between PCDDs and PCDFs in egg samples and two non-egg samples (air emissions from a lead smelter or the content of PCDD/Fs in asbestos cement fibre plates). There are egg samples from a previous IPEN report where the most likely dioxin sources were identified. The division between PCDD and PCDF congeners in toxic equivalents is used as one of the criteria for a basic classification of potential sources (Sam-Cwan 2003, Yoon-Seok 2003). However, it can be only used as basic information; further analysis of the dioxin congener pattern is needed.

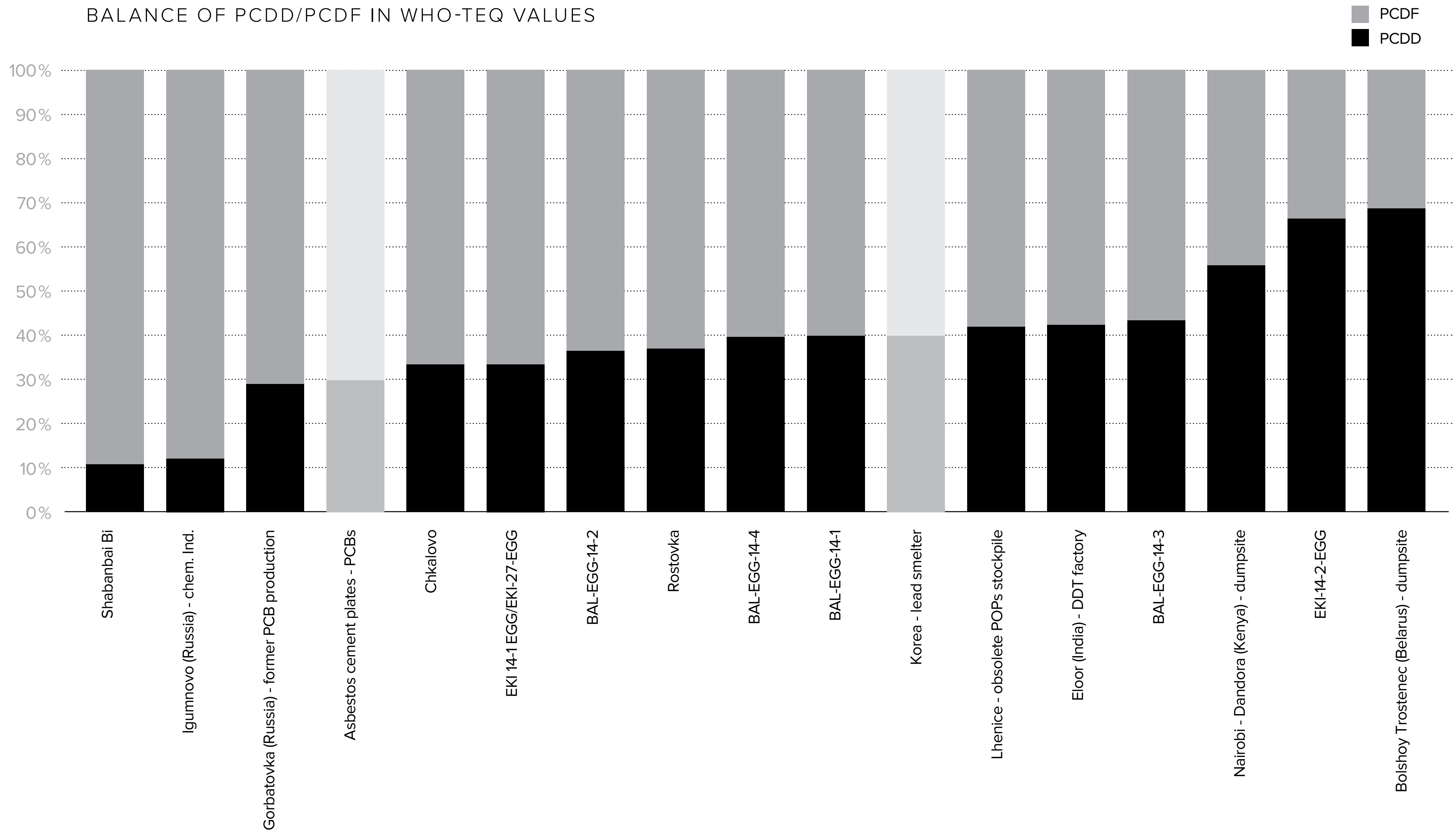
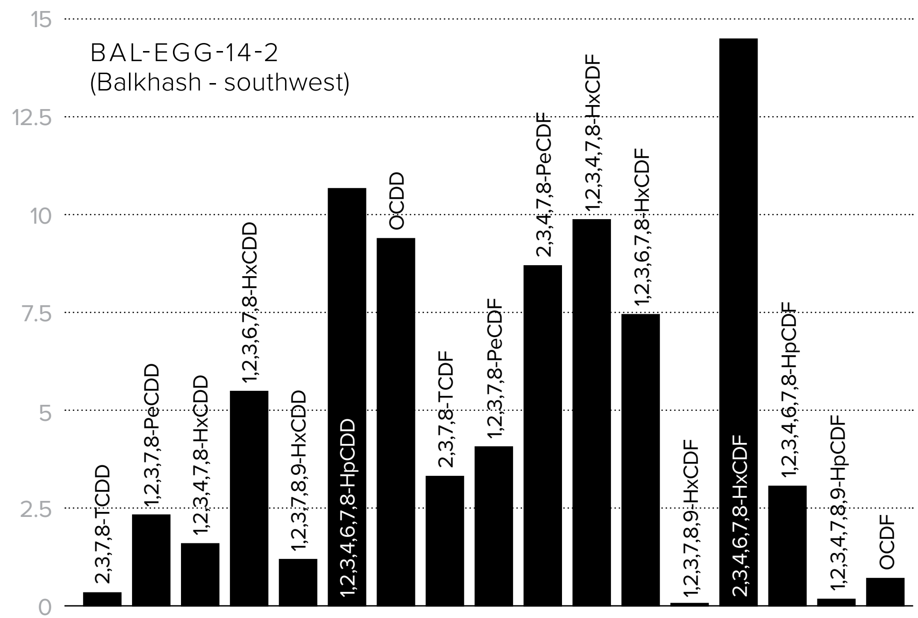


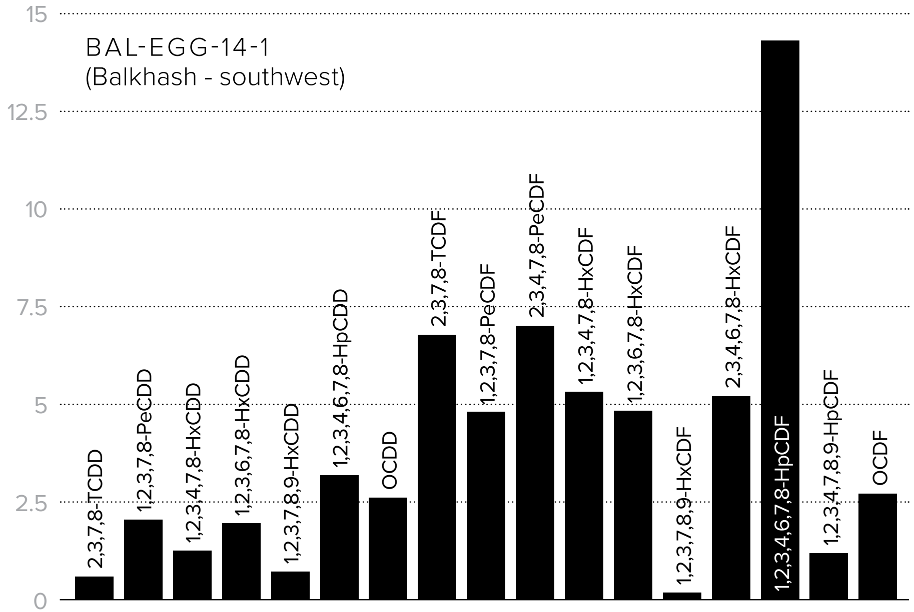
Figure 4: Share of PCDD and PCDF congeners on total WHO-TEQ values in different free range chicken eggs (in darker colours) and two other matrix samples (bars in less intense colour). Sources of information: for data on eggs (IPEN Dioxin PCBs and Waste Working Group, Eco-SPES et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Envilead et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Foundation for Realizaiton of Ideas et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Periyar Malineekarana Virudha Samithi - PMVS et al. 2005); for other data (Sam-Cwan 2003, Winkler 2015).

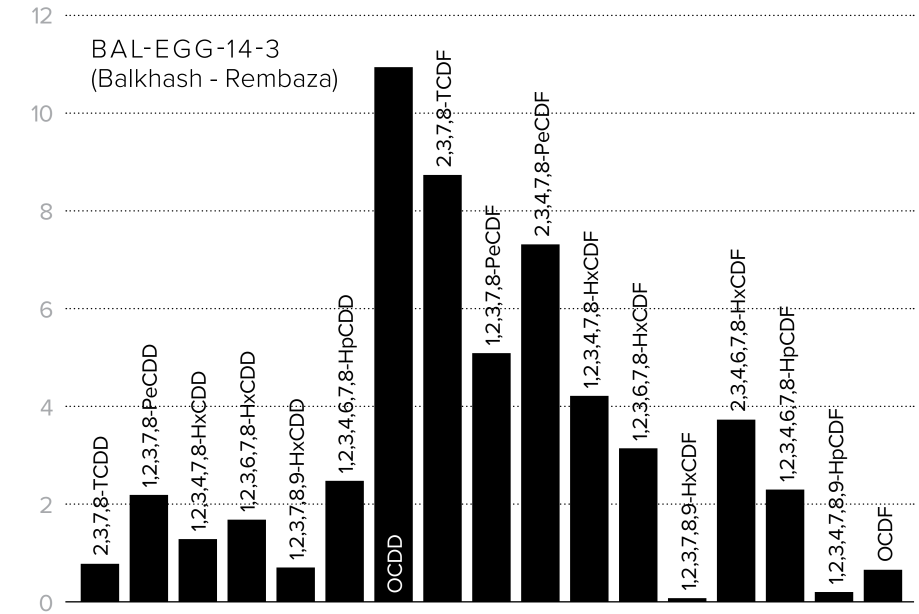
5.2.1 Balkhash

It is clear that there is not only one single source of contamination of free range chicken eggs in Balkhash city when we compare dioxin congener patterns for these samples (see graphs in Figures 5–8) although they are close to each other from Balkhash – southwest and Balkhash – Rembaza. A similar dioxin congener pattern to sample BAL-EGG-14-4 can be found in the eggs collected in Lhenice, Czech Republic (see graph in Figure 9), where the putative source of contamination is an old environmental burden, obsolete PCBs and pesticide storage. There is also a certain similarity in the relatively high levels of DDT and its metabolites in sample BAL-EGG-14-4 and Lhenice, although the total values of DDT in each pooled egg sample is different.

BAL-EGG-14-3 is close to the PCDD/Fs pattern in a sample from Helwan, Egypt (see graph in Figure 10) (IPEN Dioxin PCBs and Waste Working Group, Day Hospital Institute et al. 2005). Combustion sources, including the metallurgic industry, were marked as potential contamination sources in the case of the Helwan egg sample. We didn´t find



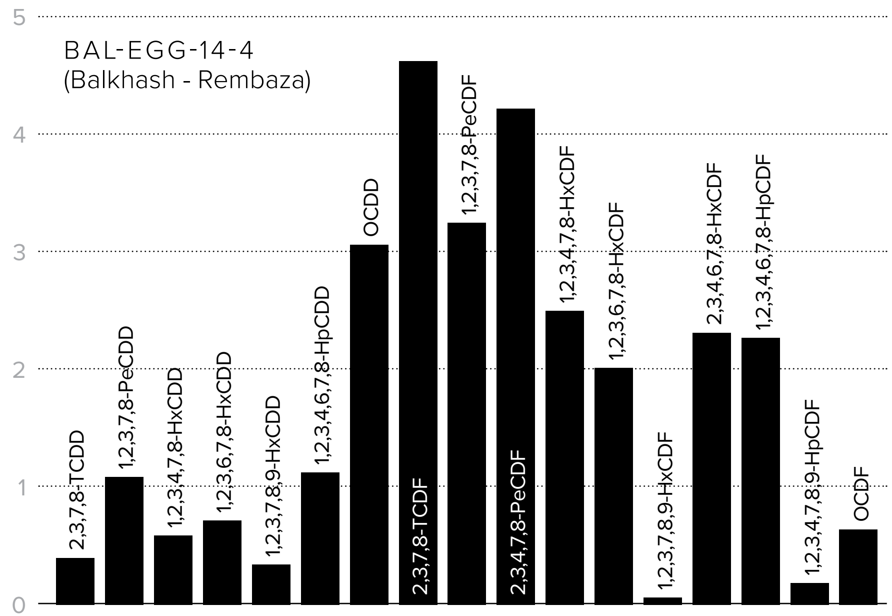




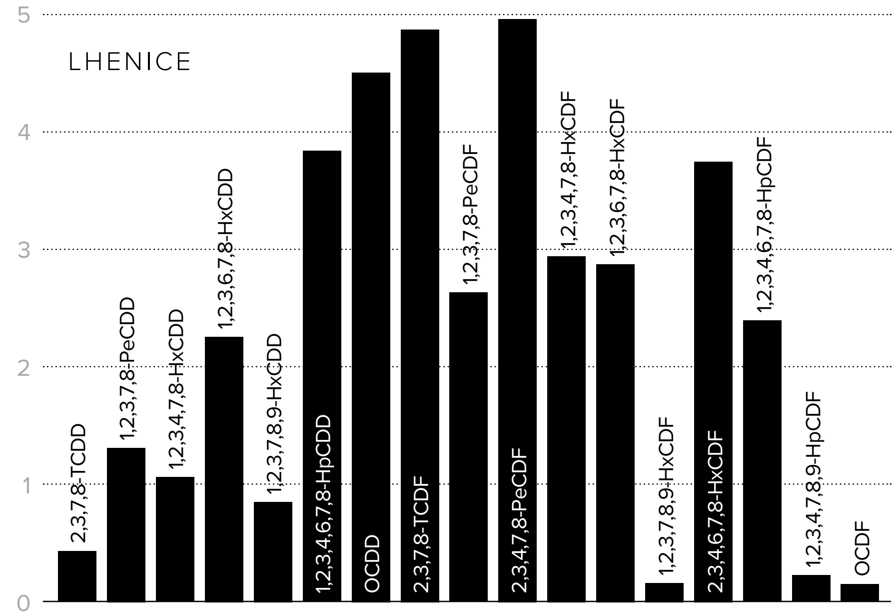
Figures 5–7: Dioxin congener patterns for free range chicken samples from the Balkhash city area.

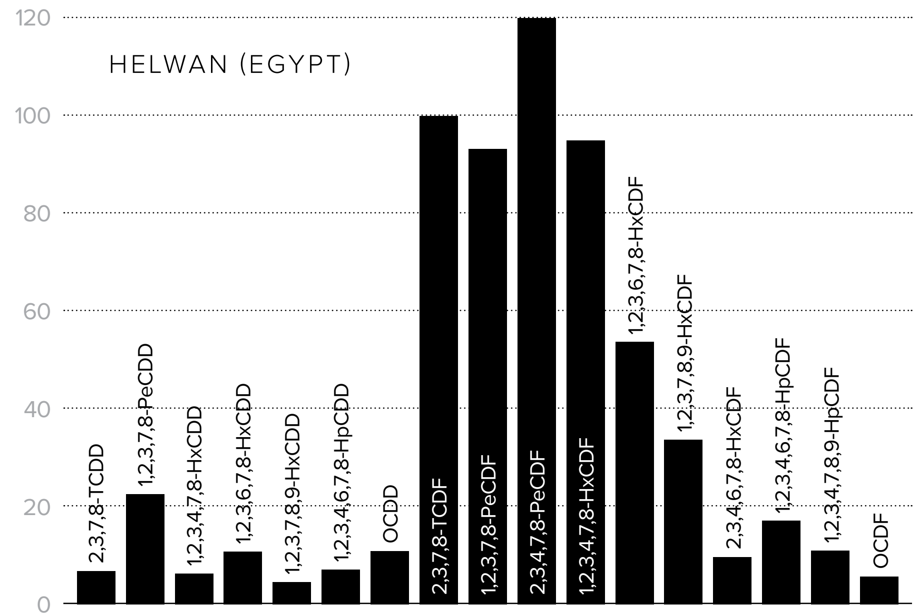
any potential single pattern for the rest of the samples from the Balkhash city area, but the prevalence of PCDFs show on some combustion sources or obsolete POPs stockpiles as sources of dioxins which can vary from open burning of waste to metallurgy.

A high level of dioxins of 264 pg WHO-TEQ g^{-1} was found in dust from a copper smelter in Balkhash, according to data published in the Kazakhstani National Implementation Plan on the Stockholm Convention (Republic of Kazakhstan 2009); however, raw data about the analysis are not publicly available. A significant level was also measured in an air sample in the smelter.



▲ **Figures 8:** Dioxin congener patterns for free range chicken samples from the Balkhash – Rembaza.





▶ **Figures 9–10:** Dioxin congener patterns in free range chicken eggs in a sample from Lhenice, Czech Republic (top) and in samples from Helwan, Egypt (bottom).

5.2.2 Area of river Nura and Shabanbai Bi

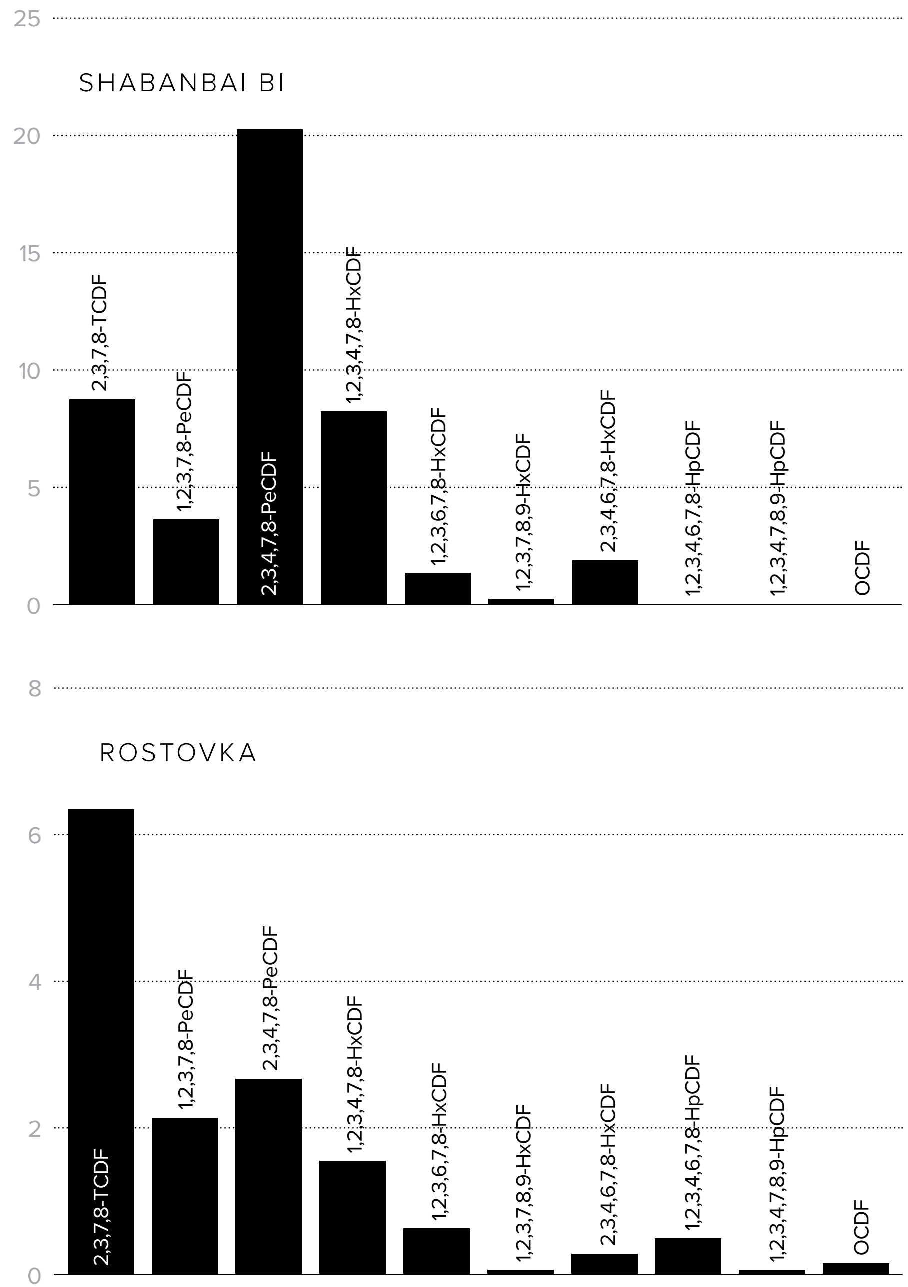
Polychlorinated dibenzofuran (PCDF) congener patterns in samples from Kazakhstan were compared with those for mixtures of PCBs: Sovtol described by Brodsky et al. (2005), Delor 103, 104, 105 and 106 as described by Taniyasu et al. (2003), and a PCBs containing material for asbestos roofs described by Winkler (2015). A similar profile for PCDF congener fingerprints for a free range chicken egg sample from Shabanbai Bi is very close to the Sovtol O3 sample or Delor 104, while profiles for chicken egg samples from Rostovka and Chkalovo are closer to Delor 106 (see graphs in Figures 11–19). In all of these three samples, DL PCBs also prevailed in comparison with PCDD/Fs as major contributors to total WHO-TEQ (see graph in Figure 3).

It seems that potential obsolete PCBs used in transformer oils or their stockpiles can be potential source of free range chicken egg contamination in Shabanbai Bi and river Nura area, or they can be present in feed used for chicken. A team from EcoMuseum has visited Shabanbai Bi in order to find the potential source of high contamination of eggs in this village, but its search was not successful. It could also be from an already removed obsolete POP stockpile, but contamination of buildings or soil left in the village. There are obsolete PCBs stockpiles as well as old transformers used in Temirtau and the river Nura area. PCDF congener pattern for asbestos roofs (Winkler 2015) is different.

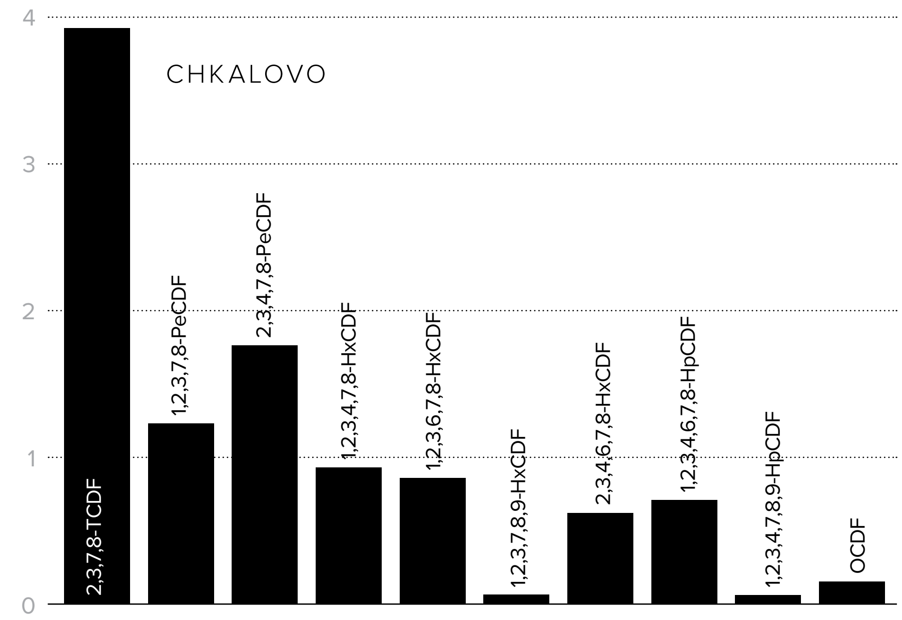
The highest mean level of 6 indicator PCB congeners was measured in ambient air in Temirtau 885 pg m^{-3} in comparison with 5 other locations in Kazakhstan in 2008 (UNEP GMP 2013). A high level of dioxins 608 pg WHO-TEQ g^{-1} was found in dust from a sinter plant of Mittal Steel in Temirtau, according to data published in the Kazakhstani National Implementation Plan on the Stockholm Convention (Republic of Kazakhstan 2009). A significant level was also measured in an air sample in the plant. Detailed PCDD/F congener patterns for these measurements were not available to us.

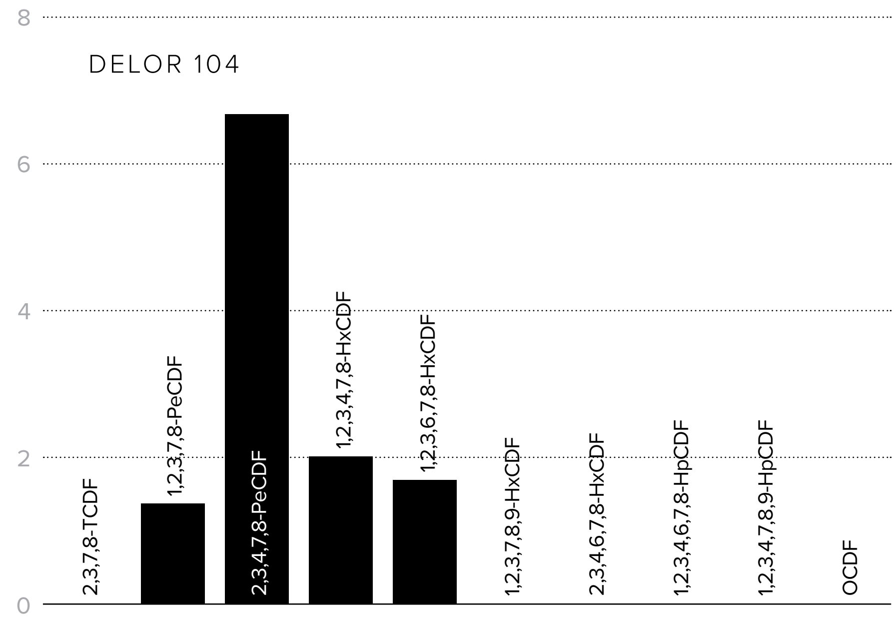
5.2.3 Ekibastuz

There are different PCDD/F congener patterns in pooled samples from Ekibastuz. This also shows an impact of different sources of contamination by dioxins at this lo-



▸ **Figures 11–12:** PCDF congeners patterns for free range chicken egg samples from Shabanbai Bi and Rostovka.


CHKALOVO
4
3
2
1
0
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
OCDF


DELOR 104
8
6
4
2
0
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
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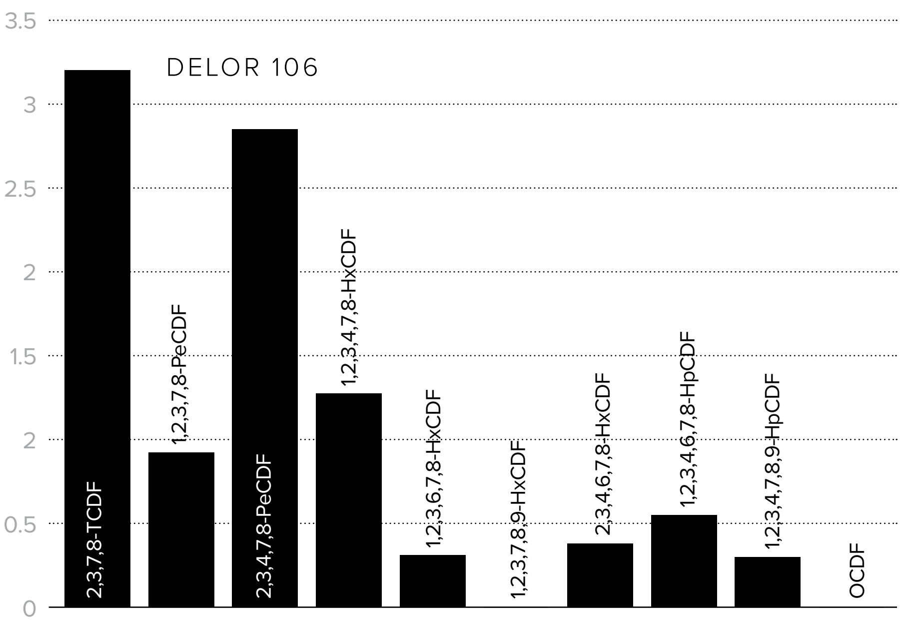
1,2,3,4,7,8,9-HpCDF
OCDF


DELOR 106
3.5
3
2.5
2
1.5
2
0.5
0
2,3,7,8-TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
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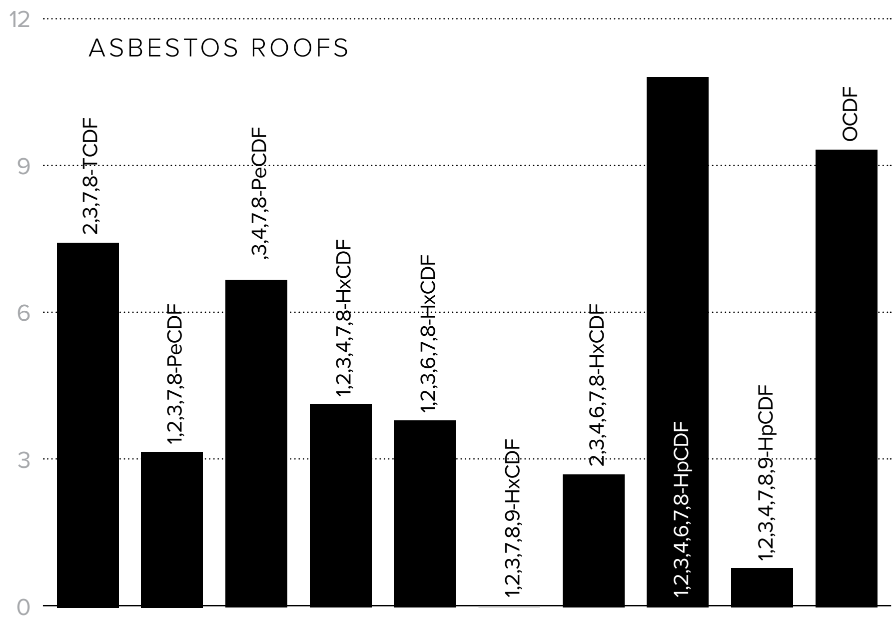
OCDF


ASBESTOS ROOFS
12
9
6
3
0
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1,2,3,7,8-PeCDF
,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
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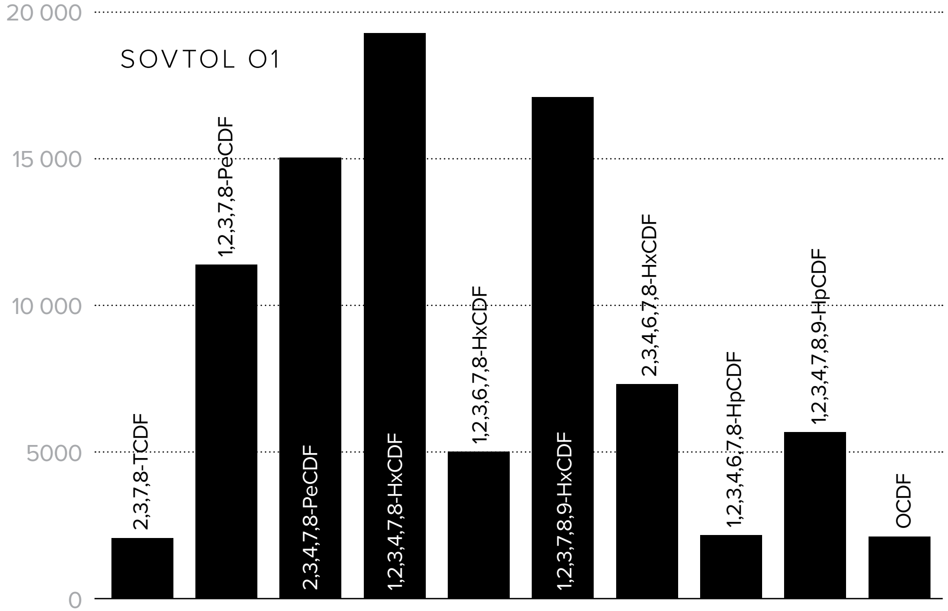
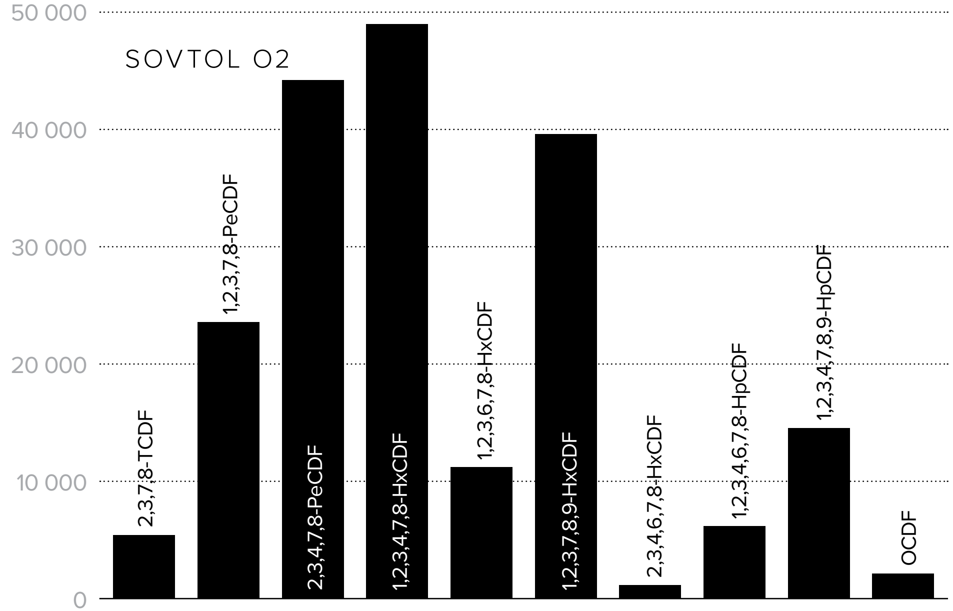
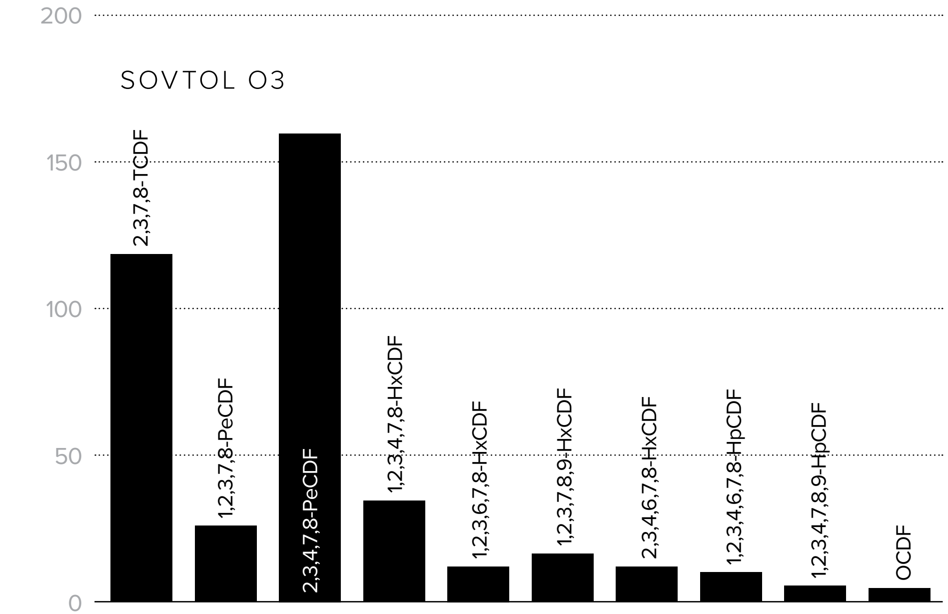
1,2,3,4,7,8,9-HpCDF
OCDF







◀ **Figures 13–19:** PCDF congeners patterns for free range chicken egg samples from Chkalovo in comparison with Delor 104 and Delor 106, according to data available in Taniyasu et al. (2003), Sovtol O1, O2 and O3 samples (Brodsky, Evdokimova et al. 2005), and asbestos roofs (Winkler 2015).

cality; however, DL PCBs cause a bigger portion of total dioxin-like toxicity in egg samples. It can be linked to historic contamination by PCBs at Ekibastuz electricity substation, although no specific PCB mixture pattern for PCDF congeners matched that found in chicken eggs in Ekibastuz.

5.3 PCBs, OCPs and their putative sources

High levels of currently banned POPs pesticides, such as DDT or HCHs, in samples from Shabanbai Bi and Balkhash show a potential presence of ongoing use of these obsolete pesticides or their presence in unknown stockpiles, either at the sites or at the location of origin of feed used for chickens.

6. CONCLUSIONS AND RECOMMENDATIONS

POPs contamination in some free range chicken eggs from Kazakhstani hot spots shows some potentially undiscovered obsolete POPs stockpiles, or so far publicly unknown sources of contamination. These results suggest the same conclusion as Muntean made for Uzbekistan in 2003: "Second, although this study and others provide some provisional data, not enough is known about the environmental fate of historical pesticide use and its current impact on human health. Research should therefore be conducted to document the environmental transformation and fate of certain pesticides and to assess their health impact. Environmental analysis should evaluate the degradation and environmental behavior of parent pesticides and their degradation or transformation products." (Muntean, Jermini et al. 2003). We can only add that for Kazakhstan such research should also be done more properly for obsolete PCB oils and other potential use of PCBs (paints, plaster, asbestos roofs etc.) although we are aware that a basic PCBs inventory has already been done or is underway. Sites contaminated by POPs should be properly remediated afterwards in order to get rid of POP contamination sources throughout the country.

High levels of PCDD/Fs and DL PCBs were found in free range chicken egg samples. Four-fifths of the samples exceeded EU MAC for PCDD/Fs and DL PCBs in chicken eggs. More regular monitoring of dioxins and DL PCBs in food samples should be undertaken by national authorities. The Cell based screening test DR CALUX(R) method has shown to be effective to find new polluted areas as well as for estimation of overall contamination of food stuff (eggs) by PCDD/Fs and DL PCBs collected from Kazakhstani hot spots.

Both Russian and EU MAC for PCDD/Fs and DL PCBs for chicken eggs used in this study were exceeded more often than those for 6 PCB congeners and OCPs. High levels of dioxins and dioxin-like PCBs in free range chicken eggs from Balkhash confirm serious contamination of the city by these pollutants. Our finding is in agreement with Kazakhstani NIP, which suggests the results of epidemiological studies among Balkhash population provide proof of the cancerogenicity and malignancy of POPs. The highest oncological disease rate in the period of 1999–2003 was observed in Balkhash (in comparison with several other locations and the Kazakhstani average) (Republic of Kazakhstan 2009). Measures to reduce dioxin and dioxin-like PCB releases from the metallurgic industry in Balkhash city, as well as in Temirtau, are crucial to overall reduction of releases of U-POPs in the studied region of Kazakhstan.

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PHOTOS

RIVER NURA

The River Nura is the main river of Central Kazakhstan. Water is widely used for household water supply, irrigation, industrial use and also for recreation and commercial fishing. The Nura has received high inputs of mercury since the 1950s, the source being the Karbid chemical factory in the city of Temirtau.

1. Former factory Karbid, the source of contamination of Nura by mercury.
2. Sampling of sediment in the river Nura in August 2013.
3. River Nura is typical steppe river. This picture shows beginning of Intumak water reservoir on Nura river where we found high levels of mercury in fish.


1.


2.


3.

EKIBASTUZ

The Ekibastuz electrical power substation was constructed for modifying alternating current (AC) to direct current (DC) using 15,000 capacitors filled with PCBs containing oils.

1. Chemical analysis of soil under the former stands of capacitors showed high levels of PCBs.
2. We took sample of the eggs from these chicken, sample is called Ekibastuz - substation.
3. Samples were taken also in the suburban areas around the substation with many dachas (cottages and gardens or orchards area).


1.


2.


3.

TEMIRTAU

In Temirtau live about 170,000 inhabitants. Steel Plant Arcelor Mittal Temirtau (AMT) is located at a distance of 500 m from the nearest houses.

1. and **2.** We sampled soil on the playgrounds in Temirtau in August 2013.
There are many such playgrounds in Temirtau.
3. Sampling of sediments at tailing pond of Karbid plant near Temirtau.
4. Inside ArcelorMittal steelworks in Temirtau.


1.

2.


3.


4.

BALKHASH

City in Karagandy Oblast, located on the northern shore of Lake Balkhash, at the Bay Bertys. Balkhash city (76,000 inhabitants) and its surroundings (30,000–50,000 inhabitants) are dominated by mining and nonferrous metallurgical enterprises. The Balkhash copper smelter is estimated to be the 22nd largest in the world.

1. The guys fishing in the canal of cooling water from power plant at metallurgical combinate.
2. In Balkhash, we also sampled the soil in the children playgrounds.
3. Sampling of bottom sediments of Lake Balkhash near metallurgical plant.


1.


2.

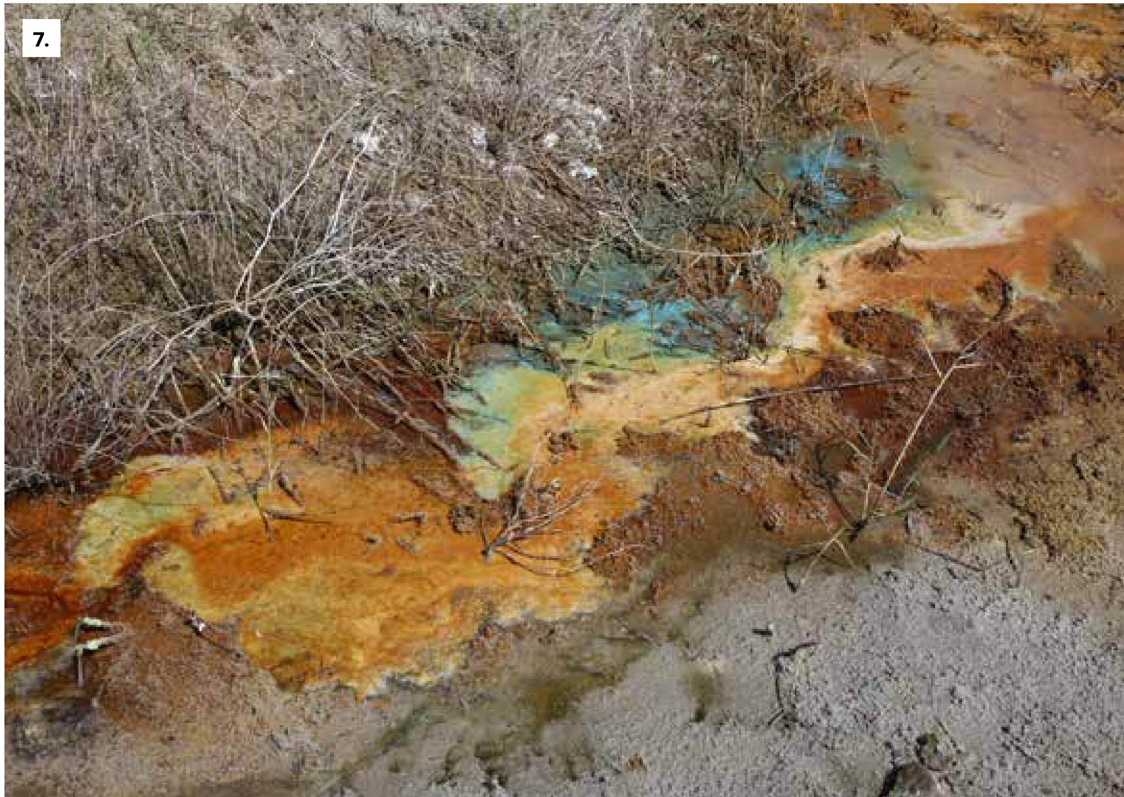

3.

4.

4. Samples taken from the outside of the tailing pond contained high concentrations of heavy metals.
5. Discharge slag heap in Balkhash
6. Samples of sediment had to be taken from several spots and then mix thoroughly.
7. This photo is from the point where the tailing pond dyke leaks on the shore of lake Balkhash. Deposits of different colors show on potential contamination by different metals.


5.


6.


7.

SHABANBAI BI

Shabanbai Bi is a village located in the southern part of the Karagandy Oblast, at the foot of Aksoran, the highest peak of the Kyzylarai mountains. We have chosen this site as a clean background locality, however the results of egg analysis have shown hidden problems.

GLUBOKOE

Glubokoe is a town in East Kazakhstan Oblast with almost 10,000 inhabitants. Five disposal sites of metallurgic slag from Itrysh Smelting Company (IMZ) belonging to Kazakhmys Corporation are located in the territory of Glubokoe.

The European Union is made of 28 Member States who have decided to gradually link together their know-how, resources and destinies. Together, during a period of enlargement of 50 years, they have built a zone of stability, democracy and sustainable development whilst maintaining cultural diversity, tolerance and individual freedoms. The European Union is committed to sharing its achievements and its values with countries and peoples beyond its borders.
The European Commission is the EU's executive body.

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