SPATIAL AND TEMPORAL TRENDS IN PERSISTENT ORGANIC POLLUTANTS SOIL CONTAMINATION IN THE CZECH REPUBLIC

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Introduction
The total area of agricultural soils in the Czech Republic is 4 284 000 ha and cover more than 54% of country area. Forests soils has 2 634 000 ha, which cover round one third of country area. Monitoring of soil properties and soil contamination is a important part of activities of Ministry of Agriculture and Ministry of the Environment. The determination of actual state of soil contamination including heavy metals and POPs is performed till 1992. This monitoring system is managed by Central Institute for Supervising and Testing in Agriculture (CISTA). Beside of this regular monitoring, MoA cover a lot of short-term, research and pilot studies concerning to soil contamination, some of them have a character of monitoring programme too. This type of soil activities is managed mainly by Research Institute of Amelioration and Soil Conservation (RIASC).

Materials and methods
System of basal soil monitoring was developed in the first part of 90´s and uses in this moment 217 permanent soil sampling sites of agricultural soils, 100 permanent areas of forest soils and 40 permanent areas in protected areas. From 1997, the contents of selected persistent organic pollutants are regularly determined. The samples are collected from 40 permanent sampling areas (5 in protected areas, 35 of agricultural soils).

Soils samples were collected every year before harvest of agricultural products. Sampling area of 1000 m^2 (25 x 40m) is used. One kilogram of soil is collected with using of special sampling scheme. Two sampling layers are collected - 0-10 cm and 10-25 cm. In protected areas, the sampling is done by diagnostic horizonts (the first mineral - surface – humic and the second mineral – undersurface). The polychlorinated biphenyls (PCBs, 7 indicator congeners), organochlorinated pesticides (OCPs – HCHs, DDTs, HCB), atrazines and polycyclic aromatic hydrocarbons (PAHs – 15 - 16 US EPA with exception of acenaphthylene). The samples were prepared, extracted and separated by standard procedures and analysis were given by GC/MS (SIM mode) (LOQ = 0,5 ppb) in the case of PCBs and OCPs and by HPLC in the case of PAHs. The labs which analyzed these samples participate on international interlaboratory tests every year. The determination of PCDDs/Fs was given by GC/MS/MS or HRMS.

Results and Discussion
Basal soil monitoring of CISTA[1]
PAHs:

- Medians of Σ of 15 PAHs in top layer are round value of 600 $ng.g^{-1}$, the values in the second layer are about 300 $ng.g^{-1}$ lower. Arithmetic means are not well-balanced.
- Contents of PAHs in 36 agricultural soils are relatively stable during the evaluated period.
- The accumulation of PAHs in higher altitudes was observed.

- The Czech limit value - 1 $\mu g.g^{-1}$ for sum of 15 PAHs was increased during 2001 in 13 cases of top layer and 6 cases of second layer.
- The mostly frequent determined PAHs were fluorantene and pyrene.
- The ratio among the individual PAHs in soils was stable.

PCBs:

- Medians of the sum of 6 PCBs congeners in agricultural soils move during last 5 years round 2 $ng.g^{-1}$ in top layer and they are lower about 0,5 $ng.g^{-1}$ in the second layer. Arithmetic mean in the tope layer ranged between 4,8 and 7,0 $ng.g^{-1}$, the values in the second layer ranged between 3,1 and 3,3 $ng.g^{-1}$.
- The limit value was increased in the case of ten observed areas. There were the areas with potential point sources of contamination and relatively stable contents of PCBs.
- The soil contents of PCBs were relatively stable in the whole set of observed set of soil samples. It is impossible to expect rapid decreasing of PCB soil contents. The reason is relatively high contents of highly chlorinated PCBs.

OCPs:

- HCHs did not detected during whole period in all samples.
- As far as HCH, the slight increasing tendency was observed in 2001 in the comparison with the year 2000, but absolute values were very low. More important was the increasing of p,p'-DDE contens (median from 5,8 to 11,8 $ng.g^{-1}$). The contents of other DDT metabolites is stable.
- The determined levels during the period 1994 – 2001 varied and it is impossible to determine any time trends.

PCDDs/Fs:

The PCDDs/Fs were determined in 38 samples during 2001.

Table 1: Contents of PCDDs/Fs (38 observed area sof basal soil monitoring) [$pg.g^{-1}$]

Parametr	Mean	Minimum	Maximum	Median	10th perc	90th perc
ΣPCDDs/Fs	274.1	32.8	1136.1	118.9	49.8	797.7
ΣP(4-8)CDDs/Fs	230.7	24.7	1082.8	91.9	33.9	706.1
ΣPCDDs/Fs TEQ	3.1	0.5	14.3	1.3	0.6	9.3

The distribution of results and a big differences between arithmetic mean and median is affected by samples with extremely high contents of PCDDs/Fs (contaminated areas and both samples from protected area). As far as protected areas, these results are in the very good agreement with the results of R-T&A projects especially from high mountains sampling sites.

- The highest PCDDS/Fs contents were observed in industrial areas and in the soil from protected areas in higher altitudes.
- The cleaning effects and under-cloud wash-out effects of long-range transported POPs can be a source of this soil contamination in protected areas. It reflects our previous and present measurements of PCDDs/Fs soil contamination of boarder high-mountains where 3-8-times higher contents of PCDDs/Fs were detected in the comparison of samples from lowland.
- The contamination of industrial areas can be given by some local, industrial sources or by sewage sludge application.
- The contents of PCDDs/Fs in soil were different if we compare various area and no observable relationships between absolute levels of PCDDs and TEQ.
- The main part of PCDDs/Fs soil contamination was done by higher chlorinated congeners (4-8 Cl in molecule).

Soil monitoring of RIASC[1]

The basic conception of this monitoring is focused on the:

- Soils from more polluted regions (North and West Bohemia, North Moravia)
- Soils from the regions with average level of contamination
- Fluvisols mainly from River Elbe basin

The samples were collected from agricultural soils, grasslands and pastures from the 6 regions of the CR during the period of 1993-2002. 1 sampling point covers area round 25 km^2. The PCDDs/Fs were determined from 1999 and 60 samples were analyzed up-to date. There were samples from industrial areas, agricultural areas, higher altitudes, flooded areas and from the soils where sewage sludge was applied long-time.

Conclusions:

- The higher levels of PAHs, PCBs and PCDDs/Fs in fluvisols collected from the inundate zone of big rivers under industrial towns and agglomeration were found.
- The atmospheric input of POPs plays very important role especially near to industrial complexes and large agglomeration (higher levels of PAHs, especially of fluoranthene and TEQ of PCDDs/Fs with quite different patterns among the regions.
- PAHs were detected near to small towns and villages where the coal is still predominant fuel in local heating systems.
- Similarly as in the case of basal monitoring of CCTIA, the higher contamination of samples from higher altitudes was observed in the case of PCDDs/Fs and also in the case of PAHs. This trend which is basically given by long-range transport of POPs were detected not only in the northern, highly polluted part of the country, but also in south part, which is generally lower contaminated (Sumava mountains).

If we will compare all tested set of soil, the soil from RIVM monitoring can be selected to three groups based on the source and intensity of contamination by PCDDs/Fs [$pg.g^{-1}$]:

- 14 – 1.6 – soils with high level of contamination, which is done by effects of industrial sources, flooded area and application of sewage sludge from WWTP,
- 1.3 – 0.5 – soils from mixed source of contamination and from relatively low polluted areas (higher mountains region),
- 0.4 – 0.1 – soils from clean areas with limited local industrial sources.

Based on this set of 60 soil samples, the background value 2.5 $pg.g^{-1}$ was defined as 90% percentil of determined values of I-TEQ PCDDs/Fs in soils.

Research and monitoring projects of R-T&A[1-3]

Few long-time research and monitoring projects is covered and manager by Consortium RECETOX-TOCOEN & Associates. Summary of the last period results is presented in Tables 2 and 3, where we can recognize the similar trends which were described in the previous two monitoring systems - higher contamination in higher altitudes and generally decreasing POPs contamination during last decade.

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Table 2: The R–T&A soil sampling areas (area characteristics, duration of sampling, number of sampling sites and up-to-date collected samples, determined pollutants)

Area	Area characteristics	Duration	Frequency	Number of sampling sites	Number of samples up to date	Observed compounds
Košetice	EMEP Central European background area	1988 – up to date	One times per every year	9	108	PAHs, PCBs, OCPs, PCDDs/Fs
Zlín	Industrial and urban area, river valley	1993, 1996, 1998, 2001	One times per these years	5-29	63	PAHs, PCBs, OCPs, PCDDs/Fs
Beroun	Industrial and urban area, river valley	2001	One times per this year	25	25	PAHs, PCBs, OCPs, PCDDs/Fs
Mokrá	Industrial source near to Brno	1993, 1998 – up to date	1993 - one times per this year, from 1998 – four times per every year	12	120	PAHs, PCBs, OCPs, PCDDs/Fs
High mountains	High mountains, background sites without local sources	1994, 1996, 1998, 2001	One times per these years	14	23	PAHs, PCBs, OCPs, PCDDs/Fs
Highways	The surroundings of Czech highways	1999	One times per this year	45	45	PAHs, PCBs, OCPs

Table 3: The soil contents of POPs from the monitoring and research activities soil sampling areas of R–T&A (PAHs, PCBs, HCHs, DDTs, HCB – [$ng.g^{-1}$], PCDDs/Fs, DL PCBs - [$pg.g^{-1}$]

Area	PAHs (16 USEPA)	PCBs (7 congeners)	HCHs (4 isomers)	DDTs (DDT + DDE + DDD)	HCB	PCDDs/Fs	TEQ	DLPCBs (77+126+169)	TEQ DL PCBs
Košetice	244.3 (5.8 – 5 412) n = 87	4.19 (0.07 – 116) n = 63	0.59 (0.02 – 182) n = 82	3.6 (0.20 – 294) n = 88	0.55 (0.04 – 9.18) n = 99	87.11 (22.8 – 1 241) n = 9	1.3 (0.3 – 16.4) n = 9	7.91 (3.05 – 234.2) n = 9	0.25 (0.08 – 5.24) n = 9
Zlín	3 145 (220 – 22 025) n = 62	16.47 (1.1 – 345.8) n = 63	0.89 (0.22 – 8.51) n = 63	9.39 (0.72 – 1 018) n = 63	3.28 (0.02 – 44.2) n = 63	307.1 (75.3 – 2 238) n = 10	2.42 (1.27 – 4.45) n = 10	53.4 (6.59 – 84.3) n = 10	0.78 (0.16 – 1.94) n = 10
Beroun	523.9 (123.1 – 6 778) n = 25	6.87 (4.36 – 29.2) n = 25	1.03 (0.34 – 1.62) n = 25	8.8 (2.19 – 216) n = 25	2.54 (0.54 – 10 295) n = 25	276.2 (98.3 – 1 279) n = 25	1.82 (0.97 – 7.11) n = 25	40.76 (11.2 – 158.7) n = 25	0.52 (0.19 – 2..92) n = 25
Mokrá	283.0 (29.0 – 2 953) n = 120	4.11 (1.78 – 27.5) n = 120	0.74 (0.11 – 64.7) n = 120	14.45 (0.80 – 6 120) n = 120	0.75 (0.06 – 8.39) n = 120	61.2 (42.2 – 703.5) n = 12	0.78 (0.42 – 13.7) n = 12	11.97 (3.04 – 172.6) n = 12	0.29 (0.11 – 4.08) n = 12
High mountains	3 213 (242 – 8 188) n = 23	26.2 (7.9 – 82.8) n = 21	1.34 (0.22 – 5.78) n = 15	55.0 (6.08 – 1 908) n = 21	2.21 (0.47 – 11.9) n = 21	1 900 (624.5 – 8 383) n = 23	28.5 (11.2 – 141.6) n = 23	242.6 (0.18 – 575) n = 15	6.4 (0 – 12.01) n = 15
Higways	192.8 (6.8 – 10 776) n = 60	3.9 (1.14 – 227.3) n = 45	1.18 (0.17 – 14.6) n = 45	12.88 (0.43 – 356.5) n = 45	0.92 (0.05 – 6.6) n = 45	Not analyzed	Not analyzed	Not analyzed	Not analyzed