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The Comparison of Soil Load by POPs in Two Major Emission Regions of the Czech Republic

Radim Vácha, Jan Skála, Jarmila Čechmánková and Viera Horváthová

Additional information is available at the end of the chapter

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1. Introduction

The Czech Republic belongs to the countries with long-term industrial history. The environmental load by persistent organic pollutants pollution has been proved to follow the industrial development, especially concerning the polycyclic aromatic hydrocarbons emissions. In the Czech Republic the industrial growth started during 19th century and in the beginning of 20th century at the time of the Austro-Hungarian Monarchy. The industrial development continued after the Monarchy collapse and the Czechoslovak Republic formation (1918 - 1938). The rapid industry growth was led by heavy industry priority in the period of socialist economy (1948 – 1990) and caused the wide environmental damages. The emission outputs reached maximum in 70th years when the daily average concentrations of SO₂ (gaseous emission) were over 50µg/m³ and in the coalfield areas of North Bohemia up to 70 - 100µg/m³ following the data of Czech Hydrometeorological Institute [1]. The loading by floating dust particles was more than 70 - 100µg/m³ and in extreme cases reached 150µg/m³.

There are two main coal mining regions in the Czech Republic (see Figure 1.). The history of brown coal mining started in North Bohemian Region in the beginning of 19th century (1819) and reached the maximum in the eighties of 20th century. The history of black coal mining in North Moravian Region is very similar and the mining activity peaked in the eighties of 20th century (about 20 millions tons per year). Opencast coal-mining activity in North Bohemia has been changing the landscape character in more intense way, however the deep mines in North Moravia has also caused environmental damages due to terrain subsidence and lagoons with coal powder and waste. Other important risk are linked to the combustion of brown coal of low quality with increased contents of sulphur and arsenic [2] in coal-fired power stations in North Bohemia and to the presence of metallurgical industry in the North

Moravian region. The load of both areas by risky elements and persistent organic pollutants gave them the designation of imission regions. The North Bohemian region covers the area of 5 districts (Decin, Teplice, Usti nad Labem, Most and Chomutov and neighbouring districts in the West Bohemian region where increased load still remains). The region is spread along the Czech-German border shaped by the Ore Mountains. The North Bohemian basin is delimited by the dislocation at the foothill of the Ore Mountains. The North Moravian region situated close to Czech-Polish border covers the area of 3 districts (Ostrava, Karvina, Frydek-Mistek). The flat character of the landscape in west part of the region (Karvina, Ostrava) passes to mountainous area forming the Czech-Slovak borderland (the Moravskoslezské Beskydy Mountains). The load of environment in both regions is historically increased with the historical pollution peak in seventies and eighties of 20th century when high content of emission-out puts in the air connected with acid rains led to perceptible damages of the environment (especially damage of the spruce forest in the Ore Mountains). The situation started to change after 1990 thanks to industrial production decrease and the necessity of technology improvement of coal-fired power stations (the installation of efficient dust particles filters in the beginning of the 21st century). The modernization of four coal-fired power stations situated in the North Bohemian region (Ledvice, Pocerady, Tusi-mice and Prunerov) has been approaching in two periods. In the 1st period (1996 – 1999) there were radically decreased the emission out puts in following extent: SO_x -92%, NO_x -50%, CO -77% and solid polluting particles -93%. The next period of modernization is running and will be finished till 2020 following precise schedule of the works. The next decrease of emission out puts will be reached in the following extent: SO_x -57%, NO_x -59%, CO₂ -31% and solid polluting particles -39%, data from [3].

The comfortless situation remains in the North Moravian region and increased contents of emission out-puts in the air are the theme of many professional and public discussions [4,5]. The special attention is paid to increased content of polycyclic aromatic hydrocarbons in environment which is connected with increased number of some inhabitant's diseases in the region [3]. The load stemmes from emission out puts from heavy industrial factories (for example the Trinec and Ostrava ironworks factories etc). There is one coal-fired power station (Detmarovice) in the region where black coal is used. The mountainous area situated in eastern part of the region serve for recreation and sport and there are no important sources of pollution. Nevertheless the increased pollution was proved in the mountains are due to imission out puts from western part of the region. Other environmental hazards in the region are linked to the existence of lagoons where around 300,000 tons of petroleum sludge have been deposited. The recent dredge and liquidation of sludge meets some technical and economical inconveniences.

The soil is one of the important environmental sinks of pollution and soil contamination can reflect long-term load by dry and wet depositions. Increased soil load by risky substances poses serious threats to environment, plant production and food security. The maintenance of suitable state of soil load by risky substances should be an interest of every society. The evaluation of soil load by risky substances must be supported by the knowledge of risky substances background values, their inputs into soils, their behaviour and fate in the soil en-

vironment, their transfer into the plants etc. The approaches to limit values system are not unified across the world, nor in European context and different philosophies may be used for the evaluation of soil contamination. There has been paid longterm attention to soil contamination issue in the Czech Republic. The potentially toxic compounds observed in Czech agricultural soils can be separated into two main groups of pollutants:

- Inorganic pollutants - potentially risky elements (REs), As, Be, Cd, Co, Cr, Hg, Cu, Mn, Ni, Pb, V, Zn, respectively Se and Tl
- Organic pollutants – persistent organic pollutants (POPs), A wide group of different organic substances, with linear or cyclic character. The current list of POPs observed in Czech legislation (Soil Protection Act) includes monocyclic and polycyclic hydrocarbons, PCBs, sum of DDT and petroleum hydrocarbons (table 1).

POPs
Monocyclic aromatic hydrocarbons
benzene, toluene, xylene, ethylbenzene
Polycyclic aromatic hydrocarbons
naphtalene, anthracene, pyrene, phluoranthene, phenanthrene, chrysen, benzo(b)phluoranthene, benzo(k)phluoranthene, benzo(a)anthracene, benzo(a)pyrene, indeno(c,d)pyrene, benzo(ghi)perylene
chlorinated hydrocarbons
PCB(28+52+101+118 +138+153+180), HCB, α -HCH, β -HCH, γ -HCH
Pesticides
DDT, DDD, DDE
Others
styrene, petroleum hydrocarbons
PCDF
2,3,7,8 TeCDF, 1,2,3,7,8 PeCDF, 2,3,4,7,8 PeCDF, 1,2,3,4,7,8 H _x CDF, 1,2,3,6,7,8 H _x CDF, 1,2,3,7,8,9 H _x CDF, 2,3,4,6,7,8 H _x CDF, 1,2,3,4,6,7,8 H _p CDF, 1,2,3,4,7,8,9 H _p CDF, OCDF PCB 189, PCB 170, PCB 180
PCDD
2,3,7,8 TeCDD, 1,2,3,7,8 PeCDD, 1,2,3,4,7,8 H _x CDD, 1,2,3,6,7,8 H _x CDD, 1,2,3,7,8,9 H _x CDD, 1,2,3,4,6,7,8 H _p CDD, OCDD

Table 1. Persistent organic pollutants observed in Czech agricultural soils

The system of limit values of soil contamination must accept sources of risky substances that influence the behaviour of risky substances in the soil (mobility, bioavailability). POPs can originate from:

- Natural sources - volcanic activity (REs, POPs), natural fires (POPs) etc.
- Anthropogenic sources – like industrial activities, transport emissions, the use of agrochemicals and biosolids in agriculture, waste water production etc.

Increased inputs of potentially toxic compounds into the soils may result in soil contamination that may negatively influence:

- The ecosystem - soil functions, contamination of aquatic systems, plants, animals etc.
- Plant production – the quantity and quality.
- Human health – via contamination of food chain, dermal or inhalation intake etc.

The efficient ways of the control and regulation of risky substances in the soil are legislative-ly mandatory limit values. The limit values of risky substances in the soil are derived on the basis of:

- Real state of soil load by risky substances reflected natural and anthropogenic diffuse load. Limit values of this kind are usually specified as “background values” of risky substances in the soil, [6] and [7].

- Experimentally derived values, that are focused on target risk following from soil use and observed environmental component (the damage of quantity and quality of plant production, the reduction of soil microbial activity etc.).

One of the most effective and sophisticated limit values systems is so called hierarchical limit values system that should be able to register target risk following the soil contamination. This system is usually used in many European countries (Germany, Netherlands and Switzerland) as system of “A, B and C limits” where

A – represents background values of risky substances in the soil. Generally, this limit value fulfils the principal of precaution.

B – is focused on target risk. The limit may be targeted on the quality or quantity of plant production (this approach is used rarely and is determined rather for small allotment producers than for agriculture) or on the decreasing of soil microbial activity and soil transformation functions etc.

C – is used as remediation (decontamination) limit that is based on the human health risk or environmental damage.

The limit values system focused on remediation needs (in the order of C limit level) are used in some countries (Great Britain, USA – EPA methodology, [8]). Given limit values of risky substances delimit risky substances concentrations that may distinctly affect human health or environment. After the exceeding of this limit the site-based risk assessment must be done and the results of risk assessment study determine next approach (the remediation, land use change). The proposal of the EU Soil Protection Act [9] is based on similar philosophy. Three steps are required on national level of member countries:

- The elaboration of soil contaminated sites register.
- The realisation of risk assessment studies on contaminated sites.
- The realisation of remediation approaches.

The directive of the Ministry of Environment of the Czech Republic No. 13/1994 Coll. [10] regulates the contents of REs and POPs in Czech agricultural soils. The limits of REs are determined for light texture soils and the other soils in the form of the aqua regia extract and the extract in 2M HNO₃ (cold method). The limit values for POPs are determined for the groups of monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons (including pesticides) and petroleum hydrocarbons. All the limit values are defined as tolerable contents of risky substances but there is no relationship to any actual risk. It brings difficulties by the evaluation and interpretation of soil load by risky substances in many cases. Moreover the limits for POPs were assessed on the base of the values taken from Nederland because no actual values of Czech soil load by POPs were available in 1994. Two years later were published the first real data about soil load by POPs in the Czech Republic [5]. Some limit values in the directive No. 13/1994 Coll. are too low (especially some individual PAHs) because they stem from Dutch legislation limits derived for sandy soils with low content of soil organic matter and are not suitable for Czech soils of different properties. There naturally arises the task of the proposal of the directive No.13 amendment based on the principal of hierarchical limit values system [11].

Three levels of the limits has been proposed:

Prevention limit – based on background values of risky substances in Czech agricultural soils. Prevention limit were proposed for REs and POPs. The exceeding of the limit shows increased anthropogenic soil load by risky substances. From the viewpoint of limit interpretation it is prohibited to use the sludge or sediment for soil fertilization in the case of limit exceeding. The proposed prevention limits for POPs based on the actual load of Czech agricultural soils [5] are presented in table 2.

Indication limit – was derived experimentally and the limit exceeding indicates the risk of increased REs transfer from the soil into the plants. Indication limit was proposed for REs only. The more detailed assessment is recommended at the locality after exceeding of indication limit. In the case of POPs the transfer from soil into plants via root intake is limited. More individual risks must be accepted for POPs indication limit and the realisation of risk assessment is recommended on the field seriously contaminated by POPs (in term of C limit level). In spite of these facts the simplified indication limits for some POPs were proposed [12], table 3. The limit values were determined as the lowest contents of risky substances in the soil that may cause any health risk. The transfer of risky substance from the soil to human bodies by dermal, oral and dietary intake was accepted.

Decontamination limit – has not been proposed yet.

The proposal of the directive No. 13/1994 Coll. amendment brings new approach to soil load by risky substances evaluation and its commencement could improve the management of contaminated sites. It could be very useful tool for the soil management in the imission regions of North Bohemia and North Moravia.

This report compares the load of two imission regions of the Czech Republic by three types of persistent organic pollutants: polycyclic aromatic hydrocarbons (PAHs), polychlorinated

biphenyls (PCBs) and DDTs (DDT, DDE and DDD). Although PCBs and DDTs have not been used in Europe since eighties, the load of soil by both groups of pollutants is still increased.

2. Materials and methods

2.1. The characterization of study area

The area of the North Bohemian region and North Moravian region is presented in Figure 1. The area of North Bohemian region is 3,184.65 km² and the area of North Moravian Region is 1,834.25km².

2.1.1. North Bohemian region

2.1.1.1. Districts

The region comprises 5 districts (NUTS 5 level): Decin, Usti nad Labem, Teplice, Most and Chomutov.

District Decin is situated on the north of region and its area is 908.58km². In the district live 132,718 inhabitants in 52 municipalities, 14 of which are classified as towns. The capital of district is the town Decin.

The density of population is 146 inhabitants/km² in the district. The agricultural land covers 40.1% of the district area and the ratio of arable land is 32.94%, it means 13.21% of the district area. The other land covers 59.9% of district area and the ratio of forest is 82.25%, this is 49.27% of district area. There are 4 geomorphologic formations in district area, Decin Upland (north-western and central part), Central Bohemian Uplands (south and south-western part), Luzicke Mountains (eastern part) and Sluknov Downs (northern part). The highest point (Penkavci vrch) has the altitude of 792 m.a.s.l. and the lowest point (the Elbe river bank in Hrensko on the border with Germany) that is the lowest point of the Czech Republic also has the altitude of 115 m.a.s.l. The Elbe river (the biggest Czech river) traverses in the west part of the district.

District Usti nad Labem is situated in south-west direction from the Decin district and its area is 404,45km². In the district live 118,194 inhabitants and 84.44% of them live in towns. The capital of district is Usti nad Labem. The density of population has value of 292 inhabitants/km² in the district. The agricultural land covers 45.66% of district area and the ratio of arable land is 29.33%, it means 13.39% of district area. The other land covers 54.34% of district area and the ratio of forest is 57.72%, this is 31.37% of district area. There are 2 most important geomorphological formations, Central Bohemian Uplands (south-western and western part) and the Ore Mountains (northern part along the border with Germany). The Elbe river flows through the district.

POPs	Preventive value ($\mu\text{g}/\text{kg}$ of dry matter)
Monocyclic aromatic hydrocarbons	
Benzene	30
Toluene	30
Xylene	30
Styrene	50
Ethylbenzene	40
Polycyclic aromatic hydrocarbons	
Fluoranthene	300
Pyrene	200
Phenanthrene	150
Benzo(b)fluoranthene	100
Benzo(a)anthracene	100
Anthracene	50
Indeno(cd)pyrene	100
Benzo(a)pyrene	100
Benzo(k)fluoranthene	50
Benzo(ghi)perylene	50
Chrysene	100
Naphtalene	50
Σ PAHs	1,000
Chlorinated hydrocarbons	
PCB Σ 7 (congeners) ¹⁾	20
PCDDs/Fs ²⁾	1
HCB	20
DDT	30
DDE	25
DDD	20
HCH (Σ α + β + γ)	10
Non polar hydrocarbons	
hydrocarbons C ₁₀ -C ₄₀ (mg/kg)	100

Table 2. Proposed preventive limit values of persistent organic pollutants in agricultural soils of Czech Republic ¹⁾ 28, 52, 101, 118, 138, 153, 180 ²⁾ value of I-TEQ PCDD/F (ng/kg)

District Teplice is situated in south-western direction from the Usti nad Labem district and its area is 469.27km². In the district there live 128,464 inhabitants in 34 municipalities, 10 of which are classified as the towns. The urbanization rate reaches 84.08% of inhabitants. The capital of district is the town Teplice. The density of population has value of 274 inhabitants/km² in the district. The agricultural land covers 34.25% of district area and the ratio of arable land is 52.01%, it means 17.81% of district area. The other land covers 65.75% of district area and the ratio of forest is 55.91%, this is 36.76% of district area. There are two

geomorphologic formations in district area, Central Bohemian Uplands (south-western and western part) and the Ore Mountains (northern part along the border with Germany).

District Most is situated in South West direction from Teplice district and its area is 467.16km². In the district live 114 795 inhabitants in 26 municipalities 6 of which are classified as towns. 88.71% of inhabitants live in the towns. The capital of district is Most. The density of population has value of 246 inhabitants/km² in the district.

The agricultural land covers 29.27% of district area and the ratio of arable land is 69.98%, it means 20.48% of district area. The other land covers 70.73% of district area and the ratio of forest is 46.85%, this is 33.14% of district area. There are two geomorphologic formations in the district area, the Central Bohemian Uplands (south-western and western part) and the Ore Mountains (northern part on the border with Germany). The coal-field area is situated under the Ore Mountains and the active open mines still exist in south-western part of the region. Large opencast mine closed in the 80s of 20th century is spread close to the Most town on the area of the former Most old town (destroyed before mining). This land is under reclamation in present time (artificial lake).

POPs	Indication value (mg/kg of dry matter)
Benzo(a) pyrene	2.0
sum PAHs ¹⁾	30.0
sum PCB ²⁾	1.0
DDT and metabolites	4.0
HCH (α, β, γ)	0.1
HCB	0.1
PCDDs/Fs ³⁾	20.0
Benzene	0.5
Ethylbenzene	5.0
Toluene	10.0
Xylene	10.0
hydrocarbons C ₁₀ -C ₄₀	500

Table 3. Proposed indication limit values of persistent organic pollutants in Czech agricultural soils ¹⁾ The sum of 16 individual PAHs (EPA) ²⁾ The sum of 7 PCB congeners (28+52+101+118 +138+153+180) ³⁾ ng/kg I-TEQ PCDDs/Fs

District Chomutov is situated in south-western direction from the Most district and its area is 935.3km². In the district live 125,758 inhabitants in 44 villages, 8 of which are classified as towns. 86.43% of inhabitants live in towns. The capital of district is Chomutov. The density of population has value of 134 inhabitants/km² in the district. The agricultural land covers 41.93% of district area and the ratio of arable land is 60.72%, it means 25.46% of district area.

The other land covers 58.07% of district area and the ratio of forest is 63.41%, this is 36.82% of district area. There are 2 geomorphologic formations in district area, Central Bohemian Uplands (south-western and western part) and the Ore Mountains (North part on the border with Germany).

2.1.1.2. North Bohemian coal field

Tectonic depression takes the area of the districts Teplice, Most and Chomutov (Figure 2). The coalfield is the relict of the Tertiary sedimentary basin filled in Miocene [13]. The layer of clay, sand and organic materials of 500 m thickness was lodged in the period of 17-22 millions years ago. The brown coal bed was developed from the peat layers laid in Tertiary marsh on the majority of basin area. The sedimentation of clay and sand prevailed in the estuary areas of rivers entering the marsh [14]. The bed is filled by river or delta sediments in these places completely. The brown coal bed was developed relatively evenly in the thickness of 25 – 45 m in the other part of the basin. The area of current rests of brown coal field has 870 km². The average altitude is 272 m.a.s. l.

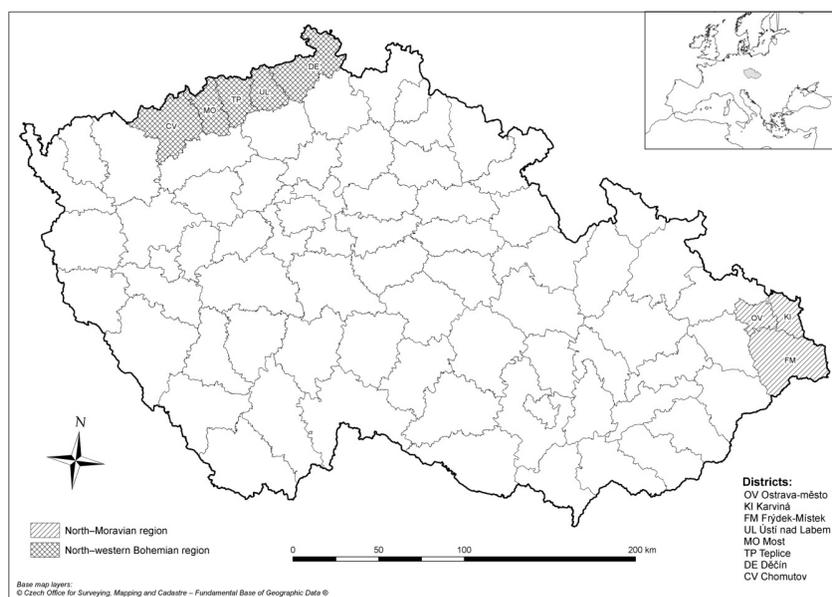


Figure 1. The area of North Bohemian Region and North Moravian Region in the Czech Republic

The mining activities have been running since 19th century and changed originally flat or downs surface relief. The process was accelerated after 1948 when the opencast mining technology on wide areas was elected. The mining is still continuing in opencast mines Bilina and Libus. The mine Bilina is the deepest mine of North Bohemian coal field with the depth of 200 m (the lowest point has the altitude of 35 m.a.s. l.). The total mining reserves were estimated at 165 millions tons in the beginning of the year 2012. The average content of ash is 26.9% and of total sulphur is 1.03% of dry matter of the coal. The open mine Libus is the largest mine of North Bohemian coal field and the total mining reserved were estimated at

240 millions tons in the beginning of the year 2012. The average content of ash is 36.8% and of total sulphur is 2.7% of dry matter of the coal. The coal is used for the production of energetic combustible mixtures. The environment is under influence of petrochemical industry in the Most district where the factory is located in Záluží u Mostu.

The North Bohemian coal field is impaired by strong anthropogenic activity when mining pits and mining depressions filled by water mining wastes in the form of table humps can be seen. The reclamations are done after landscape devastation.

2.1.1.3. The environmental data on the North Bohemian region

The area can be classified as the zone with high density of population and high concentration of the industry with increased level of imission pollutants. Following the information of Czech Hydrometeorological Institute [15] the concentration of dusty aerosol particles under $10\mu\text{m}$ (PM_{10}) were monitored on 27 localities in the region in 2009. The exceeding of 24 hours limit was observed on 7 localities. The maximum value was 63times higher than a daily limit value of $50\mu\text{g}/\text{m}^3$. Nevertheless, there was observed no exceeding of year limit value in the region.

The values of dusty aerosol particles under $2,5\mu\text{m}$ ($\text{PM}_{2,5}$) were monitored on 6 localities in region. The highest value of annual concentration $19\mu\text{g}/\text{m}^3$ is under limit value of European Direction 2008/50/EC [16].

The concentration of benzo(a)pyrene in the air was observed on 5 localities in the region and only 1 exceeding of target imission limit for annual concentration was detected in urban area of the city Usti nad Labem.

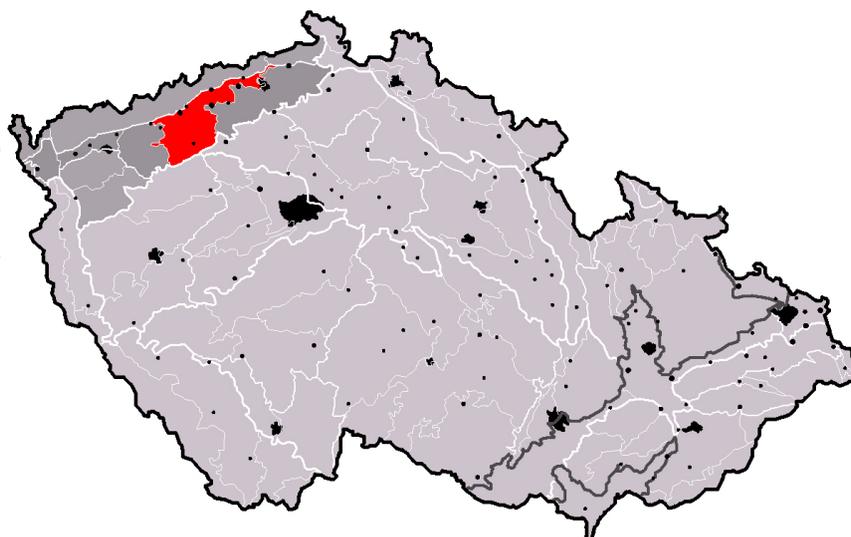


Figure 2. The North Bohemian coal field. The area in red. (the source: http://cs.wikipedia.org/wiki/Mosteck%C3%A1_p%C3%A1nev)

2.1.2. North Moravian region

2.1.2.1. Districts

The region has 3 districts: Ostrava, Karvina and Frydek-Mistek.

District Ostrava is situated in north-western part of the region and has the area of 331.53km². In the district 329,961 inhabitants live in 13 municipalities, 4 of which are classified as towns. The urbanization rate stands at 95%, indicating agglomeration character of the region. The capital of district is the Ostrava city. The density of population is 995 inhabitants/km² in the district.

The agricultural land covers 40.17% of district area and the ratio of arable land is 62.72%, it means 25.19% of district area. The other land covers 59.83% of district area and the ratio of forest is 18.18%, this is 10.88% of district area. The Ostrava-Karvina coal field is the part of geomorphologic formation shaped by the Ostrava basin and Karvina basin.

District Karvina is situated in north-eastern part of the region and its area is 356.24km². In the district 263,075 inhabitants live in 17 municipalities, 7 of which are classified as towns. 88.93% of inhabitants live in the towns. The capital of district is Karvina. The density of population has value 738 inhabitants/km² in the district. The agricultural land covers 50.77% of district area and the ratio of arable land is 68.82%, it means 34.94% of district area. The other land covers 49.23% of district area and the ratio of forest is 28.56%, this is 14.06% of district area. The district relief is shaped by geomorphologic formation of the Karvina basin as the part of the Ostrava-Karvina coal field.

District Frydek-Mistek is situated in south-eastern part of the region and its area is 1 208.49km². In the district 211,853 inhabitants live in 72 municipalities, 6 of which are classified as towns. The urbanization rate amounts to 57.2% of inhabitants living in towns. The capital of district is Frydek-Mistek. The density of population has value reaches 175 inhabitants/km² in the district. The agricultural land covers 39.38% of district area and the ratio of arable land is 48.95%, it means 19.28% of district area. The other land covers 60.62% of district area and the ratio of forest is 81.43%, this is 49.36% of district area. There are two important geomorphologic formations, the Moravskoslezské Beskydy Mountains and the Beskydy basin situated under mountainous area.

2.1.2.2. Ostrava-Karvina coal field

The Ostrava-Karvina coal field is Czech part of so called Upper Silesian coal pan spread on the area of Poland and partially of the Czech Republic that comprises coal fields in the Karvina, Ostrava and Beskydy basins. Ostrava-Karvina coal field is the largest coal field in the Czech Republic where black coal is extracted by deep mining technology. The Ostrava-Karvina coal field is separated in south part from the Beskydy basin by the Bludovický break and has two parts (the Ostrava and Karvina basin) divided by the Orlová fault structure.

More than 300 km² is used for mining in Czech part of the Upper Silesian field and next 400 km² are considered to be perspective. The coal bearing layers in the rest of field area are not

situated in accessible mining depths. Majority of mining activities runs in the Ostrava-Karvina coal field and only the Paskov mine one mine (Paskov) is open in the Beskydy coal field. There were identified two major coal layers in the Ostrava-Karvina coal field: Ostrava with general thickness of 2,880 m and Karvina with general thickness of 1,200 m. The average bed thickness of the Ostrava layer is 73 cm, whereas the most average thickness has the coal bed Prokop (2-4 m) with maximum more than 12 m. The average coal seam thickness of the Karvina layer is 180 cm and the most average thickness (504 cm) has also the coal bed Prokop with maximum up to 15m. The total amount of already extracted coal in the Ostrava-Karvina coal field is estimated at about 1,7 billions tons. In Czech part of the Upper Silesian field operate four deep mines and one mine stays in preserved regime at present time.

The mine CSM has the total area of 22.12km² and estimated activity will run to 2028.

The mine Karvina has the total area of 32.21km².

The mine Darkov has the total area of 25.9km².

The mine Paskov has the total area of 105.68km² including preserved mine Frenstat (63.17km²).

The North Bohemian coal field is impaired by strong anthropogenic activity, especially the land subsidence is one of the most common and risky effects of the mining industry having impact on the regional environment. Other environmental hazards are connected to remaining existence of lagoon of by-products after black coal processing. The reclamations are running in the region at present time.

2.1.2.3. The environmental data on North Moravian region

The region can be characterised as the zone with high density of population (especially in the Ostrava and Karvina agglomeration) and with the presence of industrial activities mainly metallurgy. Following the information of Czech Hydrometeorological Institute [15] the concentration of dusty aerosol particles under 10µm (PM₁₀) in the region is the highest in the Czech Republic. The exceeding of limit values was detected on most of measured localities in the Ostrava and Karvina districts. It was observed that the concentrations of pollutants in the air rapidly increase during cold period of year influencing annual average value of pollution. The daily limit of PM₁₀ concentration was exceeded more than 100 days a year on the most loaded localities in the Ostrava district. The target value for annual average concentration of dusty aerosol particles under 2.5µm (PM_{2.5}) given by European Directive 2008/50/ES (25µg/m³) was exceeded on all observed localities in the North Bohemian region in 2009.

The limit concentration of benzo(a)pyrene (1ng/m³) is permanently exceeded on most area of the North Bohemian region and multiple exceeding were observed on most localities. The maximum was detected in the Ostrava region (nine multiple of the limit).

2.2. Terrain works methodology

The plan of soil sampling was done first using map sources. The systematic soil sampling scheme based on the equidistance net of sampling points was prepared to maximally maintain the regular character of sampling. However the study targeted only agricultural soils and thus forest soils, urban soils and mining areas were excluded from sampling plan. The numbers of samples in individual districts of the North Bohemian and North Moravian imission regions are presented in table 4. The samples were taken out in the period of 2000 – 2005. The intensity of sampling was, on average, 1 sample/km² depending on the area of the district, number of samples and presence of forest and urban soils and mining areas. The potential sources of contamination were determined (industrial zones, mining zones, power stations) as well as the base meteorological data.

The soil samples were taken out from humic horizons of agricultural soils. The depth of the soil layer for sampling was between 5 and 15 cm. Each sample was collected from 10 partial samples on the locality. The sampling was done in minimal distance of 50 m from road. The samples were stored and transported in jars and frozen by the temperature –18 °C after the transport. Every locality was described and geographic coordinates were assessed using GPS. The determined soil characteristics, including soil type, soil subtype and soil sort (soil texture), pH value [17] and the content of C_{org} [1518], were compared with the contents of POPs. The POPs analysis was realised in accredited commercial laboratories.

North Bohemian imission region					North Moravian imission region		
179					106		
Decin	Usti n/L	Teplice	Most	Chomutov	Ostrava	Karvina	Frydek-Mistek
27	33	47	39	33	40	33	33

Table 4. The numbers of soil samples taken out in the North Bohemian and North Moravian regions and in individual districts.

2.3. Persistent organic pollutants analysis

The methodology of POPs analysis is following for individual groups.

BTEX (benzene, e-benzene, toluene and xylene)

Method used: EPA Method 8260 B [19]

Equipment: Gas chromatograph with mass spectrometer (GC/MS)

Principle

The soil samples are extracted by methanol and defined volume of extract is dosed into re-distilled water after 24 hours. The final solution is analyzed by the system GC/MS using Headspace dozer. The individual substances are defined on the base of comparison of retention time and mass spectrum of analyzed substance considering mass spectrum of standard.

PAHs – polycyclic aromatic hydrocarbons

Method used: methodology TNV 75 8055 [20]

Equipment: High-performance liquid chromatograph with fluorescence detector (HPLC)

Principle

The solid sample analyse comprises the exsiccation using waterless sulphate and the extraction procedure in the acetone solution. The raw extract is analysed without purifying. PAHs are determined by the high-performance liquid chromatography with fluorescence detection (mobile phase – acetonitrile/water). One instrument measured some PAHs portions during isocratic elution under invariable wavelength and the second plant detected the other PAHs portion on equal terms. Two detectors in series assemble the instrument configuration thus two different wavelengths are involved in the detection. Such procedure minimises the difficulties with the gradient elution and with the alteration of the wavelength setting during analyse by the division of unpurified samples.

The concentration levels of individual compounds, the sum values of the compounds (the PAHs sum), the sum value of 2-3 nuclei PAHs and of 4-6 nuclei PAHs were used for the assessment of the load of soils and plants. The sum of toxic equivalency factors for PAHs (the TEF PAHs sum) was involved as well to take into account various toxicological characteristics of individual PAHs compounds. The TEF PAHs sum is defined as the sum of the products of the concentration of each compound multiplied by the toxic equivalent value for carcinogenic compounds. There were used following compounds:

Benzo(a)pyrene and Dibenzo(a,h)anthracene - toxic equivalent value = 1

Benzo(a)anthracene, Benzo(b)fluoranthene and Indeno(1,2,3-cd)pyrene - toxic equivalent value = 0,1

Benzo(k)fluoranthene - toxic equivalent value = 0,01

PCB7 – polychlorinated biphenyls, seven indicator congeners (28, 52, 101, 118, 138, 153, 180)

Method used: EPA Method 8082 [21]

Equipment: Gas chromatography with ECD detector (GC/ECD)

Principle

Dry soil sample is extracted by n-hexan. Extract is dozed after re-cleaning into gas chromatograph where the separation on capillary column and the detection on ECD detector are processed. The software identifies individual congeners on the base of comparison of retention times in calibrated solutions and samples.

DDT sum – sum of DDT, DDE and DDD

Method used: EPA Method 8082

Equipment: Gas chromatography with ECD detector (GC/ECD)

Principle

The dry sample is extracted by dichlormethane using intensive shaking and after volatilization is transferred into n-hexan. 1µl of the extract is dozed into gas chromatograph where the separation on capillary column and the detection on ECD detector are processed. The software identifies individual substances on the base of comparison of retention times in calibrated solutions and samples.

2.4. Results evaluation

The data were processed by the use of elementary statistical methods (Microsoft Excel) and geographic information systems (ESRI ArcGIS 9.2) was used for visualisation of soil load by sum of PAHs and benzo(a)pyrene in agricultural soils. The map outputs are based on the existence of contour lines connecting the points with identical concentration of observed substances. The Inverse Distance Weighting function was used for spatial interpolation. The areas of graduated concentrations connected with the other map layers (base geographical map etc.) create the map output.

3. Results and discussion

3.1. Soil load by polycyclic aromatic hydrocarbons (PAHs)

The comparison of regional load by PAHs shows very clear conclusion: The load of the North Moravian region by PAHs is demonstrably higher. The fundamental statistical data of soil load by sum of PAHs show table 5 (North Bohemian region) and table 6 (North Moravian region). The most loaded district is the Ostrava district with longterm metallurgical tradition where 85% of soil samples overcome preventive limit (1mg/kg) for sum of PAHs in Czech agricultural soils (reflecting background value). The observed maximal values differ ten times between the regions. The differences could be also found from the viewpoint of structural characteristics of contamination. While the participation of toxic benzo(a)pyrene in total load by PAHs reaches about 7% in the North Bohemian region, its participation in the load reaches almost 17% in the North Moravian region (table 7). The load of individual district by PAHs can be documented by the comparison of number of exceeding of proposed indication limit for benzo(a)pyrene and sum of PAHs [12]. There was observed only one limit overrun among the North Bohemian samples, the exceeding was distinctive for benzo(a)pyrene and sum of PAHs (table 8). In the North Moravian region (table 9), there were documented seven localities exceeding indication limit for benzo(a)pyrene or sum of PAHs. Only two localities show exceeding for both indicators and maximum observed value is generally ten times higher than in the North Bohemian region. On the other hand must be accepted that soil load by PAHs was caused by floods on three localities (Stara Karvina) in the North Moravian region. Nevertheless, the problems with increased load by carcinogenic benzo(a)pyrene in the North Moravian region also follow from this comparison.

District	Samples number	Samples number increased	Samples increased %	Maximum value (mg/kg)
Decin	27	2	7.4	5.71
Usti/Labem	33	4	12.1	5.68
Teplice	47	11	23.4	7.67
Most	39	7	18	46.52
Chomutov	33	3	9.1	3.88
Together	179	27	15.1	46.52

Table 5. The load of agricultural soils by sum of PAHs in North Bohemian Region

District	Samples number	Samples number increased	Samples increased %	Maximum value (mg/kg)
Ostrava	40	34	85	28.1
Karvina	33	15	45,5	37.81
Frydek-Mistek	33	14	42,4	336.2
Together	106	63	59,4	336.2

Table 6. The load of agricultural soils by sum of PAHs in North Moravian Region

	Benzo(a)pyrene			Fluoranthene		
	Samples number increased	Samples increased %	Maximum value (mg/kg)	Samples number increased	Samples increased %	Maximum value (mg/kg)
North Bohemia	13	7.3	8.39	30	16.8	5.43
North Moravia	53	50	32.5	52	49.1	68.3

Table 7. The load of soil by benzo(a)pyrene and fluoranthene in North Bohemian and North Moravian Regions

The stronger impact of load by PAHs on health problems of inhabitants in the Nord Moravian region was presented by some authors [4,5]. Spatial distribution of POPs in both region is presented by contour maps where the load by benzo(a)pyrene and fluoranthene (the most widespread PAH substance) is visualised by GIS tools. The load by benzo(a)pyrene in the North Bohemian and North Moravian region shows Figure 3. The load in the North Bohemian region is given mainly by point sources of contamination and just two points with higher contents of sum of PAHs were found, the first near the Decin town and the second one in north-western part of the region. The load in the North Moravian region by carcinogenic benzo(a)pyrene shows surface contamination mainly in the field area around the Ostrava city, increased load is obvious in the vicinity of the Trinec town (ironworks) and the

load of region spreads to the Moravskoslezské Beskydy Mountains in the east of region. The similar trend can be seen in the case of fluoranthene in the North Moravian region, but more visible surface load can be seen in the North Bohemian region in comparison with benzo(a)pyrene (Figure 4). Very probably, more massive load by fluoranthene, that is typical for burning processes, is given by fossil combustibles in towns more than by industrial activities in the North Bohemian region. Moreover, the comparison of layout of coal-fired power stations in the region of North Bohemia (black squares indicate the areas of coal-fired power stations) and the presence of areas with increased load by fluoranthene indicates important role of their activity. Only one coal-fired power station in the North Moravian region (Detmarovice) situated close to border with Poland does not influence the load of region by PAHs as shows the map.

The quality of the load is evaluated on the base of ratio of PAHs substances with 2 nuclei, 3-4 nuclei and 5-6 nuclei. Table 10 presents the values of the sum of medians of individual substances grouped on the base of nuclei number. This value indicates not only the quality of the load but also the quantity (cumulative effect of observed concentrations). Only the quality of the load is defined by the values of medians of the groups PAHs differentiated by nuclei numbers. The both characteristics demonstrate significantly increased load by more nuclei substances in the North Moravian region in comparison with the North Bohemian region and increased toxicity of the load in the North Moravian region by PAHs consecutively.

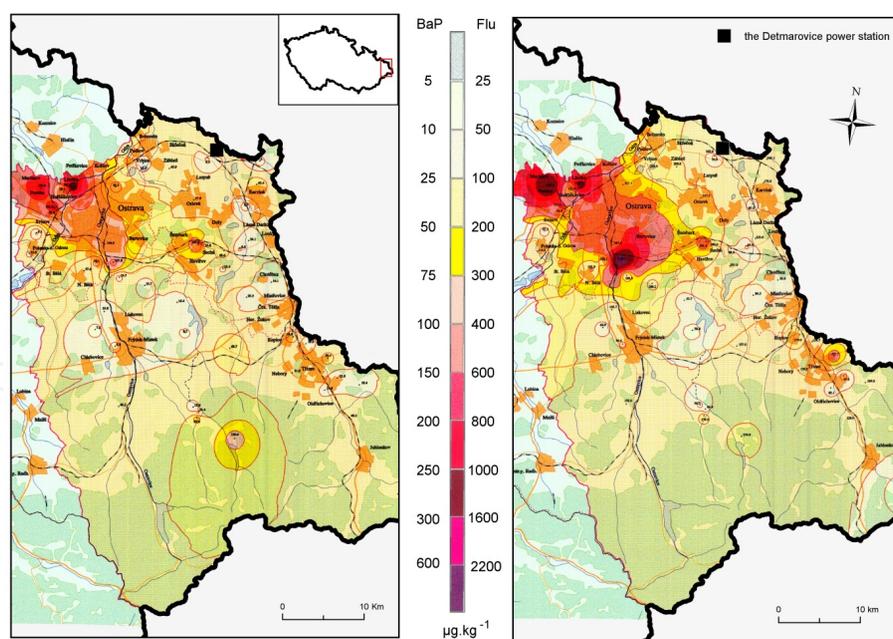


Figure 3. The load of the North Moravian Region by benzo(a)pyrene and fluoranthene ($\mu\text{g/kg}$)

The recent development in the North Moravian region proved no decreasing temporal tendency of air pollution by dust particles and also PAHs, because there spatially coincide various pollution sources in the region and the situation needs more complicated approach in

comparison with the North Bohemian Region where technology improvement in coal-fired power stations influenced positively air quality.

Locality	District	Benzo(a)pyrene (mg/kg)	Sum of PAHs (mg/kg)
Horni Jiretin	Most	8.39	46.52

Table 8. The localities of the North Bohemian region with the load by PAHs exceeding proposed indication limit for benzo(a)pyrene and sum of PAHs in agricultural soil

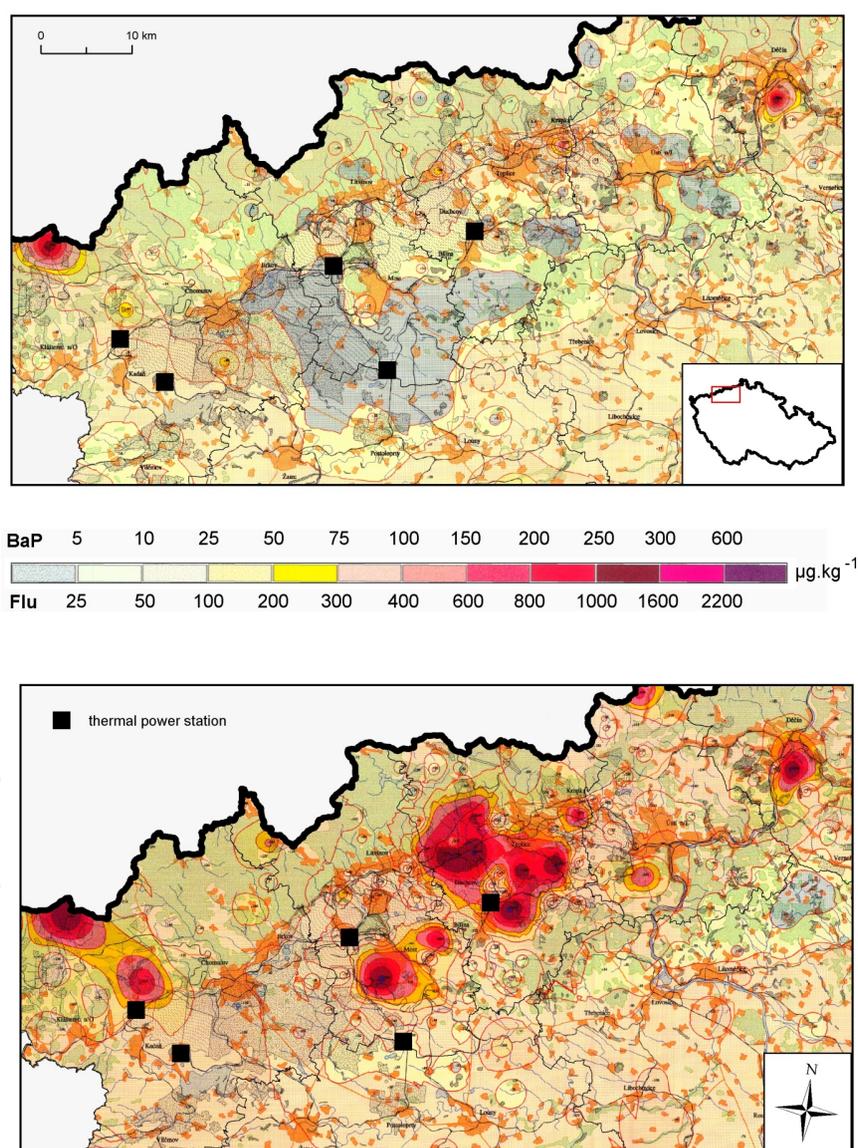


Figure 4. The load of the North Bohemian Region by benzo(a)pyrene and fluoranthene (µg/kg)

3.2. Soil load by monocyclic aromatic hydrocarbons (MAHs)

The soil load by individual substances (benzene, toluene, xylene, e-benzene) from the group of monocyclic aromatic hydrocarbons (MAHs) present tables 11 (North Bohemian Region) and 12 (North Moravian Region). The comparison shows that more loaded by MAHs is the North Bohemian region. The most loaded district is Most where petrochemical factory (Zaluzi u Mostu) is situated. The region Most shows not only the highest number of limit exceeding but also the highest maximal values. E-benzene is the substance with maximal detected value (0,9 mg/kg) at all. Opposite, no exceeding of e-benzene limit in the soil was observed in the North Moravian region where only very slight exceeding of preventive value of benzene, toluene and xylene was observed. Only exceeding of preventive limit was observed and no exceeding of indication limit was detected in the soils of both regions. It is evident that the load by monocyclic aromatic hydrocarbons immediately relates to chemical industry and there is no correlation with the load by polycyclic aromatic hydrocarbons connected with burn processes.

Locality	District	Benzo(a)pyrene (mg/kg)	Sum of PAHs (mg/kg)
Przno	Frydek-Mistek	2.31	23.12
Paskov I	Frydek-Mistek	32.5	336.17
Paskov II	Frydek-Mistek	0.19	95.68
Ostrava-Arnostovice	Ostrava	2.98	28.06
*Stare Mesto Karvina I	Karvina	2.72	25.01
*Stare Mesto Karvina II	Karvina	3.18	27.89
*Stare Mesto Karvina III	Karvina	3.56	37.81

Table 9. The localities of the North Moravian region with the load by PAHs exceeding proposed indication limit for benzo(a)pyrene and sum of PAHs in agricultural soil * The load by PAHs after floods – fluvial load

	North Bohemian Region			North Moravian Region		
	2n	3-4n	5-6n	2n	3-4n	5-6n
Sum of substance. medians (mg/kg)	0.002	0.192	0.018	0.0006	1.337	0.173
Ratio	1	92.6	9	1	2227.8	288.2
Medians of n-groups (mg/kg)	0.002	0.01	0.008	0.0006	0.153	0.0437
Ratio	1	5	4	1	255.1	72.8

Table 10. The sum of medians and medians of PAHs substances in soil differentiated by nuclei number

District	Samples number	Samples number increased	Samples increased %	Maximum value (mg/kg)
Decin	27	0	0	0.02 e-benzene
Usti/Labem	33	0	0	0.04 e-benzene
Teplice	47	1 benzene 1 toluene 4 xylene 6 e-benzene	2.13 benzene 2.13 toluene 8.51 xylene 12.77 e-benzene	0.08 benzene 0.08 toluene 0.12 xylene 0.1 e-benzene
Most	39	3 benzene 3 toluene 6 xylene 6 e-benzene	7.7 benzene 7.7 toluene 15.4 xylene 15.4 e-benzene	0.11 benzene 0.15 toluene 0.48 xylene 0.90 e-benzene
Chomutov	33	0	0	0.04 e-benzene
Together	179	4 benzene 4 toluene 10 xylene 12 e-benzene	2.23 benzene 2.23 toluene 5.59 xylene 6.70 e-benzene	0.11 benzene 0.15 toluene 0.48 xylene 0.90 e-benzene

Table 11. The load of soils by individual monocyclic aromatic hydrocarbons in the North Bohemian region

3.3. The load of soils by chlorinated hydrocarbons (PCBs, DDTs)

The soil load by sum of seven PCB congeners (28, 52, 101, 118, 138, 153, 180) in the North Bohemian and North Moravian region are presented in tables 13 and 14. There is distinctive difference between the loads of the regions when the North Moravian region is loaded much more. More than 25% samples exceeded proposed preventive limit for PCB7 in agricultural soils in the North Moravian region. Only 3.9% samples exceeded preventive limit in the North Bohemian region. The most loaded district from both regions is the district Ostrava where 42.5% samples exceeded preventive limit. The maximal value was detected in the sample from the district Decin in the North Bohemian region. The value 0.52 mg/kg is 26 multiple of proposed preventive limit (0.02 mg/kg) and about one half of proposed indication limit (1 mg/kg) for PCB7 in the soil. The sources of PCB in the environment are concentrated in industrial areas and usually relate to the presence of dumps and waste incinerators [22]. PCB load may relate to historical environmental burdens when PCB revolatilization from soil depends on weather conditions. These processes very probably reflect the soil load of the Ostrava district with high concentration of human activities. The increased soil load was for example confirmed in the urban area of the Prague city by our investigation and general load of Czech agricultural soils moves in the interval of 1.19 – 20.11 µg/kg (geometric means calculated for individual districts of the Czech Republic). The average PCB7 contents in humic horizons of Czech agricultural soils ranged between 5.5 µg/kg (2000 – 2003) and 8.43 µg/kg (2004) following the data of Czech National Stocktaking [23].

District	Samples number	Samples number increased	Samples increased %	Maximum value (mg/kg)
Ostrava	40	0 benzene	0	0.017 benzene
		1 toluene	2.5 toluene	0.031 toluene
		1 xylene	2.5 xylene	0.039 xylene
		0 e-benzene	0 e-benzene	0.009 e-benzene
Karvina	33	1 benzene	3.03 benzene	0.032 benzene
		0 toluene	0 toluene	0.010 toluene
		0 xylene	0 xylene	0.009 xylene
		0 e-benzene	0 e-benzene	0.004 e-benzene
Frydek-Mistek	33	0 benzene	0 benzene	0.020 benzene
		0 toluene	0 toluene	0.003 toluene
		0 xylene	0 xylene	0.010 xylene
		0 e-benzene	0 e-benzene	0.002 e-benzene
Together	106	1 benzene	0.94 benzene	0.032 benzene
		1 toluene	0.94 toluene	0.031 toluene
		1 xylene	0.94 xylene	0.039 xylene
		0 e-benzene	0 e-benzene	0.009 e-benzene

Table 12. The load of soils by individual monocyclic aromatic hydrocarbons in the North Moravian region

District	Samples number	Samples number increased	Samples increased %	Maximum value (mg/kg)
Decin	27	4	14.82	0.52
Usti/Labem	33	2	6.06	0.08
Teplice	47	0	0	0.01
Most	39	1	2.56	0.05
Chomutov	33	0	0	0.01
Together	179	7	3.91	0.52

Table 13. The load of soils by sum of PCB₇ in the North Bohemian region

District	Samples number	Samples number increased	Samples increased %	Maximum value (mg/kg)
Ostrava	40	17	42.5	0.43
Karvina	33	5	15.15	0.13
Frydek-Mistek	33	5	15.15	0.26
Together	106	27	25.47	0.43

Table 14. The load of soils by sum of PCB₇ in the North Moravian region

District	Samples number	Samples number increased DDT/DDE/DDD	Samples increased % DDT/DDE/DDD	Maximum value (mg/kg) DDT/DDE/DDD
Decin	27	0/0/0	0/0/0	0.001/0.001/0.001
Usti/Labem	33	1/0/0	3.03/0/0	1.13/0.001/0.001
Teplice	47	4/4/3	8.5/8.5/6.4	1.21/0.15/0.26
Most	39	6/1/0	15.4/2.6/0	0.06/0.03/0.01
Chomutov	33	1/0/0	3.03/0/0	0.04/0.001/0.001
Together	179	12/5/3	6.7/2.8/1.7	1.21/0.15/0.26

Table 15. The load of soils by DDT and its metabolites in the North Bohemian region

DDT and its congeners have been still registered in agricultural soil of the Czech Republic in spite of DDT use finished in 1974 [22]. DDT decomposition is generally reflected by slowly increased contents of DDE in soils. This trend is more visible in the North Moravian region where the ratio of DDT/DDE/DDD has value 3.5/4/1 while in the North Bohemian region has value 4/1.7/1 (indicating relatively more recent load). We have the hypothesis about non legal use of high doses of DDT in the North Bohemian forests (the Ore Mountains) during the bark beetle calamity in the eighties of 20th century (unsworn information). The level of soil load by DDT and its metabolites is comparable in both regions. Only the Decin district in the North Bohemian region, where no exceeding was observed, differs from the other districts. This fact shows no gap with our hypothesis because the Ore Mountains range does not reach the Decin district area. The general trends of DDTs concentration are complicated in the soils of the Czech Republic because a strong oscillation of DDTs values was observed [23]. Nevertheless the data of Czech National Stocktaking show the decreasing number of DDT exceeding of preventive limit during 2000 – 2002 years (from 60 to 18) and increasing number of DDE exceeding of preventive limit (from 14 to 24).

Only the maximal values of DDTs in the soils of both regions exceed preventive limits and the maximum 1.21 mg/kg reaches 30.25% of proposed indication limit value.

District	Samples number	Samples number increased DDT/DDE/DDD	Samples increased % DDT/DDE/DDD	Maximum value (mg/kg) DDT/DDE/DDD
Ostrava	40	3/3/0	7.5/7.5/0	0.35/0.18/0.005
Karvina	33	2/4/1	6.01/12.1/3.03	0.069/0.032/0.049
Frydek-Mistek	33	2/1/1	6.01/3.03/3.03	0.057/0.033/0.022
Together	106	7/8/2	6.6/7.55/1.89	0.35/0.18/0.049

Table 16. The load of soils by DDT and its metabolites in the North Moravian region

4. Conclusion

The data of soil load by observed POPs groups in two environmentally affected areas indicate generally higher load of the North Moravian region in comparison with the North Bohemian region. This result is especially supported by the comparison of soil load by polycyclic aromatic hydrocarbons. The load relate to spatial coincidence of various pollution sources connected with high concentration of metallurgy and with high urbanization rate in the Ostrava agglomeration. The load of soil by polyaromatic hydrocarbons has diffuse character and exceeding of proposed preventive limit value (based on PAHs background values in Czech soils) was detected on most observed localities. The exceeding of proposed indication limit value for PAHs in soil (derived from human health risks) was detected in the North Moravian region as well. Markedly increased soil load was also monitored in the case of PCBs in the North Moravian region where the effect of increased urban environment plays important role. Nevertheless, the intensity of the load by PCBs is lower and only preventive limit values were exceeded. The different trends were proved for two POPs groups – monoaromatic hydrocarbons and DDTs and its metabolite. While soil load by DDTs is comparable in both regions (with some qualitative differences) the load of agricultural soils by MAHs is markedly higher in the North Bohemian region and especially in the Most district. This is the consequence of petrochemical industry situated close to the Most town. The recent development in both regions may be evaluated as better in the North Bohemian region where the investment into technologies in coal-fired power stations decreased the load of environment by contaminants. The adverse emission situation in the North Moravian region with increased concentration of metallurgy is still remaining.

5. Lists of abbreviations

C_{org}-Content of organic carbon

DDT-Dichlorodiphenyltrichloroethane

MAHs-Monoaromatic hydrocarbons

PAHs-Polyaromatic hydrocarbons

PCB7-Sum of 7 polychlorinated biphenyls congeners

PCDDs/Fs-Polychlorinated dibenzodioxins/furans

PM₁₀-Particulate matter in air of size <10 μm

PM_{2.5}-Particulate matter in air of size < 2.5 μm

POPs-Persistent organic pollutants

REs-Risky elements

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Author details

Radim Vácha*, Jan Skála, Jarmila Čechmánková and Viera Horváthová

*Address all correspondence to: vacha@vumop.cz

Research Institute for Soil and Water Conservation, Prague, Czech Republic

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