EXPLORING THE WAYS HOW CONTAMINATED SOILS AFFECT A GLOBAL FATE AND CYCLING OF POPS – CONCEPTUAL APPROACH

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Introduction

A widespread production and use of persistent organic pollutants (POPs) in industrialized regions together with their environmental persistence led to the intensive contamination of soils [1]. Soil plays an important role in the global fate and distribution of POPs. Based on the physicochemical properties of the individual POP, on the sorption capacity of soil, temperature and other meteorological conditions [2-4], the soil bodies currently represent a long-term storage system for some chemicals, while they act as a pollution source for the others [5]. A re-volatilization is one of the most important elimination pathways and contaminated soils should be considered an important source of POPs to the atmosphere [6-8]. The significant shifts in the soil-air equilibrium status can to be expected in the connection with potential climate changes. For the study of these consequences, we need a detailed assessment of soil as a secondary source of POPs to the atmosphere and based on this, we can try to evaluate the country specific contribution to the global inventory of the atmospheric POPs.

The Czech Republic, as a model country for this study, is considered to be one of the most industrially developed among new member states of the European Union. On the other hand, it is also a country whose industrial development in the last forty years has led to a variety of negative environmental implications and a country, which produced some of POPs (PCBs, organochlorine pesticides such as technical hexachlorocyclohexanes (HCHs) and lindane (γ-HCH), DDT and hexachlorobenzene (HCB). All these POPs are still detectable in abiotic and biotic environmental compartments, including humans.

At the same time, the Czech Republic is a country with vast information on contamination of the environmental matrices based on an intensive POPs monitoring and research projects. One of the most important activities is a long-term POPs monitoring in the background station of the Czech Hydrometeorological Institute in Kosetice. This observatory is a part of the Environmental Monitoring and Assessment Programme (EMEP) as the only station in the Central, Southern and Eastern Europe measuring persistent organics. The POP levels in a variety of environmental matrices (ambient air, wet deposition, surface water, sediment, soil, moss, and needles) are monitored there. This unique data set has been also used for the field validation of the POP transport models in the EMEP MSC-EAST [9-11].

This comparison of modelling results with monitoring data indicated a significant underestimation of the POP concentrations in all measured departments [11]. EMEP MSC-EAST model is based on the emission factors derived from a measurement at major industrial sources leaving out a contribution of secondary sources (re-volatilization from constructions, soils and water). Thus, we can hypothesize that this omission results in the observed bias in predicted POP concentrations. To confirm this hypothesis, an inventory of the secondary sources (contamination levels of the soil and water bodies) as well as a quantification of associated volatilization fluxes is needed [12].

To quantify a contribution of non-industrial sources to contamination of the atmosphere by persistent, toxic substances, and to assess associated risks, we have to accomplish several steps: (1) a country wide inventory of soils, their properties and contamination levels based on available monitoring data, (2) a model estimating total burdens and associated risks for human and wildlife, (3) a laboratory experiments on quantification of volatilization fluxes from soils with various properties and contamination levels, (4) a model estimating a contribution of contaminated soils to ambient air pollution based on the measured soil burdens and laboratory-derived emission factors.

Materials and methods

A total number of 103 soil samples were analyzed for their content of POPs and heavy metals. Methods of soil sampling and sample analysis were described recently [12-14]. One-way ANOVA models discriminating different types of land use according to the levels of pollutants were used.

Results and discussion

Soil inventory

While HCHs and HCB were found at highest levels in arable soils, the enhanced accumulation of PCDDs/Fs, PCBs, PAHs and DDTs were observed in high altitude forest soils. Concentrations of these compounds strongly correlated with a soil organic carbon content, but it was not the only explanation for elevated levels in mountain soils since a significant difference between highland and mountain forest soils was detected.

Results clearly differentiated between arable, grassland and forest soils, and showed that due to the global atmospheric transport, the mountain ecosystems can reach the contamination levels higher than the ones found in urban and industrial regions. It has been confirmed that mountain soils can accumulate persistent organic pollutants over extended time periods as a results of the long-range atmospheric transport, the scavenging effect of coniferous forests and the high organic carbon content of forest soils. It has been also demonstrated that mountain soil is an appropriate matrix to compare an impact of distant pollution sources on various regions and comparison of POPs spatial distribution [15].

More good quality time trend data on the POP residues in soils from different parts of the globe are needed but a long-term research on the soil forming processes is equally important for better understanding of the slow changes in the soil ecosystem and associated POP cycling in the global environment.

Estimation of the soil emission fluxes

Soil data described above can be further used for an inventory of the soil burden and associated risks. However, such detailed information on the extent of contamination as well as the soil quality makes it also possible to assess an inventory of the volatilization fluxes of POPs from polluted soils to air, and to estimate an extent to which soil, as a secondary source of the pollution, is responsible for elevated atmospheric levels of POPs. To complete such model, the volatilization fluxes of organic compounds have to be quantified for soils with various land use, organic carbon content and level of contamination. Since the Czech Republic represents a typical industrial country of the mild climate, such information on both, soil burdens and atmospheric fluxes, would significantly contribute to the on-going inventories of persistent toxic compounds in the environment [5,16].

A systematic tool for estimation of an impact of contaminated soils on the air quality was a laboratory study using a volatilization chamber, designed for a direct measurement of the soil-air exchange of persistent organic pollutant (POP). This chamber was applied for determination of the volatilization fluxes of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). An influence of a soil type and land use, physicochemical properties of selected compounds and their concentrations in soils, a temperature and wind velocity on the partitioning of PCBs and OCPs between soil and air was investigated. The volatilization fluxes were determined for 13 model compounds at 3-5 concentration levels, for two soil organic carbon contents, three temperatures and two wind velocities. As expected, the higher fluxes were measured for more volatile compounds, for soils with lower organic carbon contents or higher contamination, at higher temperatures and higher wind velocities.

This large dataset acquired from the laboratory experiments was further modified using results of the field studies focused on the influence of the soil use and vegetation cover on the extent of volatilization. It has been shown that permanent grass cover limits the volatilization loss to 50% while plowing and cultivating of soil causes a significant increase, especially for more volatile compounds. Generated data can be used for a model inventory of an impact of the secondary pollution sources on the air contamination as well as for development of various distribution and transport models.

To compare the fluxes from arable and grass covered soils, two independent techniques were applied. A volatilization flux from permanently grass covered field was measured using a hat sampler positioned 10 cm above the ground. The same measurement was repeated after the grass removal and plowing the field. The volatilization fluxes of various compounds from the grass covered soil reached only 25-75% of the one from the open field. To confirm this result, an intact, grass covered block of soil was collected from the same site and placed into the laboratory volatilization chamber. These values can be applied as the compound-specific correcting factors for modification of the laboratory-derived volatilization fluxes when modeling a soil-air exchange for various soils and seasons of the year.

To prevent the overestimation of the atmospheric burdens resulting from using a pre-cleaned air in the laboratory simulations, the volatilization fluxes have to be calculated only for the sites where the fugacity fraction higher than 0.5 indicates a net volatilization from soil. Such detailed model for polychlorinated biphenyls and organochlorine pesticides is currently under development. A preliminary study performed on PCB 153 indicated a total burden of 61 tons of this compound in Czech soils with the annual volatilization flux of 169 kilograms.

Assessing spatial POPs soil contamination and related health risk in the Czech Republic
This part of the study aims to discuss possibility of applying spatial GIS data models to facilitate spatial analytical modelling. GIS is a tool that has the potential to overcome some limitations by combining spatial data from diverse sources. It allows description and analytical interactions, develops predictive models, and provides support for decision making. GIS is widely applied for environmental modelling [17-19]. We defined the following goals:

a) To summarize available POP levels and model the spatial distribution in soils of the Czech Republic;
b) To calculate the POP burdens in soils based on the first step;
c) To estimate the risk potentials of contaminated soils for humans.

A total of 3782 soil samples were analyzed for the contents of POPs (selected PCBs and OCPs) in frames of various monitoring programmes and screening studies. The first part of the samples originates from the bazal monitoring of soils of the Ministry of Agriculture CR. This consists of 216 agricultural sites. The second part provides the soil samples from various projects of the RECETOX Centre representing mainly grasslands (242 localities).

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Risk Assessment
Applied methodology combines quantitative human health risk assessment and spatial basal GIS methods to produce an assessment of risks to human health from exposure to contaminated land, in a manner which preserves the spatial distribution of risks and provides a measure of uncertainty in the assessment. Intake of soil contaminants and consequent risk is calculated using an adaptation of the SSL model. These maps provide a powerful visual tool for the risk managers, enabling efficient targeting of risk reduction measures to different locations.

Analysis was performed using maximal levels of individual chemical compound during whole sampling period (1998-2006). This approach guarantees the worst case scenario within consequential risk assessment. Datasets were divided in 2 parts which involve 1) agriculture locations and 2) forest soil locations.

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This approach can identify areas with high need to decrease exposure resulting to decreasing health risks. It is obvious, not only improving sampling homogeneity, but also identification highly populated places should be the priority of risk assessors to reduce health risks in population. These maps then provide a powerful visual tool for risk managers, enabling efficient targeting of risk reduction measures to different locations, and for national monitoring net improvement.

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