

## **Introduction**

The basic idea of this session is to exchange experiences of POPs monitoring in soils including sampling techniques and evaluation strategies. Up to now, different and even not harmonized experimental strategies rarely allow to compare results or use data for regional or global models.

Since more than two decades, POPs are monitored in environmental media and especially in soils. Whereas harmonized methods for ambient air monitoring such as active and passive samplers or accumulation monitors such as spruce needles, kale, or bulk deposition samplers are used to give an image of the pollution on a short time scale, due to their heterogeneity, their accumulation and long-term storage potential soils ask for more specific and dedicated sampling and analytical methods.

Also, compared to water and air, soil processes act on a long-term scale and therefore accumulation of POPs is less sensitive to environmental influences such as UV-light, temperature variance, and others. On the other hand, accumulation and fate of POPs in soils are largely influenced by the vegetation cover and the land use of (e.g. natural, agricultural, silvicultural soils, housing or industrial area).

POPs have been extensively studied in the atmosphere and atmospheric depositions specifically in urban areas in conjunction with the impact on agricultural or forest soils (see refs 1 - 11). Some of these studies suggest a dependency between POP concentrations and environmental/local parameters, such as altitude, latitude, population density, or soil total organic carbon (TOC). However, in most cases it is difficult to make the proof as the areas studied are relatively small or the data basis is in a statistical sense limited. Also, direct comparison of published data is often complicated by varying sampling strategies, such as sampled horizons and soil depths, as well as varying target compounds.

Considering this, the question arises if we need a best practice guidance for generating representative, reliable and comparable data from soil monitoring. Further, the question arises how these data can be used for verifying past and present releases (inventories), match with other monitoring data, or estimate critical loads to secure the health of soils in the future.

## **Materials and methods**

In Germany, as consequence of the soil legislation and the technical rules for sampling and analytical procedures given therein, the sampling protocol of most studies and soil inventories is similar. In a recent inventory (second forest soil inventory, see refs 12 - 14) the sampling for about 2000 locations has been performed within 3 years by about 20 different sampling teams following an identical standardized operating procedure (SOP) which has been evaluated during a pretest.

On each plot, material from eight satellite points was combined to one composite sample. Distances between sampling center and satellite points were 10 m. Samples were taken from the organic layer (Of/Oh-horizons) excluding the litter horizon (Ol), as well as from the mineral soil in 0-5 cm and 5-10 cm depth. Special care was taken to separate the humic layer from the mineral layer. In many cases, specifically when lacking a dense network of roots, a 30x30 cm metal frame was applied to the soil surface and the humic layer was gently removed from the underlying soil horizon. Alternatively, hand auger equipment was used to sample the organic and the mineral layer in a single step. Here the differentiation of humic layer and mineral layer was performed visually. The mineral soil was sampled with sampling rings (100 and 250 cm). The samples were transferred to 1 L brown-glass bottles, sealed with alumina foil and stored until further pretreatment at 20 C. To remove larger particles, the raw field samples were sieved by 5 mm (organic layer) and 2 mm (mineral soil) mesh size, homogenized, and kept in a cooled storage until further analytical pretreatment

Additionally, on each sampling spot, a soil pit was dug in the center of the sampling plot to gain a pedological description of the site and to take material for soil physics tests. Finally, each plot is characterized inter alia by the abundances of the chemical pollutants, the soil and humus type, the type of forest stand (deciduous, coniferous, mixed), types of soil horizons and their thicknesses and bulk densities, TOC, and pH. These data allow us to evaluate not only the pollution in terms of contents (mass concentrations as mg/kg) but also in terms of stocks and loads. The latter figures are more relevant e.g. when relating emission scenarios to the effective deposition. The following example may elucidate the relevance of accompanying data of soil physics.

### Results and discussion

In Table 1 the contents show a significant decrease by depth from the humic horizon to the subsequent horizons / layers. The highest concentration of PCBs is generally found in the humic horizon. When calculating the stocks which are the thickness and density corrected data, the ratio between humic horizon and mineral horizon inverts. The highest stock is found in the top mineral soil layer with a sharp decrease by depth to the subsequent layer.

Conclusively, it comes into consideration if data not sampled by horizons and with lacking information about soil physics data can really give a true image of the pollution of soil. Also, it becomes increasingly difficult to compare results of different studies which apply different sampling strategies or do not report in detail the accompanying information.

Table 1: comparison of contents and stocks. Medians (ng/g d.m. and ng d.m./square meter) of indicator PCBs for 440 sampling plots in German forest soils.

soil layer	Content (ng/g)	Stock (ng/sqm)
Humic horizon	13	30
mineral soil 0-5 cm	3	90
mineral soil 5-10 cm	1	30

The paper will rise some guiding questions (and will give indications of its relevance) which are to be considered before any practical start of a soil inventory study, e.g.:

- identify the purpose of the study, e.g. (to derive background values or identify hotspots or levels of contamination; accidental or long-term monitoring,
- identify the group of POPs, their chemical properties
- size of soil samples
- sampling strategies, composite samples versus single samples, sampling by depth and/or by horizons
- sampling patterns
- which data on soils physics are needed
- sampling time, sampling frequency
- sample pretreatment: drying, sieving, grinding
- Extraction and separation: acid pretreatment, extraction solvent
- QA/QC
- Reporting

The paper will refer to recent publications and standardized test guidelines such as the ISO 18400 series (soil quality – sampling procedures) and other soil related standards.

### Acknowledgements

This study was possible as a result of the cooperation between the federal and state authorities for forest and environment. Specifically, forest soil samples were taken by the authorities of the German states and provided for this study. Financial support by the research fund of the Federal Environment Agency (UBA) is gratefully acknowledged (FKZ 3707 71 201).

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