Stockholm Convention POPs in abiotic and biota samples from Mongolia

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1 Introduction

Mongolia is a Party to the Stockholm Convention on Persistent Organic Pollutants (POPs) since 2004 and for the first time, took part in the UNEP-coordinated regional project to support the implementation of the global monitoring plan (GMP) under the Convention (UNEP, 2015). Mongolia participated in all subprojects and recruited teams to participate in the air, human milk and water sampling networks as well as in interlaboratory assessments, and capacity building activities. The GMP has defined ambient air and water as core matrices for environmental occurrence and transport and human milk or human blood for human exposure. Results for POPs in these core matrices have been published recently (Surenjav et al., 2022).

On the other hand, many countries are interested in determining POPs concentrations in foodstuffs, including for regulatory purposes, or sediment and soil. Within the UNEP/GEF GMP2 projects, these additional samples were named 'national samples' (for long: samples of national interest to the participating country). A separate SOP addressing soil, sediment, meat, fish, dairy products or eggs was developed and applied for these projects (UNEP, 2017). These so-called national samples were analyzed in the project's central laboratories for the POPs and their transformation products as recommended in table 2.2 of the GMP guidance document (UNEP, 2021).

From the POPs pesticides, hexachlorocyclohexanes (HCH) have been used in Mongolia widely under the common name of "Dust" consisting of either α-HCH (12%) or an HCH emulsion (16%) that had been used from 1958 to 1985 as an insecticide in livestock ectoparasites (for mites, scabs, ticks, bloodsuckers, etc.), as well as for disinfecting animal shelters and ordure. HCH in powder form was mainly spread over small animals by hand, whereas big animals and cattle were driven into a cubicle where they were smoked by burning HCH. In addition, usage of hexachlorobenzene (HCB), chlordane, aldrin, dieldrin, and heptachlor was reported to have been used from 1969 to 2003 (Mongolian Academy of Sciences (MAS), 2022).

The occurrences, relative abundances, and distribution of 26 POPs listed in either annex A, B, or C of the Stockholm Convention were analyzed in abiotic and biota samples from Mongolia. Five of the listed POPs were not included in this project: chlordecone, polychlorinated naphthalenes, short-chained chlorinated paraffins, pentachlorophenol, and dicofol.

2 Materials and Methods

Origin and characteristics of the samples: The Institute of Chemistry and Chemical Technology of the Mongolian Academy of Sciences (MAS) was responsible for the national implementation of the project including selection and collection of matrices. All the national samples are prepared following the protocol for the "Sampling and Pre-treatment of National Samples within the UNEP/GEF Projects to Support the Global Monitoring Plan of POPs" (UNEP, 2017). When preparing the national samples, close contact was maintained with the expert laboratories in the Netherlands and Sweden. The national samples were chosen according to the most consumed foods for the everyday life of Mongolians. In addition, soil samples close to the animal wash basin of a veterinary clinic and water were collected and analyzed. The two river water samples are not included in this paper and have been reported already in a recent publication (Surenjav *et al.*, 2022). The matrices and the analytes are shown in Table 1.

Chemical analysis: Chlorinated POPs included aldrin, dieldrin, endrin, hexachlorobenzene (HCB), pentachlorobenzene (PeCBz), mirex, chlordecone, hexachlorobutadiene (HCBD), α-endosulfan, α-hexachlorocyclohexane (α-HCH), β-HCH, and lindane (γ-HCH) as single compounds and five POPs that consist of more than one compound: Dichlorodiphenyltrichloroethanes (DDTs) included analysis of *o,p'*- and *p,p'* isomers of DDT, DDD, and DDE and are reported as DDTs; PCB_6 includes PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180, toxaphenes included three Parlar congeners, namely Parlar 26, 50, and 62; chlordanes include *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, and oxychlordane; heptachlor includes heptachlorepoxide. Brominated flame retardants included hexabromobiphenyl 153, three stereoisomers of hexabromocyclododecane, α-HBCD, β-HBCD, and γ-HBCD; penta- and octabromodiphenyl ethers were combined to $PBDE_6$ and included PBDE 47, PBDE 99, PBDE 153, PBDE 154, PBDE 175/183. Dioxin-like POPs (dl-POPs) comprise 7 congeners of PCDD, 10 PCDF, and 12 dioxin-like PCB (dl-PCB) and were reported as TEQs using the 2005 WHO toxicity equivalency factors (van den Berg et al., 2006). Perfluoroalkyl substances

(PFAS) included perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and hexane sulfonic acid (PFHxS).

National samples were analyzed by E&H VU Universiteit Amsterdam for brominated and chlorinated POPs using gas chromatography with capillary columns coupled to mass selective detectors (GC/MS or GC/MSMS). dl-POPs were analyzed by an accredited commercial laboratory in Germany following established and validated methods using high resolution gas chromatographic columns (HRGC) coupled to sector-field high-resolution mass spectrometers (HRMS). PFAS were analyzed by MTM Research Centre at Örebro University using UPLC/MS-MS instrumentation.

Dairy samples, one milk, one mare milk, and four butter samples were analyzed for dl-POPs and PFAS only, the butter sample also for brominated flame retardants.

Table 1: Identity of samples and analytes

#	Type	Matrix	Sample_IDs	OCPs	PCB_6 HCB etc	BFRs	dl-POPs	PFAS
1-4	Dairy	Butter	Butter1, Butter2, Butter3, Butter4			X	X	X
5-8	Egg	Egg	Egg1, Egg2, Egg3, Egg4	X	X	X	X	X
9	Fish	Fish	Fish1			X	X	X
10	Fish	Fish	Fish2	X	X	X	X	X
11-12	Fish	Fish	Fish3, Fish4	X	X		X	X
13-16	Meat	Meat	Beef, Mutton, Chicken1, Chicken2	X	X	X	X	X
17	Meat	Meat	SheepTail				X	X
18-19	Meat	Meat	HorseMeat, Pork	X	X			
20	Dairy	Milk	Milk (cow)				X	
21	Dairy	Milk	MareMilk				X	X
22	Plant	Fruit	SeaBuckthorn1	X	X			
23	Plant	Oil	Seabuckthorn2				X	X
24	Plant	Oil	Flax	X	X			
25-28	Soil	Soil	Soil1, Soil2, Soil3, Soil4	X	X			X

3 Results

Aldrin, endrin, chlordane (including isomers and transformation products), heptachlor (including isomers and transformation products), PBB 153, and PFHxS were not quantified in any of the 28 samples. Toxaphene (sum of three as Parlar #26, #50, #62) was found in only one fish sample (Fish1 at 0.04 µg/kg f.w.).

The scale of the brominated and chlorinated POPs (Br/Cl-POPs) – all at ppb level – is shown in Figure 1, left and the pattern in Figure 1, right. The cow milk and the mare milk samples were not analyzed for Br/Cl-POPs and the butter samples and Fish1 not for the chlorinated POPs. It can be seen that in fish and chicken, PCB_6 was most prominent whereas could not be quantified in eggs (N=4) or plants (N=2). In addition, chlorinated industrial chemicals such as HCB, PeCBz, and HCBD were found in meat and eggs; to a lesser extend in fish. The soil samples contained small amounts of PCB_6 (0.1 µg/kg-4.5 µg/kg), HCB (0.1 µg/kg-8.2 µg/kg), PeCBz (4.7 µg/kg-74 µg/kg), and HCBD (<LOQ-0.41 µg/kg) but very high concentrations of certain organochlorine pesticides. Soil1 was highly contaminated with DDTs (9 880 µg/kg) and had also the highest value for PeCBz. Soil2 had quantifiable levels of most chlorinated POPs with 419 µg/kg of α-HCH. Soil3 had more β-HCH (3 406 µg/kg) and lindane (2 321 µg/kg) than α-HCH (573 µg/kg). Soil4 had extreme values for the three HCHs with 13 062 µg/kg for α-HCH, 2 600 µg/kg for β-HCH, and 29 300 µg/kg for lindane. These results confirmed the earlier use of pesticides in the veterinary sector.

Figure 2 is a graphical representation of the measured values for each Br/Cl-POPs and sample colored by the type of sample. The comparatively high concentrations of DDTs, α-HCH, β-HCH, lindane, α-endosulfan, HCB, and PeCBz in soil can be seen. Highest concentrations of PCB_6 and $PBDE_6$ were found in fish. Interestingly, in the butter samples, PBDE 209 was higher than $PBDE_6$. Striking is the presence of HCBD in almost all types of samples. Among the drins, only dieldrin could be quantified and only in three egg samples and one soil sample; all at very low concentrations.

The barplots for dl-POPs and PFAS, the POPs that were quantified at ng/kg scale, are shown in Figure 3. The fish were mainly contaminated with PFOS and PFOA whereas the chicken had the dl-POPs present. The Mongolian biota samples showed very low concentrations of all dl-POPs (Figure 3, upper row); many results were below the limit of quantification. If quantified, PCDD were found in terrestrial foodstuffs like meat, dairy and egg but not in fish, whereas PCDF and especially PCB were also found in fish. Soil samples were not analyzed for dl-POPs (see Table 1). PFOS was higher in fish than PFOA, but PFOA had higher detection frequencies. Fish2 had the highest PFOS value (309 ng/kg f.w.). The sea buckthorn oil contained only dl-PCB; the fruit was not analyzed for dl-POPs nor PFAS; it also did not contain any quantifiable Br/Cl-POP.

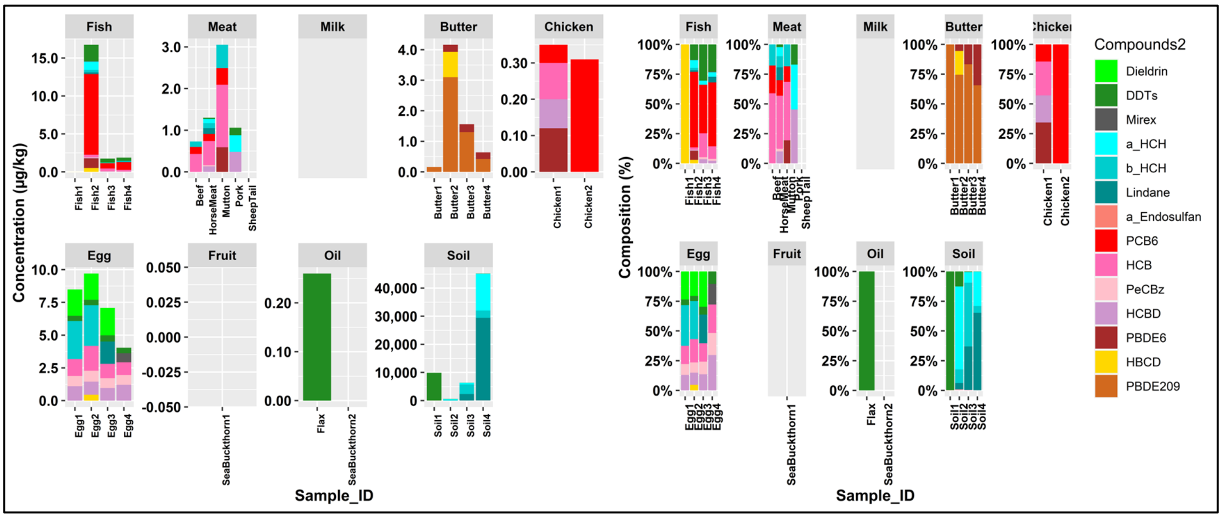


Figure 1: Stacked barplots for chlorinated and brominated POPs: scales in µg/kg (left) and pattern at 100% (right). National samples are grouped according to matrix

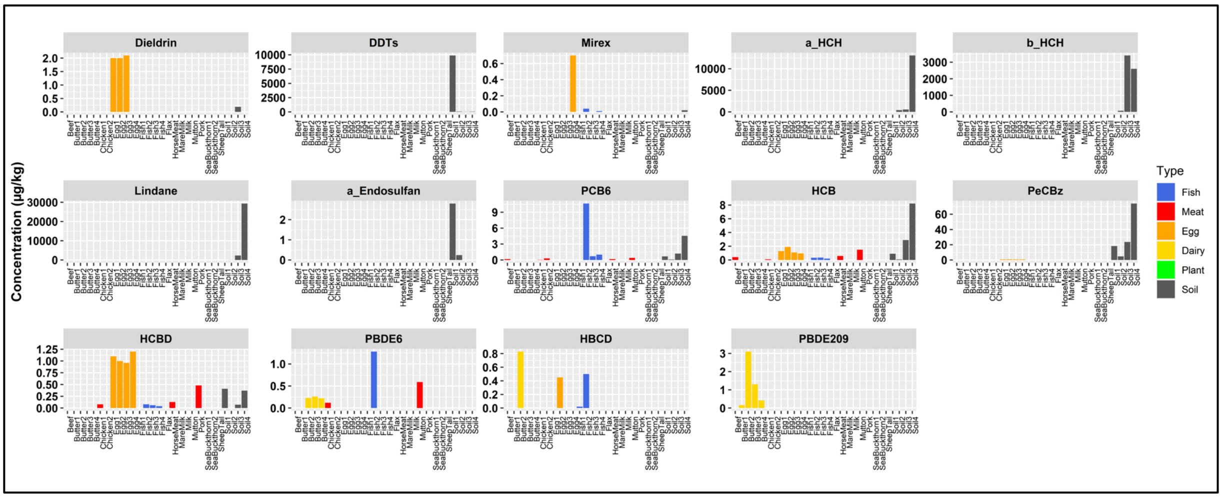


Figure 2: Barplots for Br/Cl POPs according to type of samples

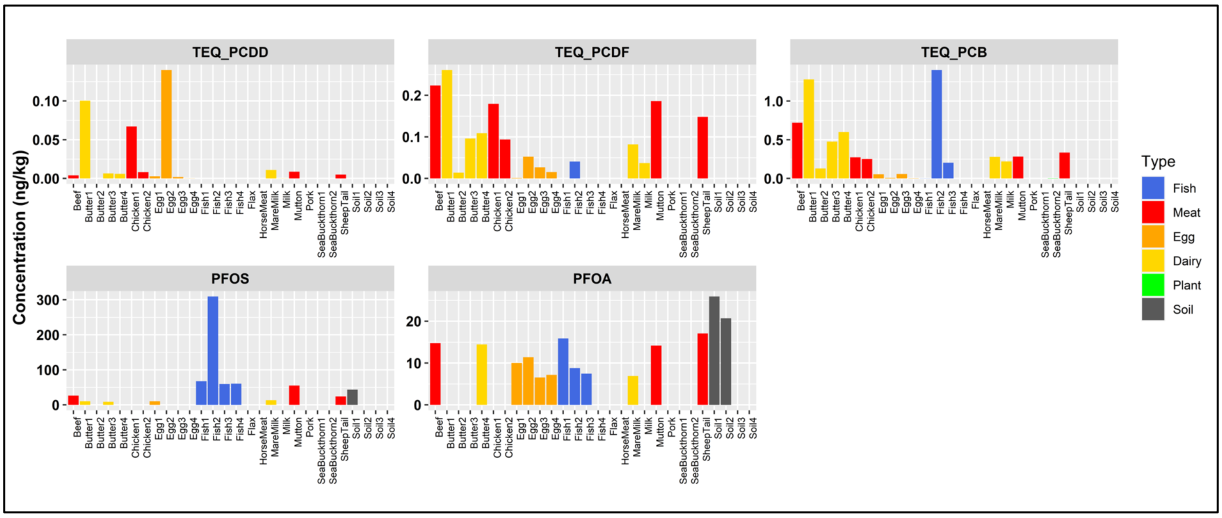


Figure 3: Barplots for dl-POPs and PFAS according to type of samples

The graphs from the principal component analysis in Figure 4 show the complex pictures as to their chemical composition and scale of the POPs quantified in the Mongolian samples. The PCA at left explains 50% of the results for Br/Cl-POPs. Especially the intentional industrial chemicals, $PBDE_6$, PCB_6, HBCD but also HCBD, drive the 2nd dimension of the graph. The fish samples are wrapped into a narrow ellipses along the y-axis whereas the soil samples are located in the 2nd and the 4th quartile and characterized by β-HCH and HCB; the extreme dot represents Soil4. Meat, butter and egg samples form small distinct ellipses. The graph for dl-POPs and PFAS represents 67% of the samples. Among the variables, TEQ_PCB has the largest contribution to Dim1 whereas PFOS contributes largely to the positive and TEQ_PCDD to the negative y-axis. The outlier in the 1st quartile corresponds to Fish2 (309 pg/g for PFOS) and Butter1 (1.28 pg TEQ/g for TEQ_PCB) in the 4th quartile. Meat samples form a circle around the origin whereas egg and soil samples are wrapped by narrow ellipses.

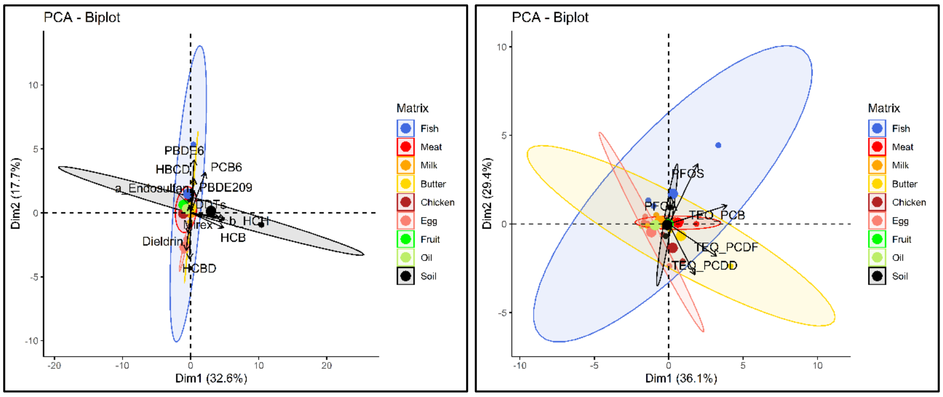
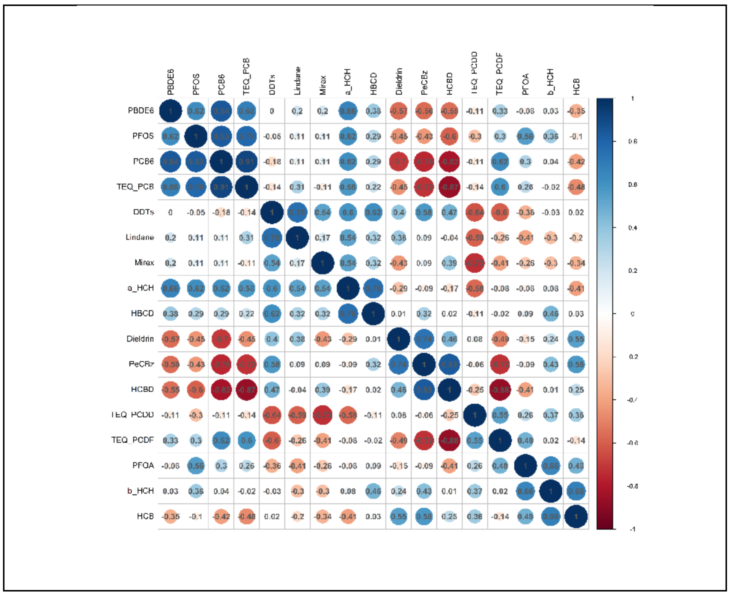


Figure 4: PCA with ellipses around the matrices for Br/Cl-POPs (left) and dl-POPs/PFAS (right) (n=28)



	PBDE6	PFOS	PCB6	TEQ_PCB	DDTs	Lindane	Mirex	a_HCH	HBCD	Dieldrin	PeCBz	HCBD	TEQ_PCDD	TEQ_PCDF	PFOA	b_HCH	HCB
PBDE6	1	0.62	0.84	0.68	0	0.2	0.2	0.66	0.38	-0.57	-0.56	-0.55	-0.11	0.33	-0.08	0.03	-0.35
PFOS	0.62	1	0.83	0.79	-0.05	0.11	0.11	0.62	0.29	-0.45	-0.43	-0.6	-0.3	0.3	0.56	0.36	-0.1
PCB6	0.84	0.83	1	0.91	-0.18	0.11	0.11	0.62	0.29	-0.7	-0.76	-0.82	-0.11	0.62	0.3	0.04	-0.42
TEQ_PCB	0.68	0.79	0.91	1	-0.14	0.31	-0.11	0.58	0.22	-0.45	-0.72	-0.87	-0.14	0.6	0.26	-0.02	-0.48
DDTs	0	-0.05	-0.18	-0.14	1	0.76	0.54	0.6	0.62	0.4	0.58	0.47	-0.64	-0.6	-0.36	-0.03	0.02
Lindane	0.2	0.11	0.11	0.31	0.76	1	0.17	0.54	0.32	0.38	0.09	-0.04	-0.59	-0.26	-0.41	-0.3	-0.2
Mirex	0.2	0.11	0.11	-0.11	0.54	0.17	1	0.54	0.32	-0.43	0.09	0.39	-0.73	-0.41	-0.26	-0.3	-0.34
a_HCH	0.66	0.62	0.62	0.58	0.6	0.54	0.54	1	0.76	-0.29	-0.09	-0.17	-0.58	-0.08	-0.08	0.08	-0.41
HBCD	0.38	0.29	0.29	0.22	0.62	0.32	0.32	0.76	1	0.01	0.32	0.02	-0.11	-0.02	0.09	0.46	0.03
Dieldrin	-0.57	-0.45	-0.7	-0.45	0.4	0.38	-0.43	-0.29	0.01	1	0.74	0.46	0.08	-0.49	-0.15	0.24	0.55
PeCBz	-0.56	-0.43	-0.76	-0.72	0.58	0.09	0.09	-0.09	0.32	0.74	1	0.83	-0.06	-0.72	-0.09	0.43	0.58
HCBD	-0.55	-0.6	-0.82	-0.87	0.47	-0.04	0.39	-0.17	0.02	0.46	0.83	1	-0.25	-0.88	-0.41	0.01	0.25
TEQ_PCDD	-0.11	-0.3	-0.11	-0.14	-0.64	-0.59	-0.73	-0.58	-0.11	0.08	-0.06	-0.25	1	0.55	0.26	0.37	0.36
TEQ_PCDF	0.33	0.3	0.62	0.6	-0.6	-0.26	-0.41	-0.08	-0.02	-0.49	-0.72	-0.88	0.55	1	0.48	0.02	-0.14
PFOA	-0.08	0.56	0.3	0.26	-0.36	-0.41	-0.26	-0.08	0.09	-0.15	-0.09	-0.41	0.26	0.48	1	0.66	0.48
b_HCH	0.03	0.36	0.04	-0.02	-0.03	-0.3	-0.3	0.08	0.46	0.24	0.43	0.01	0.37	0.02	0.66	1	0.68
HCB	-0.35	-0.1	-0.42	-0.48	0.02	-0.2	-0.34	-0.41	0.03	0.55	0.58	0.25	0.36	-0.14	0.48	0.68	1

Figure 5 shows the correlation coefficients for 17 POPs that were quantified in eight biota samples (four eggs, one each in fish, beef, mutton, chicken). The size of the circle indicates scale of correlation; blue colors indicate positive correlations, red colors negative correlations. It can be seen that $PBDE_8$, PFOS, PCB_6, and TEQ_PCB are strongly positive correlated and have strong negative correlations with dieldrin, PeCBz, and HCBD. The TEQ_PCDD are strongly negative correlated with DDTs, lindane, and mirex. PFOA, β-HCH, and HCB showed strong positive correlations.

Figure 5: Spearman correlation coefficients for 17 POPs

4 Discussion

These results from the national samples should be assessed in relation to the global data from these UNEP/GEF GMP2 projects and complement a previous publication describing the results of POPs in Mongolia (Surenjav *et al.*, 2022). In general, it was found that for Mongolia, POPs concentrations tend to be low, especially in biota samples. The legacy industrial chemicals, PCB_6, HCB, PeCBz, and HCBD, could be found in some of the foodstuffs. Dieldrin was present in egg samples. The soil samples demonstrated that locally, very high POPs contamination can be found; especially DDTs, α-HCH, β-HCH, and lindane indicating past applications.

5 Conclusions

The present study was the first systematic survey to monitoring POPs and resulted in a prioritization of POPs, which will lead to follow-up studies and creation of national chemical analytical capacities to be used in future programmes.

6 Acknowledgments

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