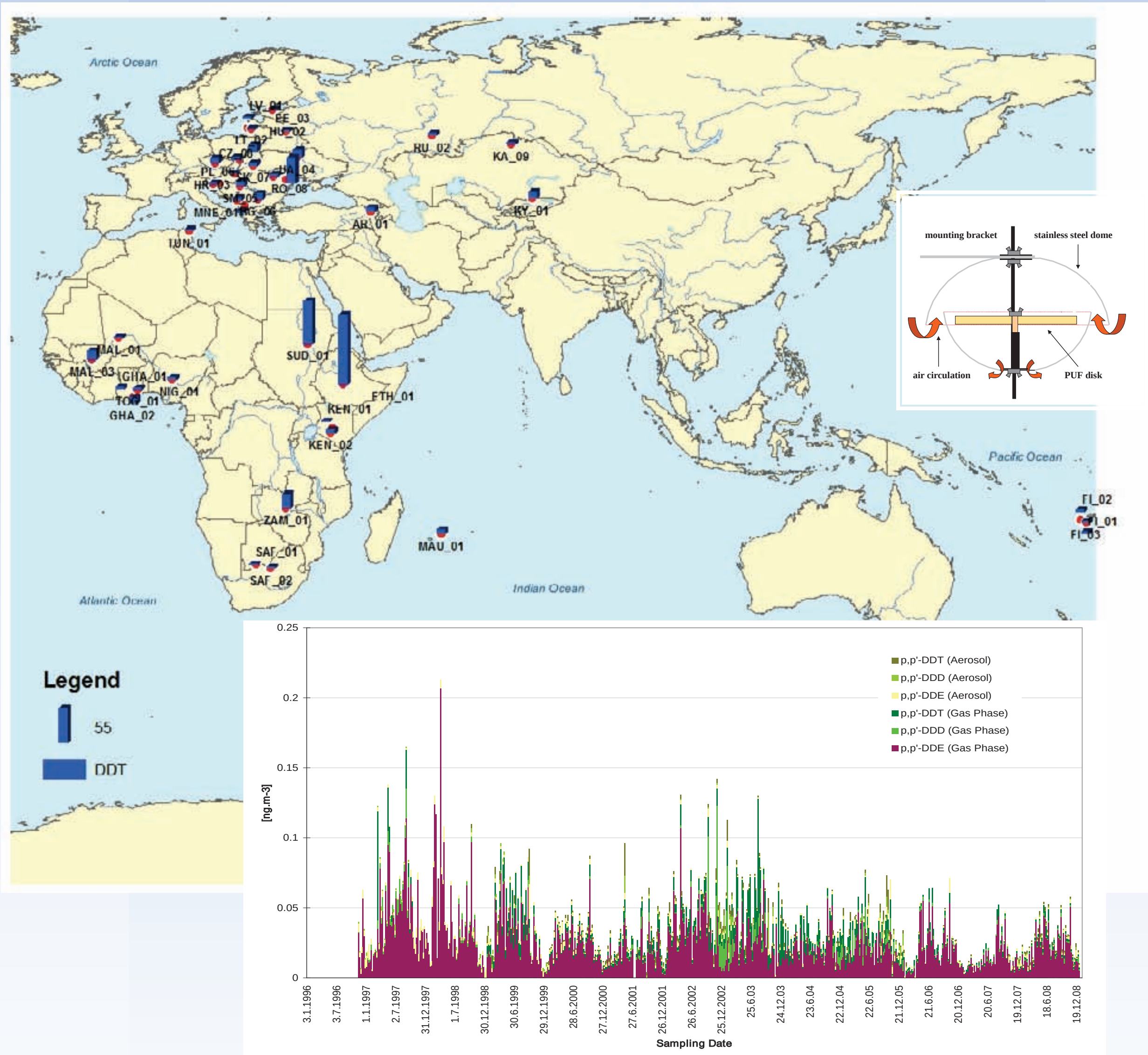
RECETOX

RESEARCH CENTRE FOR ENVIRONMENTAL CHEMISTRY AND ECOTOXICOLOGY

Towards the Global Monitoring of POPs

Contribution of the MONET Networks



Jana Klánová, Pavel Čupr, Ivan Holoubek, Jana Borůvková, Petra Přibylová, Radovan Kareš, Jiří Kohoutek, Alice Dvorská, Jiří Komprda

Masaryk University
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This report summarizes results of the ambient air monitoring activities in the Central and Eastern European region (CEEC), Central Asia, Africa and Pacific Islands driven by RECETOX as the nominated Regional Center of the Stockholm Convention for the region of Central and Eastern Europe under the common name of the MONET networks. For many of the participating countries these activities generated first data on the atmospheric levels of POPs.

A term of "**persistent organic pollutants**" (POPs) represents several classes of organic contaminants including polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and other industrial and agricultural chemicals. Dwue to their wide distribution, ability to bioaccumulate in the biotic tissues, and potential harmful effects such as immunotoxicity, neurotoxicity, developmental toxicity, carcinogenicity, mutagenicity, and endocrine disruption potentials, POPs have remained in the center of scientific attention for the last decades. Polycyclic aromatic hydrocarbons (PAHs) are often included in this group of compounds because of their potential for long-range transport even though their physicochemical properties do not suggest the persistency and bioaccumulation potential.

The **Stockholm Convention** (SC) on Persistent Organic Pollutants (POPs) entered into force on the May 17, 2004 with the main objective to protect human health and the environment from persistent organic pollutants by reducing or eliminating their releases into the environment. According to Article 16 of the SC, its **effectiveness shall be evaluated** starting four years after the date of its entry into force, and periodically thereafter at intervals to be decided by the Conference of the Parties (COP). **Global Monitoring Plan** (GMP) has been developed with an objective of evaluating whether the POPs actually were reduced or eliminated on the global scale. GMP should outline a strategic and cost effective approach built on **existing monitoring programs** to the extent possible. It has to be simple, practical, feasible and sustainable. Design has to go beyond the first monitoring report and address long-term needs for attaining appropriate representative data in all regions to achieve global coverage.

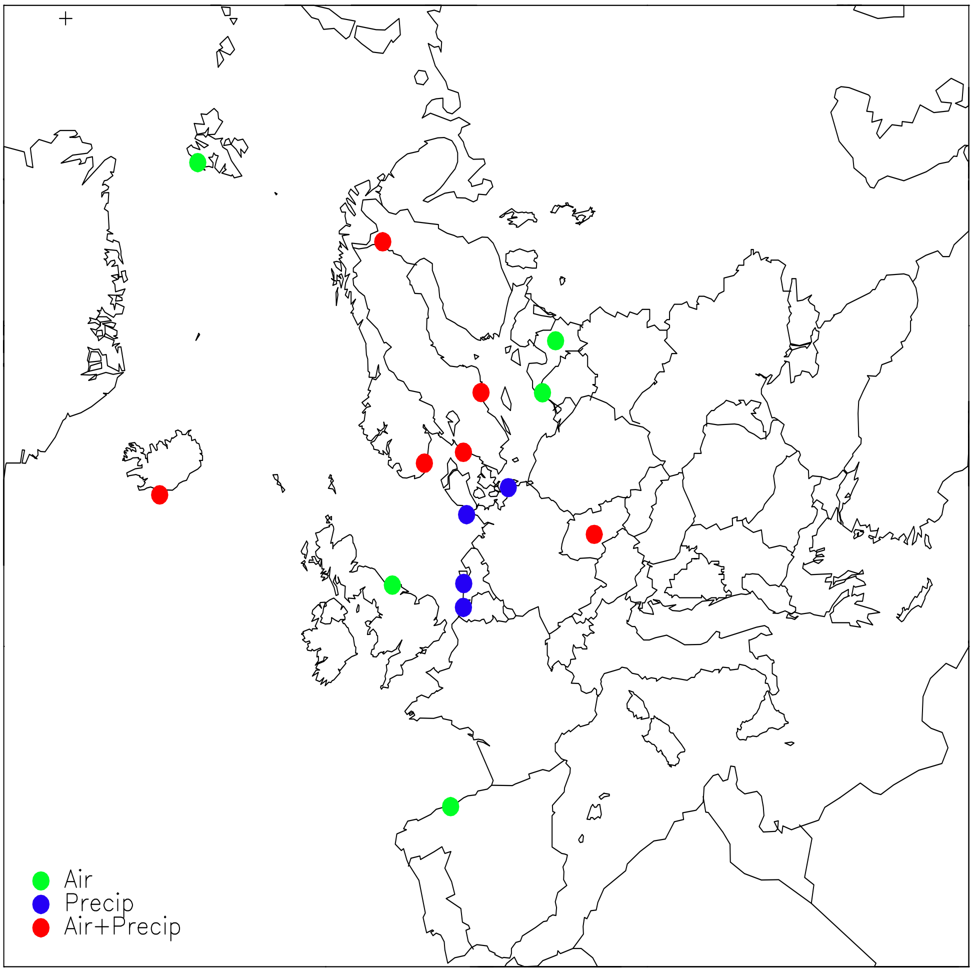


Figure 1: EMEP POPs monitoring network.

One of the programs coordinating such monitoring effort on multiple sites is the **European Monitoring and Evaluation Programme** (EMEP). It was established with the main goal of providing the governments and subsidiary bodies under the Convention on Long Range Trans-boundary Air Pollution (CLRTAP) with qualified scientific information supporting development and evaluation of the international protocols. A map of the EMEP stations reporting on the POP levels in atmosphere and precipitation is presented in Fig. 1. **Kosetice observatory** of the Czech Hydrometeorological Institute located in the southern Czech Republic (N49°35´; E15°05´) is the only site where POPs are being determined in some additional matrices as well. The samples of ambient air, wet deposition, surface water, sediment, soil and biota, as the key components of the environmental system, have been collected for the last 20 years at this station.

A **typical seasonality** in the atmospheric concentrations of POPs can be seen in Figs. 2-6. The PAH levels show a characteristic pattern (Fig. 2) prompted by higher occurrence of these compounds in the cold seasons when they are produced by various combustion processes. The highest atmospheric levels of PAHs found in January and February were as much as three orders of magnitude higher than the lowest ones measured in July and August.

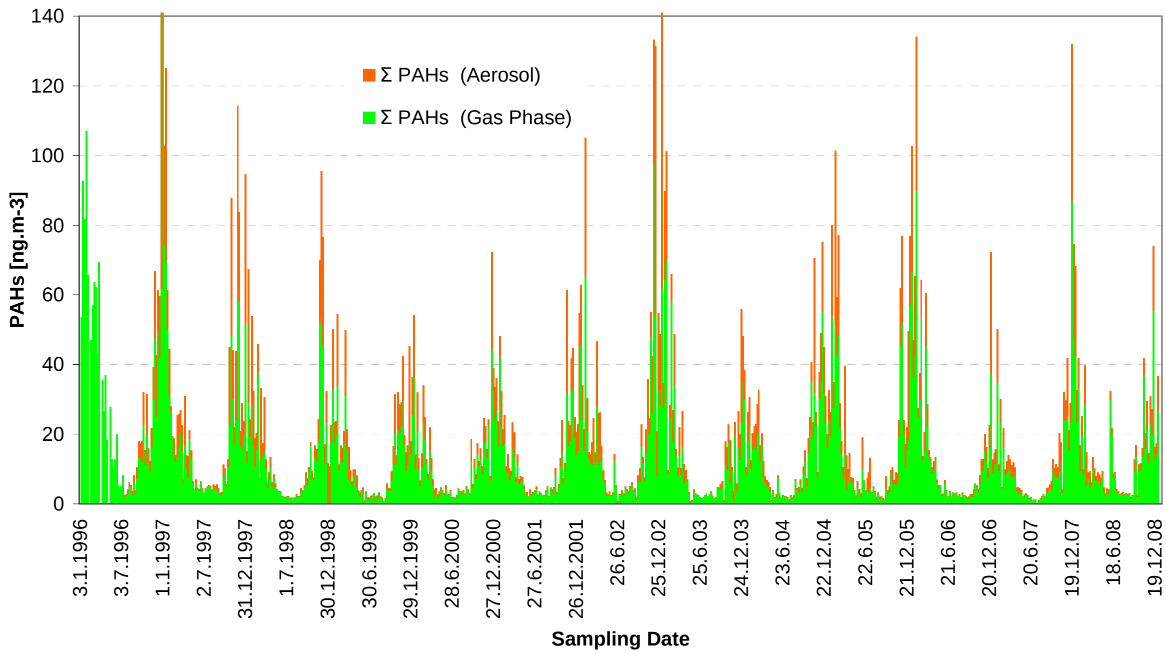


Figure 2: Polyaromatic hydrocarbons (PAHs) in ambient air (ng m^{-3}), Kosetice observatory, 1996-2008 (weekly sampling).

PCB and OCP concentrations displayed a very different profile (Figs. 3-6). Most of these compounds were banned in Europe and their maxima are not connected to their production or seasonal application. They are present in atmosphere due to **volatilization from the old deposits** (soils, sediments, wastes) or due to long-range atmospheric transport from the regions where they are still being applied. In agreement with this hypothesis, elevated levels of organochlorines are observed in summer when increasing temperatures enhance evaporation of these compounds. Even though this seasonality is not as well pronounced as it is in the case of PAHs, it can still be detected for PCBs in Fig. 3, and for pesticides in Figs. 4 - 6.

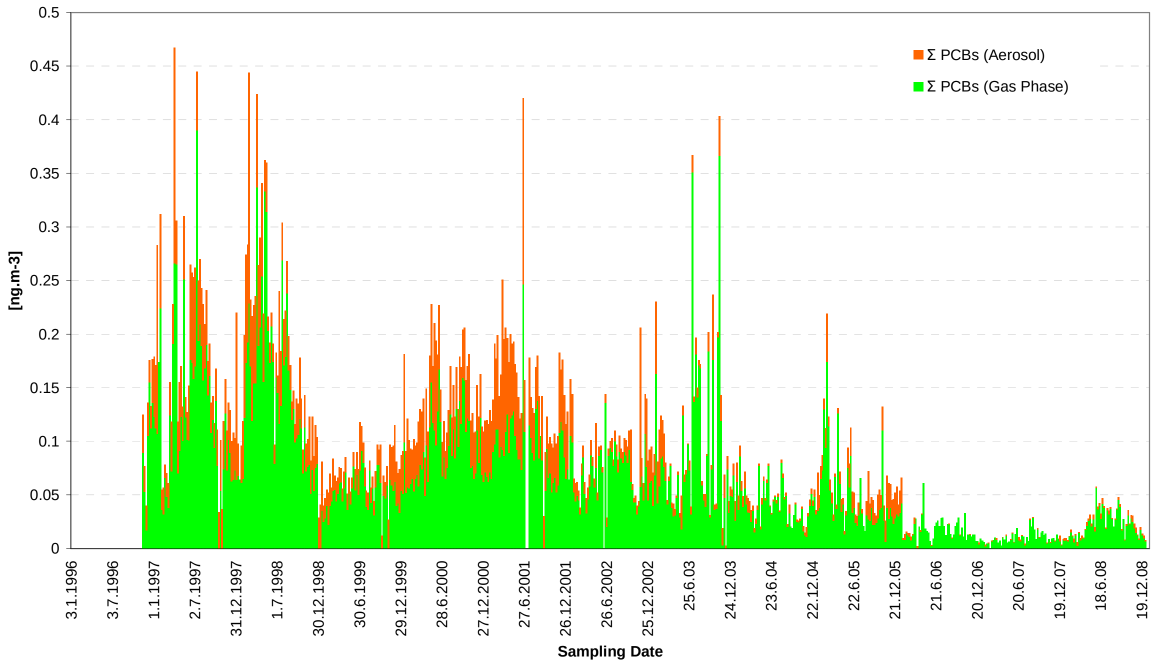


Figure 3: Polychlorinated biphenyls (PCBs) in ambient air (ng m^{-3}), Kosetice observatory, 1996-2008 (weekly sampling).

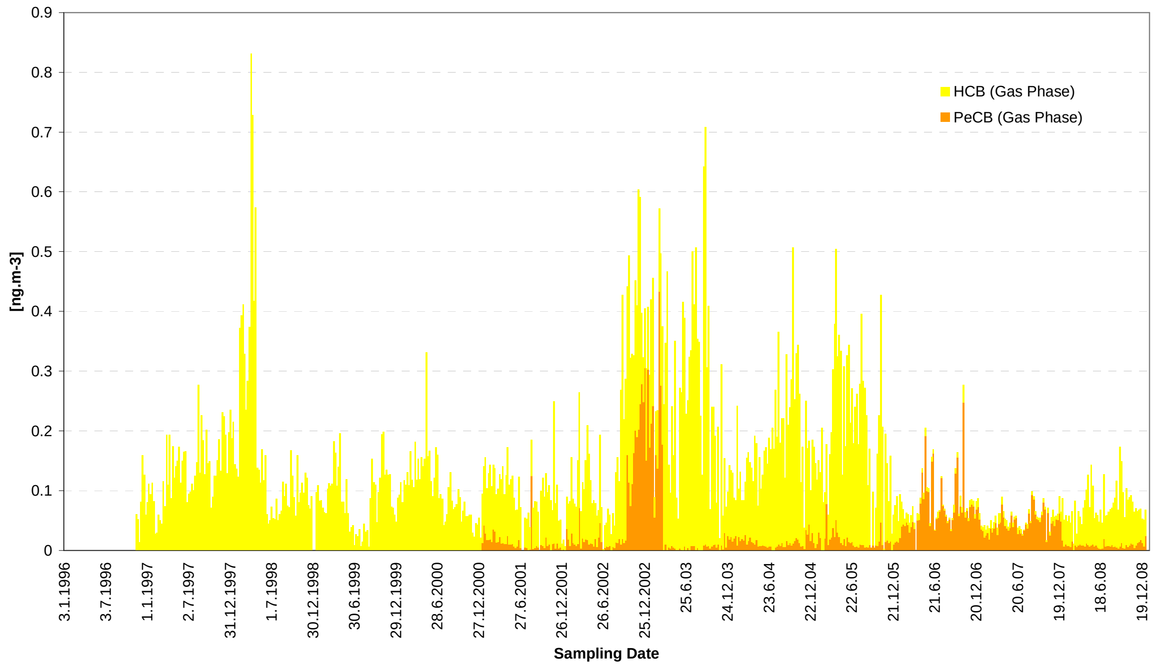


Figure 4: Hexachlorobenzene (HCB) and Pentachlorobenzene (PeCB) in ambient air (ng m^{-3}), Kosetice observatory, 1996-2008 (weekly sampling).

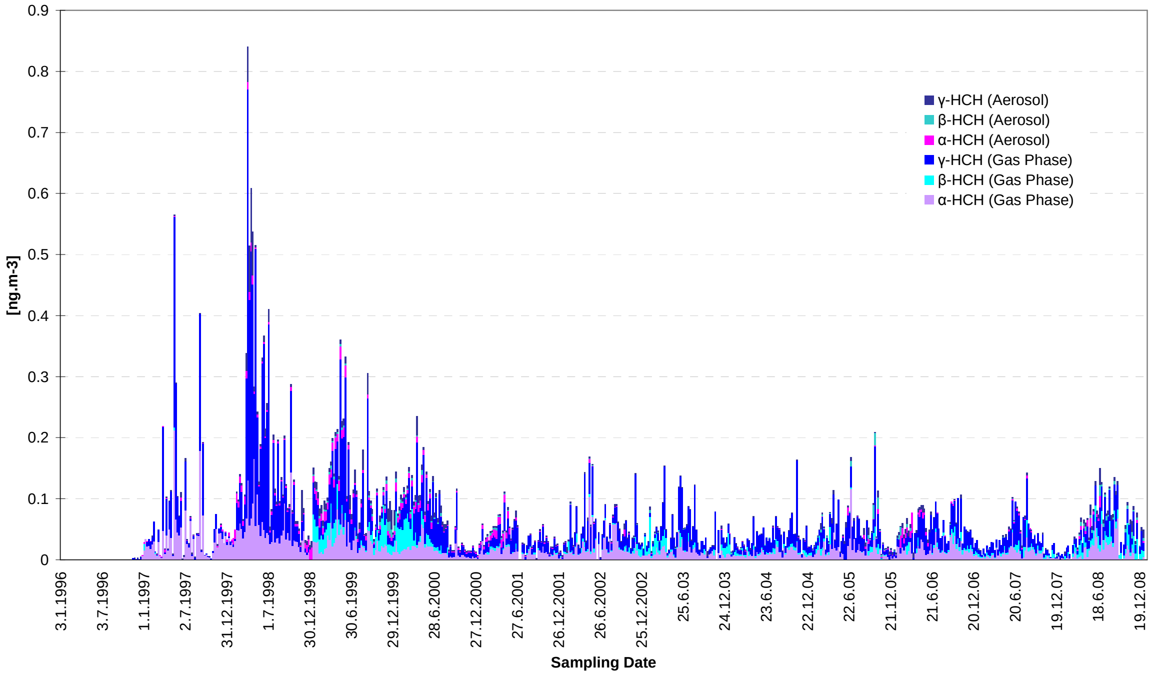


Figure 5: Hexachlorocyclohexanes (HCHs) in ambient air (ng m^{-3}), Kosetice observatory, 1996-2008 (weekly sampling).

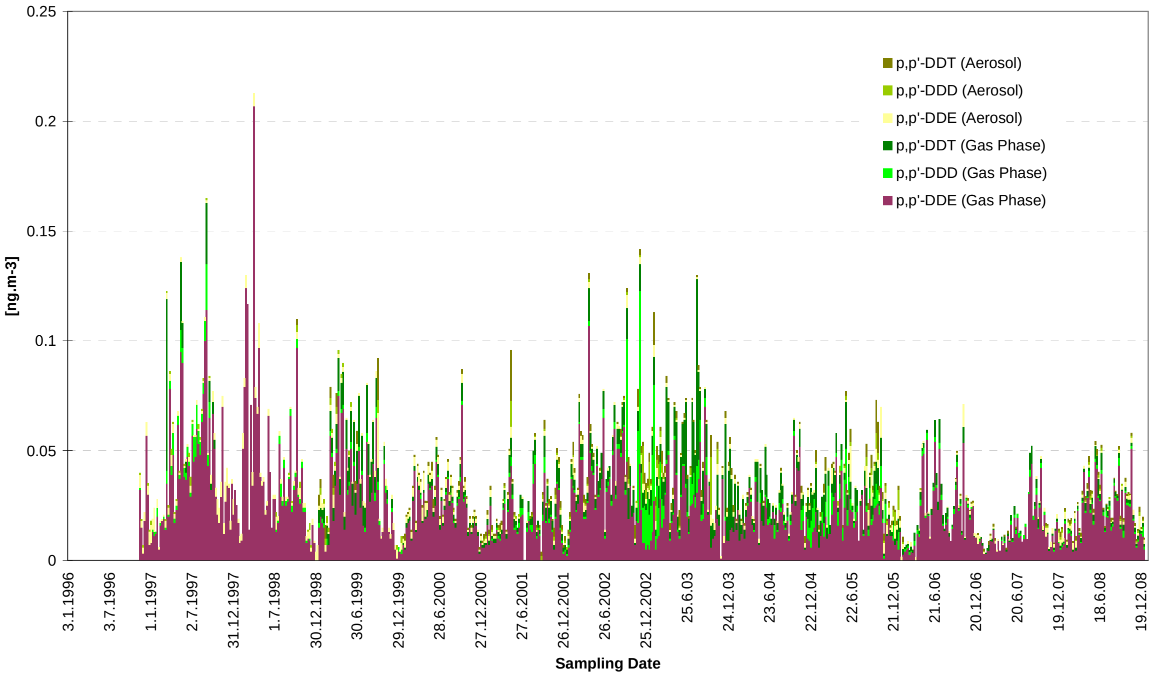


Figure 6: DDTs in ambient air (ng m^{-3}), Kosetice observatory, 1996-2008 (weekly sampling).

Annual median air concentrations were calculated for all subgroups (PAHs, PCBs, HCB, HCHs and DDTs) and resulting values were compared to evaluate the **long-term trends** for each group of compounds and the period of 1996-2008 (Fig. 7). While PAH levels have been quite stabile in the last decade, PCBs showed generally decreasing trends. Pesticides fluctuated showing highest atmospheric concentrations in two periods immediately following the major floods (1997 and 2002).

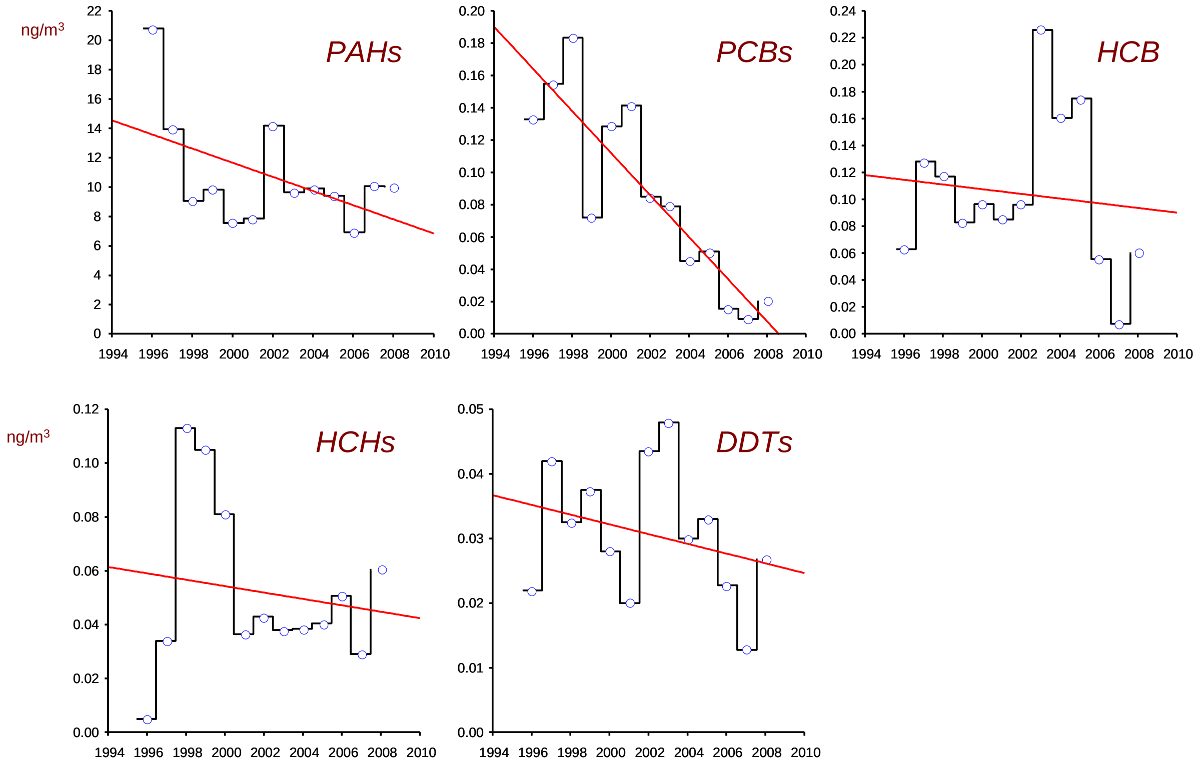


Figure 7: Time related trends of the atmospheric levels of POPs in Košetice.

Monitoring data from Kosetice can be used for an **assessment of sources** and distribution processes, and for validation of long-range transport and environmental fate models (Fig. 8).

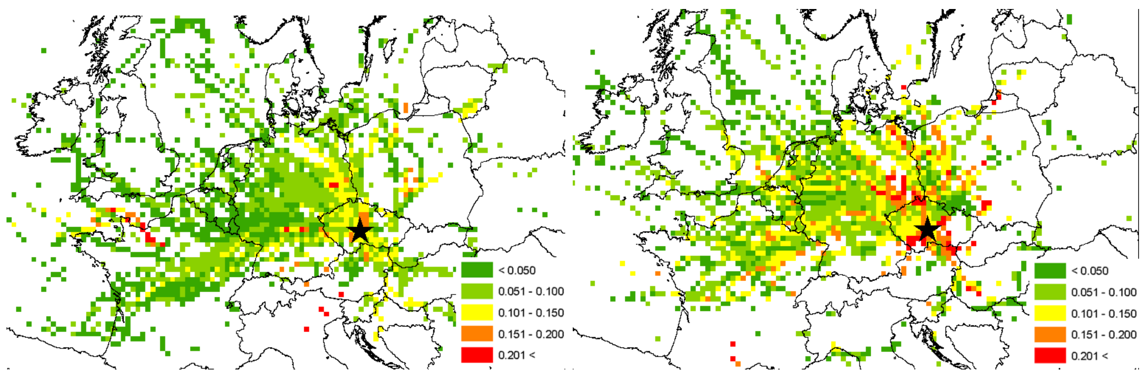


Figure 8: Distribution of ground source loadings for HCB in two time periods (1997-99 and 2004-06) derived from the air mass back trajectory analysis. The dark green colour depicts areas with the lowest contribution to HCB levels measured in Kosetice, whereas dark red depicts areas of the highest contribution.

The **integrated monitoring program** allows for comparison of the long-term trends of the POP levels in various matrices. The atmospheric samples are most homogenous due to efficient mixing of air. On the other hand, they are most variable in time due to the fast response of atmosphere to any changes in point and diffusive sources. The moss or needle samples respond very well to current atmospheric levels of POPs. The sediment and soil samples offer the long-term record of the POP contamination because they act as an efficient sink of the POP pollution. However, we need to be aware that matrices with high accumulation potential can also turn from the sinks to the sources of POPs.

As can be seen in Fig. 9, **time related trends of POPs** vary between the compounds and matrices. For PCBs, significantly decreasing trend was observed not only for air, needles and moss, but also for sediment and soil. In contrast, decreasing trends were not significant for pesticides in most of the matrices.

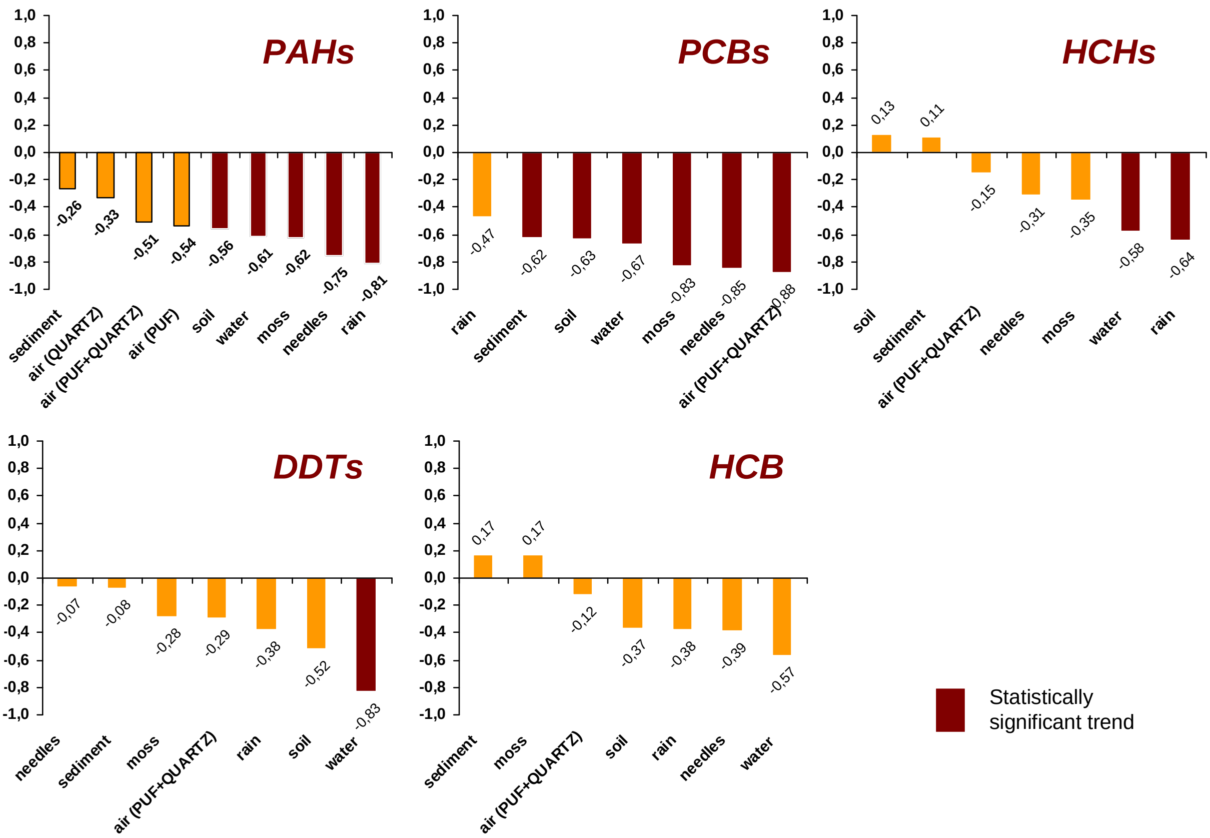


Figure 9: Time related trends of POPs in various matrices from Kosetice (trends range from 1 - decreasing trend, to 1 - increasing trend).

Long-term data from the multimedia sampling can be also used for **evaluation of various environmental models**. A fugacity model, for instance, was applied to explain observed decadal trends in concentrations of polycyclic aromatic hydrocarbons measured in Kosetice soil. Weekly air concentrations were used as input data for the unsteady state model; concentrations in soil were calculated and compared to experimental data. General agreement between measured and predicted soil concentrations of PAHs was observed. Temporal trends in PAH concentrations in Kosetice can be related to changes in residential heating. Predicted soil concentrations of volatile PAHs namely acenaphthylene, fluorene and phenanthrene were in better correspondence with observed data than concentrations of less volatile PAHs i.e. dibenzo(ah)anthracene, benzo(a)pyrene and benzo(ghi)perylene. These discrepancies between the model results and field data are probably a result of the simplified description of degradation and aging processes in soil. The results from our dynamic multicompartmental model confirmed our hypothesis about unsteady state conditions between the air and soil, and suggested that commonly used simple steady state model should be only applied as a predictive tool in a small region when local sources and sinks are well described.

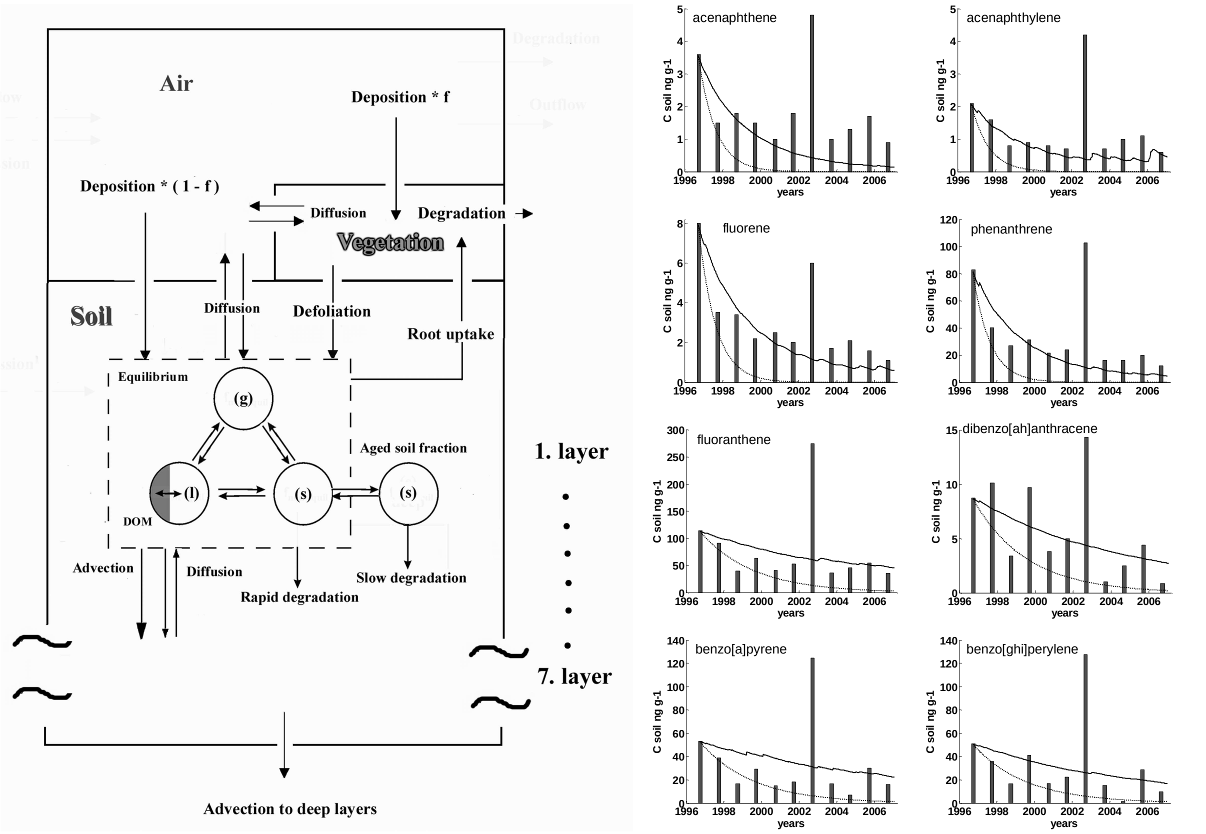


Figure 10: Long term temporal trends of the soil concentrations: a **<u>comparison of the model simulation with the soil concentrations</u>** measured in Kosetice.

Since the high volume air samplers as expensive devices requiring reliable power supply as well as trained operators are not widely available, the air monitoring of POPs has only been conducted at limited number of sites. In the last years, however, new demands resulted in development of the range of **passive air samplers** (PAS) as new tools for the air quality monitoring. PAS offer a cheap and versatile alternative to the conventional high volume air sampling and they have been currently recommended as one of the methods suitable for the purpose of new long-term monitoring projects. As PAS tend to provide information on the long-term average conditions in the atmosphere and ignore variability on a shorter time scale data, they are particularly suited to complement the high volume air measurements and serve in the evaluation of multimedia fate and transport models. Based on their unquestionable advantages, passive samplers were recommended by the Preliminary Ad-hoc Technical Working Group for the Global Monitoring Plan as a **suitable tool for the Global monitoring of POPs in ambient air**.

Passive air sampling device used in the following studies consists of two stainless steel bowls attached to the common axes to form a protective chamber for the polyurethane foam filter. The filter is attached to the same rod and it is sheltered against the wet and dry atmospheric deposition, wind and UV light. Exposure times between four and twelve weeks enable determination of many compounds from the POP group. Average sampling rate was estimated to be **3.5 -7 m^3/day** which roughly corresponds to **100-200 m^3** of the air sampled during four weeks of deployment.

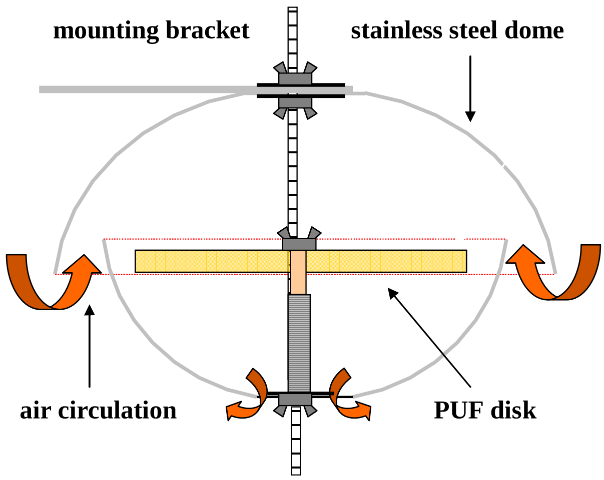


Figure 11: Scheme of the passive air sampler.

The passive samplers have been continuously co-employed with the high volume samplers as a part of the atmospheric monitoring of POPs **in Kosetice since 2003**. That allowed for the field calibration of PAS not only for the gas-phase chemicals but also for the particle-bound compounds. Five years of data are showing the same seasonal fluctuations as well as temporal trends as the results of the high volume monitoring (Fig. 12).

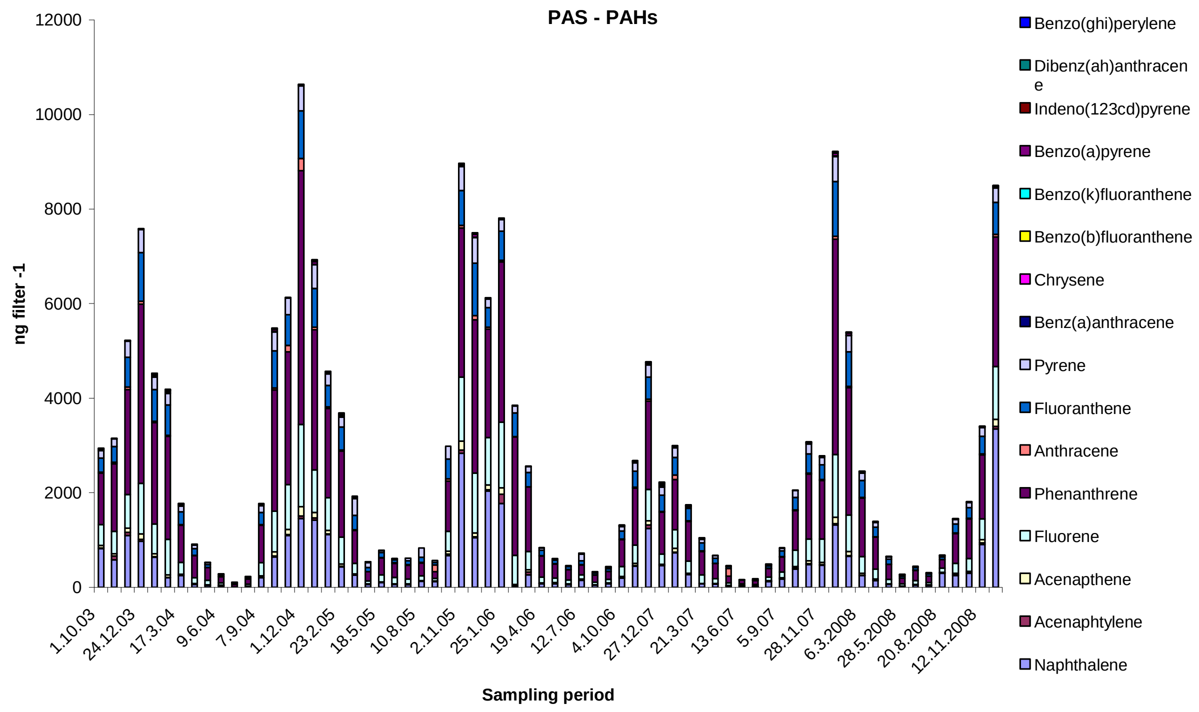


Figure 12: PAHs in ambient air (ng filter^{-1}), Kosetice observatory, 2003-2008 (passive sampling).

Based on these positive results, the **National POPs monitoring network** based on the PAS technique has been established in the **Czech Republic (MONET-CZ)**. In 2004, a number of sites in the vicinity of various sources (chemical, petrochemical and cement industry, traffic, domestic heating) was monitored to evaluate their impacts and pollution trends. Redundant sites were omitted in 2005, and new source types were added (municipal, medical and danger waste incinerators, remediation technologies). A new set of 15 background sampling sites was included in cooperation with the Czech Hydrometeorological Institute. This set consisted of the mountain sites along the Czech borders and it was meant to evaluate an impact of transboundary transport in this region. The new design of the MONET network containing 37 sites (including 15 backgrounds) was introduced and initiated in **January, 2006**. It has been maintained since, collecting every year thirteen 28-day samples from each site.

Results from the first **3 years of the MONET network** for selected groups of compounds (background sites only) are presented in Figs. 13-17 (winter months are shown in yellow, summer months in red color). Typical seasonal trends showing the winter maxima were observed for PAHs. For DDTs, fall concentrations were consistently the highest. Seasonal maxima of HCHs varied from site to site. Interestingly, HCB concentrations were higher in the winter rather than summer suggesting that combustion sources (seasonal residential heating) were more significant source of HCB than summer evaporation from diffusive secondary sources. No clear temporal trends have been observed yet. Remaining rural, urban and industrial sites are shown (together with the Central and Eastern European sites) in the plot-and-whisker graphs in the following figures.

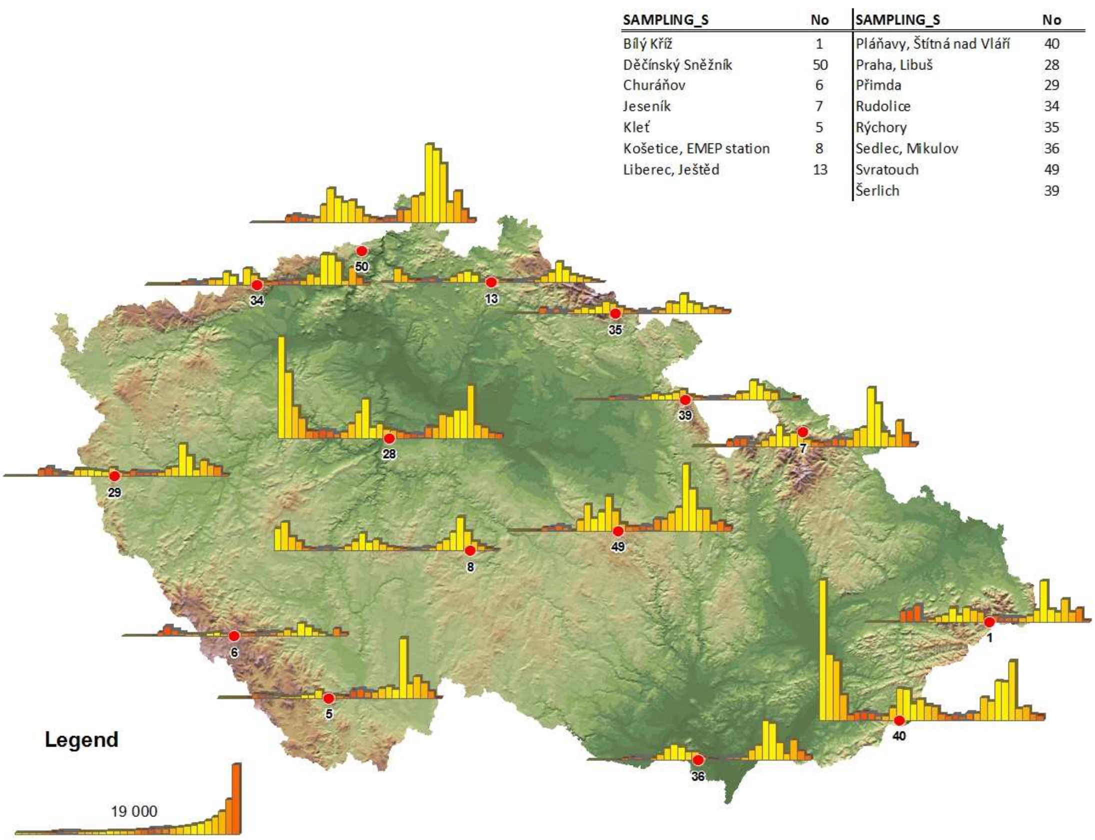


Figure 13: Passive air sampling 2006-2008, MONET-CZ, PAHs (ng filter^{-1}).

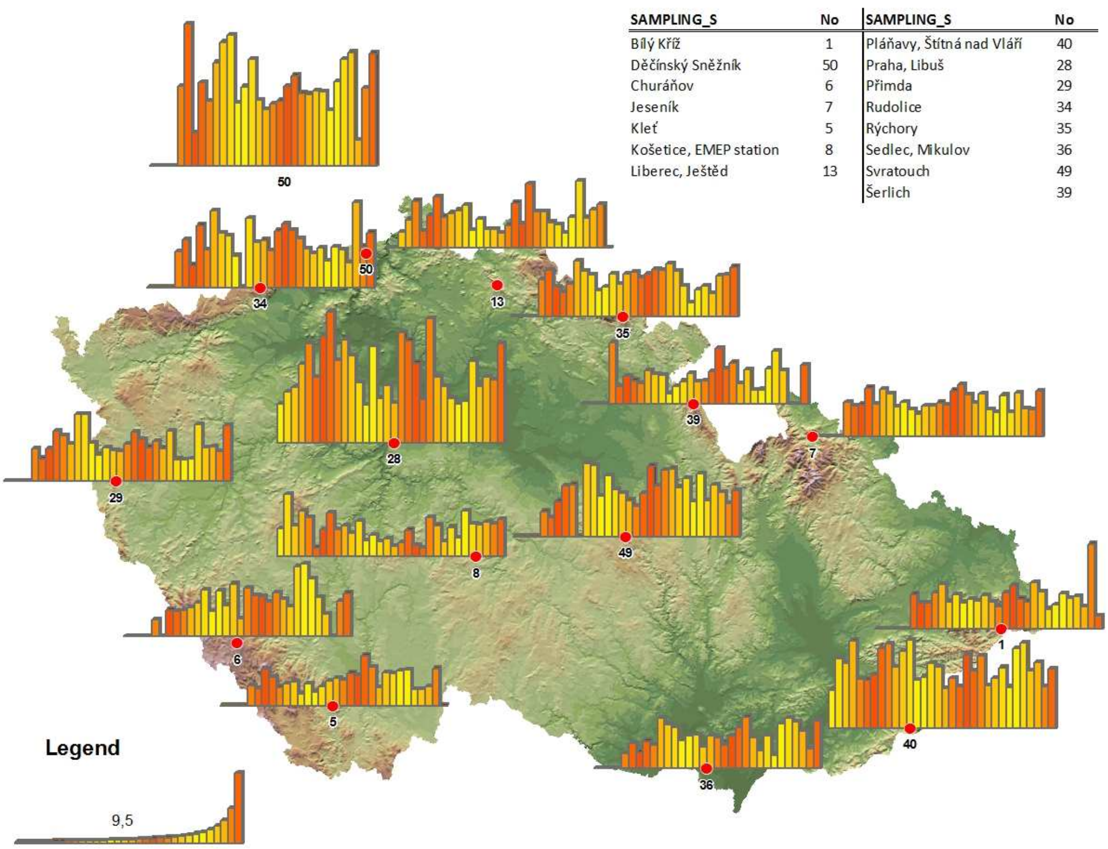


Figure 14: Passive air sampling 2006-2008, MONET-CZ, PCBs (ng filter^{-1}).

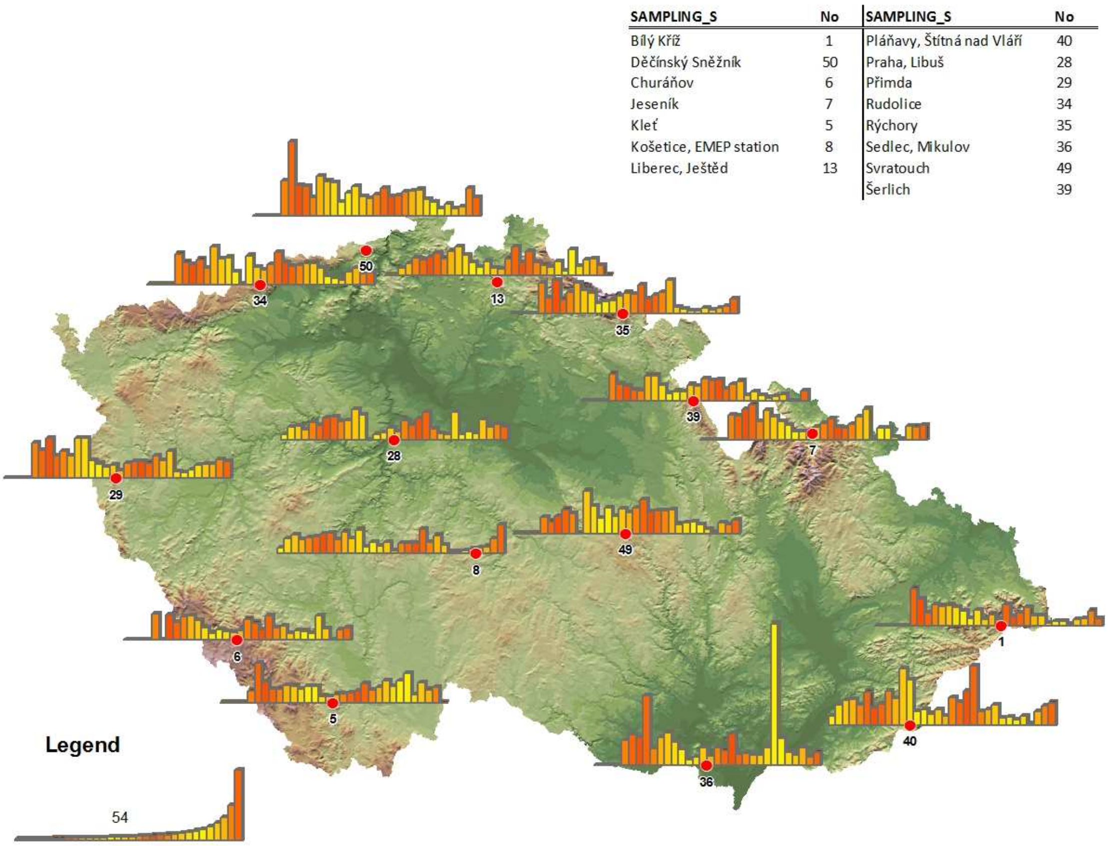


Figure 15: Passive air sampling 2006-2008, MONET-CZ, HCHs (ng filter^{-1}).

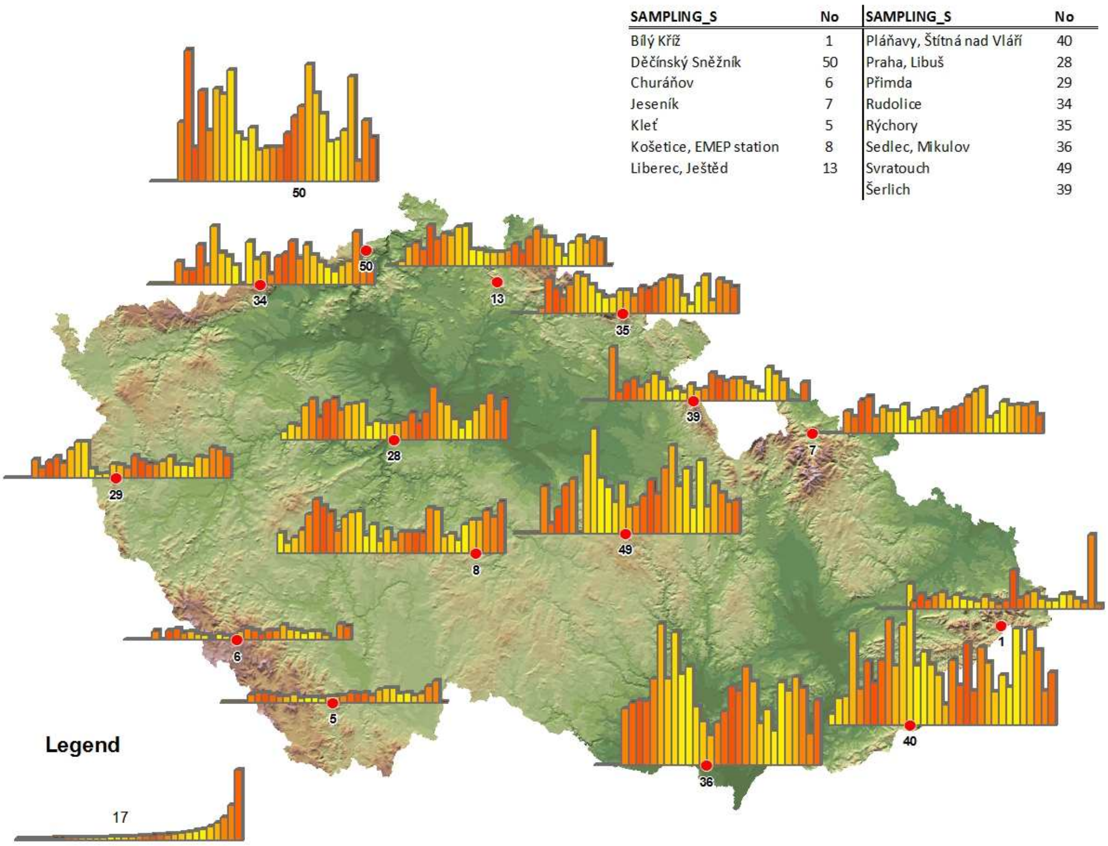


Figure 16: Passive air sampling 2006-2008, MONET-CZ, DDTs (ng filter^{-1}).

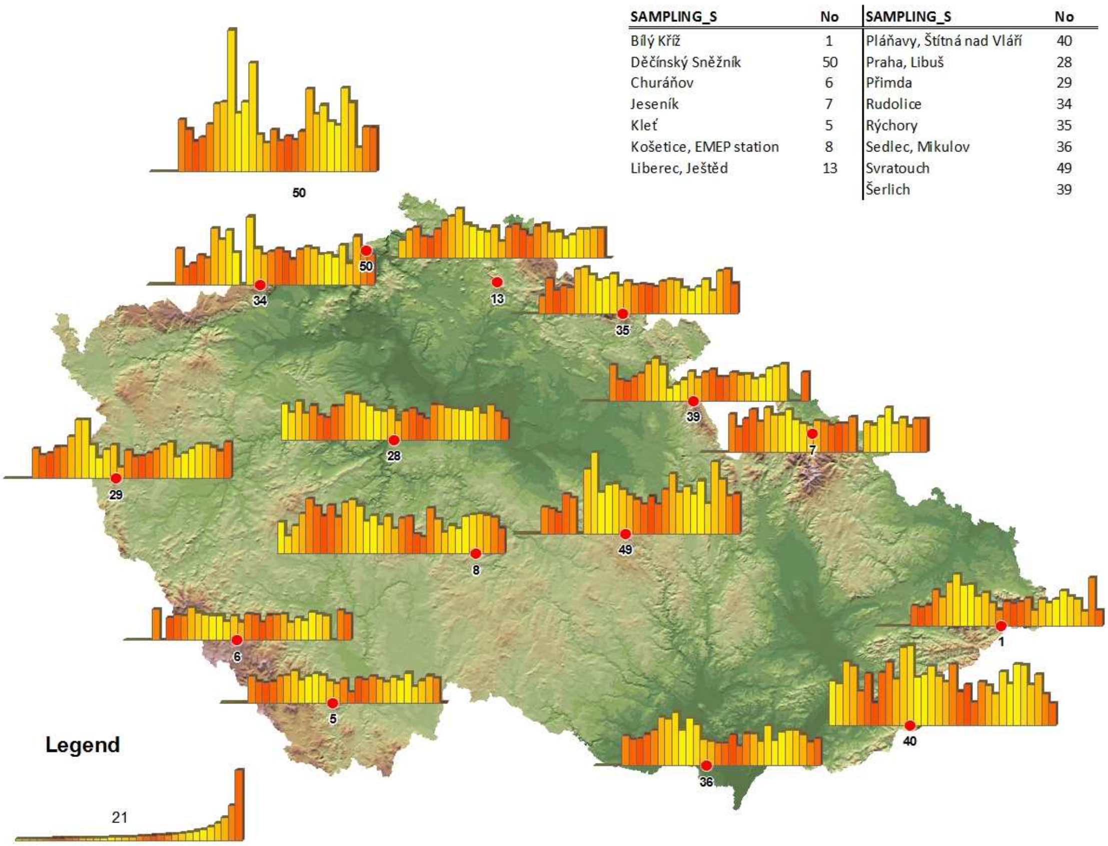


Figure 17a: Passive air sampling 2006-2008, MONET-CZ, HCB (ng filter^{-1}).

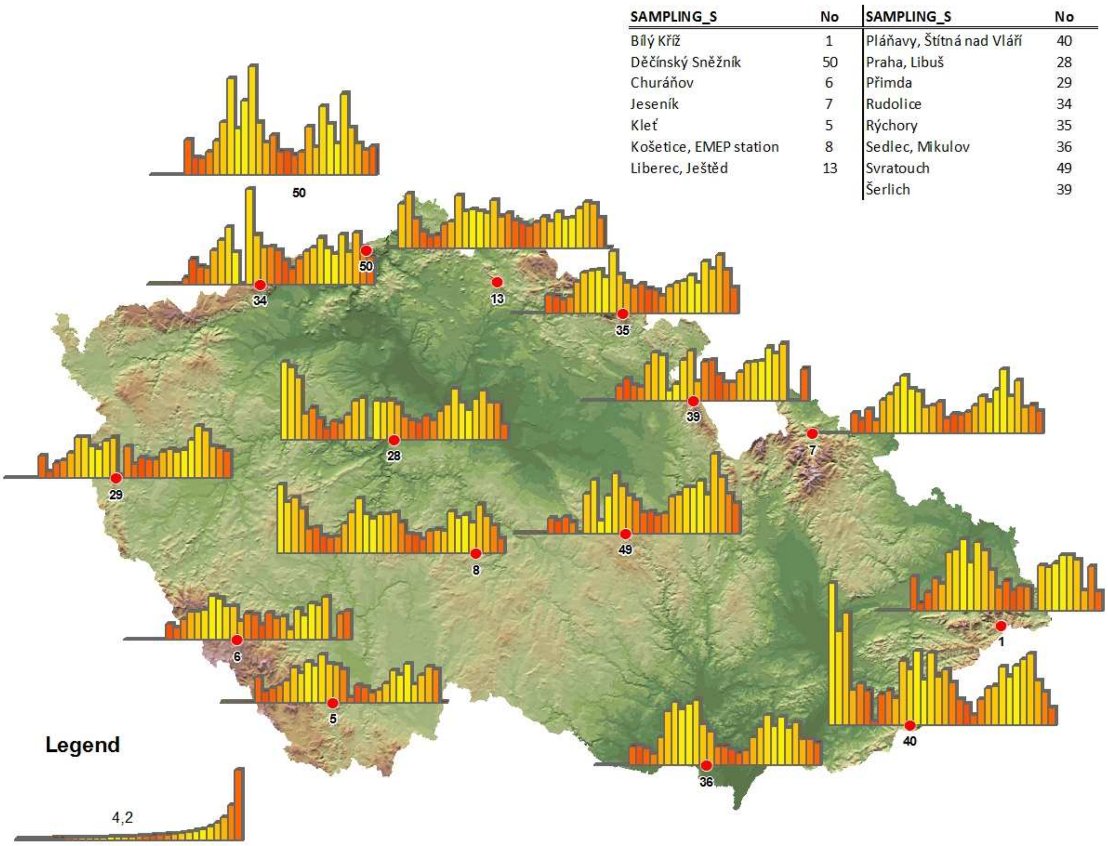


Figure 17b: Passive air sampling 2006-2008, MONET-CZ, PeCB (ng filter^{-1}).

As **Central, Southern and Eastern Europe** is the region with a lack of data on the atmospheric POP, three screening campaigns were organized between 2006 and 2008 (MONET-CEECs). A philosophy was the same as for the model network in the Czech Republic: 5-20 sampling sites were selected per country (according to the size of each country) and they were monitored for 5 months. Industrial, agricultural, urban and rural sites were included together with the backgrounds. The goal was not only to determine the background levels but also to provide information on the extent of pollution. Variability of the atmospheric concentrations of selected POPs for the range of the sampling sites is presented in the following box-and-whisker plots. In addition to the Central and Eastern European region (CEEC), 26 sites from the **African continent** (MONET-AFRICA) and 21 sites from the **Central Asia** (former Soviet Union countries as a part of MONET-CEECs) were monitored in 2008 and 3 sites from the **Pacific Islands** between 2006 and 2007 (MONET-PIs).

Extremely high concentrations of **PAHs** were found in Bucuresti (Romania) where the median values went up to 100 µg filter^{-1} and Kamenogorsk (Kazakhstan) where they reached 30µg filter^{-1}. At most of the other sites, the median concentrations did not exceed 5 µg filter^{-1} with occasional fluctuations up to 20 µg filter^{-1} with the exception of the big cities (Sofia (Bulgaria), Beograd (Serbia), Skopje (Macedonia), Galati and Timisoara (Romania), Cairo (Egypt), Asela (Ethiopia)) and industrial sites (mostly in the vicinity of refineries) as Jurinka (Czech Republic) where the medians reached 10-15 µg filter^{-1}.

Median concentrations of **PCBs** stayed below 20 ng filter^{-1} at most of the sites. Extreme concentrations were measured in Kazakhstan where the median values were at several sites in tens to hundreds of µg filter^{-1} (up to 237 467 ng filter^{-1}). Higher than other countries was also Romania with most of the sites higher than average and several reaching 1 µg filter^{-1}. Median concentrations exceeding hundreds of nanograms of PCBs per filter were also measured in Dakar (Senegal). Elevated levels were, however, found in all biger cities: Amberd (Armenia), Karaganda (Kazakhstan), Niksic (Montenegro), Banja Luka (Bosnia), Celje (Slovenia), Kyiv (Ukraine) or at the sites connected to production or application of PCBs (Colorlak paint factory in the Czech Republic, Zastava Kragujevac in Serbia).

Levels of **HCHs** were generally low (median value below 30 ng filter^{-1}) except for the sites where it was produced or stored. The highest median levels were measured at several sites in Romania (Turda 2.3 µg, Onesti 1 µg filter^{-1}), similar extreme (2.5 µg filter^{-1}) was also found at Kitengela site in Kenya. Hundreds of nanograms of HCHs per filter were measured in Ufa and Chapaevsk in Russia, near the Spolana chemical factory in the Czech Republic or in Skopje, Macedonia. There were countries as Kyrgyzstan or Romania where all the sampling sites had elevated PCB levels.

Median levels of **DDTs** stayed below 100 ng per filter at most of the sites. There were, however, the sites with medians more than an order of magnitude higher. The highest median level was found at Kitengela site in Kenya (2.5 µg filter^{-1}), the values higher than 100 ng filter^{-1} were also found in Dakar (Senegal) (360 ng filter^{-1}), Asela (Ethiopia), Bamako (Mali), Kyiv (Ukraine), several sites in Bucuresti (Romania) or Kyrgyzstan.

Median values of hexachlorobenzene (**HCB**) were below 10 ng filter^{-1} at most of the sites. Concentrations several times higher were found in Ivansedlo (Bosnia), Ufa and Chapaevsk in Russia, Kyiv (Ukraine) and Cairo (Egypt). The highest median level was measured in the vicinity of the chemical factory Spolana in the Czech Republic (88 ng filter^{-1}), and near the chemical complex in Chapaevsk. The sites with the highest median levels of pentachlorobenzene (PeCB) as a degradation product of HCB coincided with those with the highest levels of HCB (Spolana, Chapaevsk) but elevated concentrations were also found at all sites of Kyrgyzstan, in Asela (Ethiopia), Kitengela and Dandora (Kenya).

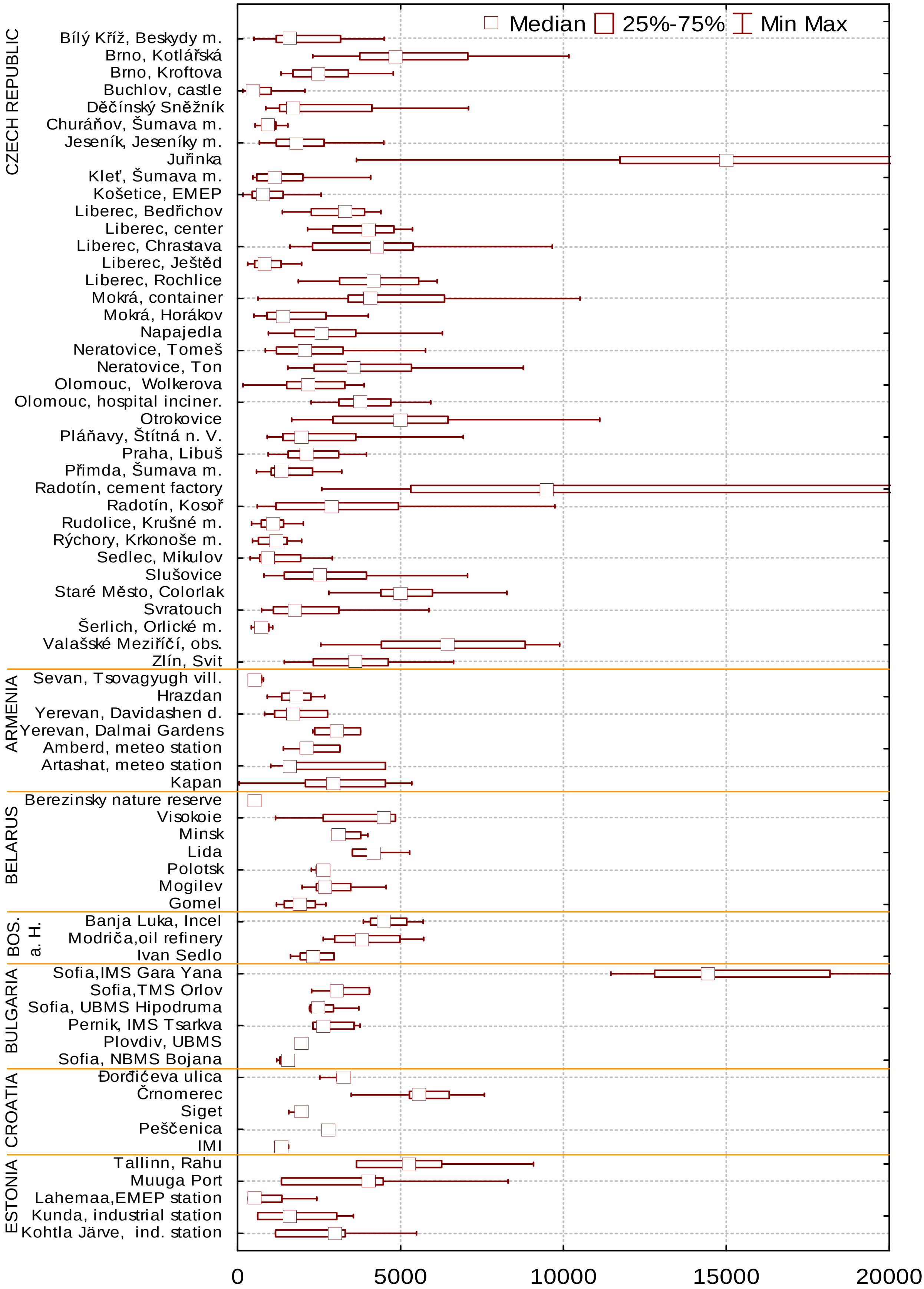


Figure 18: PAH levels in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

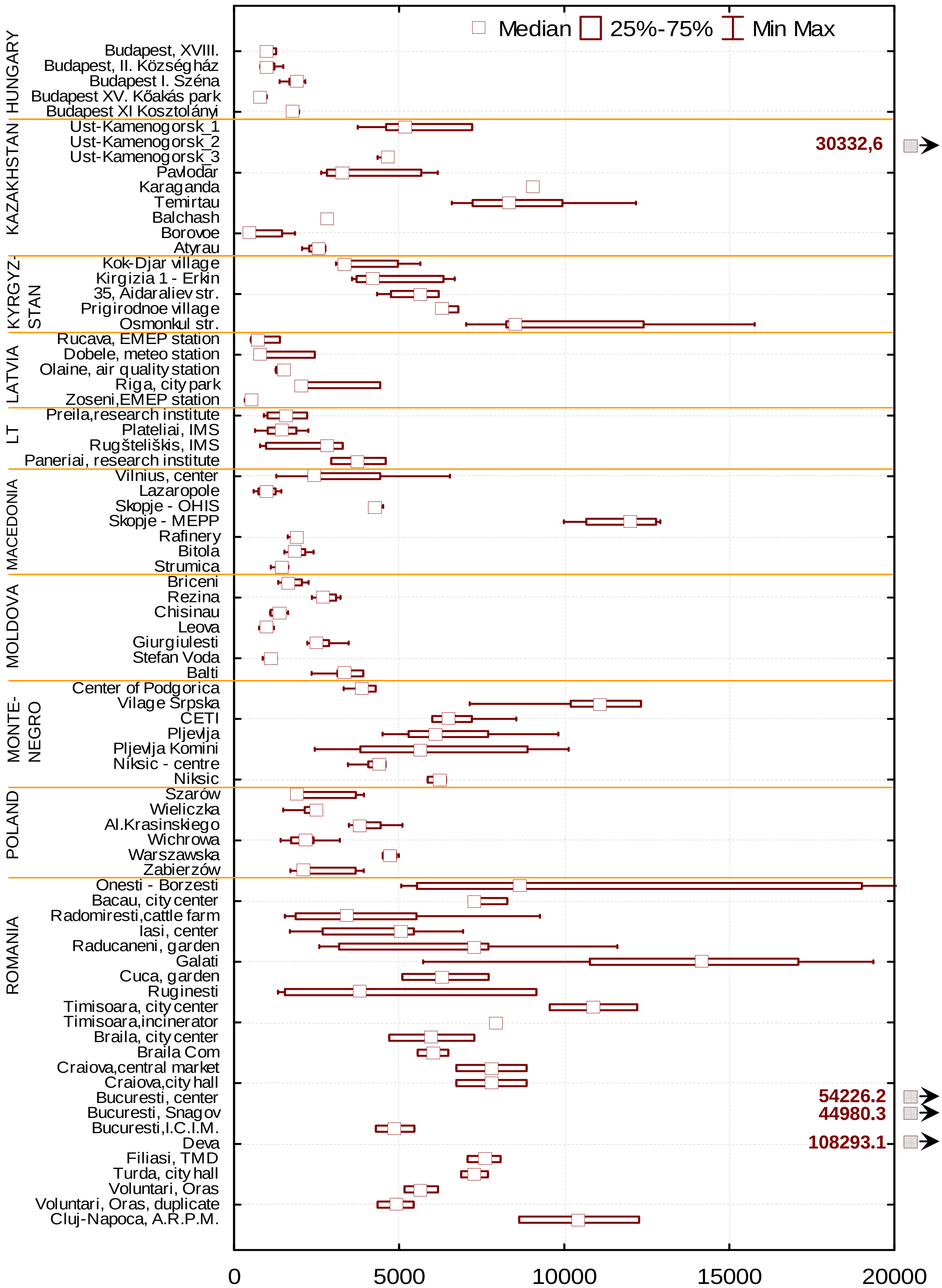


Figure 19: PAH levels in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

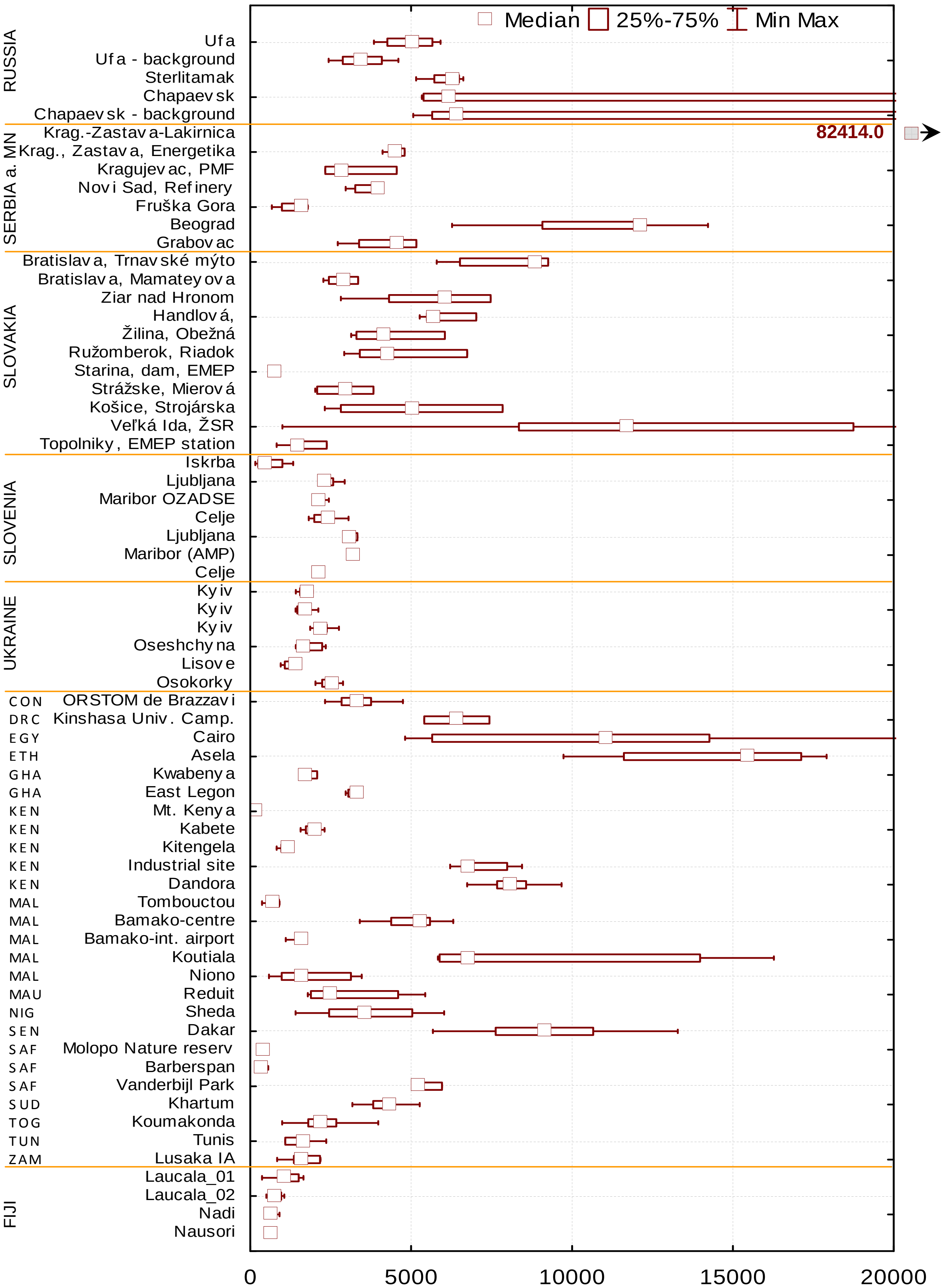


Figure 20: PAH levels in ambient air (PAS, ng filter[-1]), 2004 – 2008.

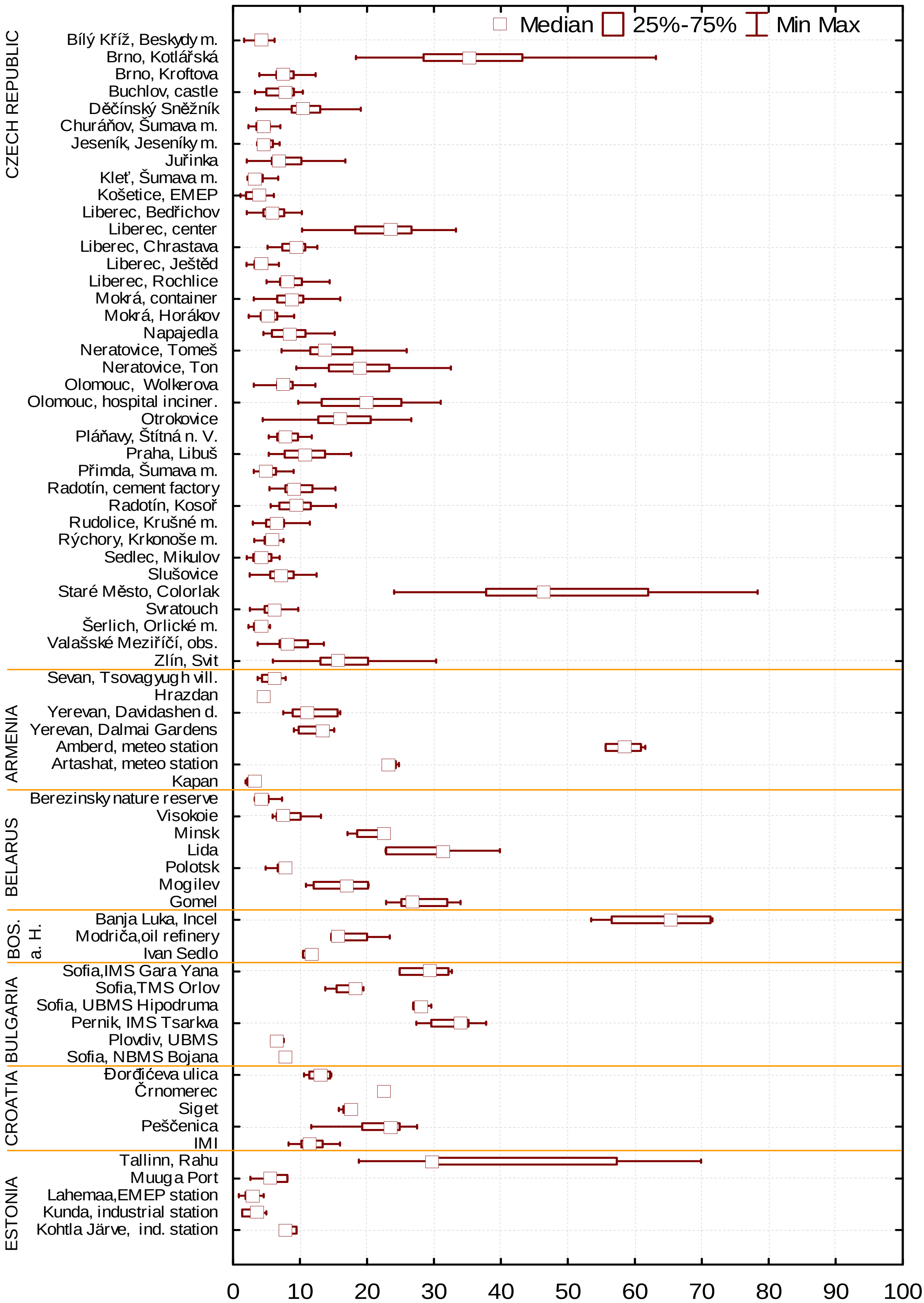


Figure 21: PCB levels (7 indicators) in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

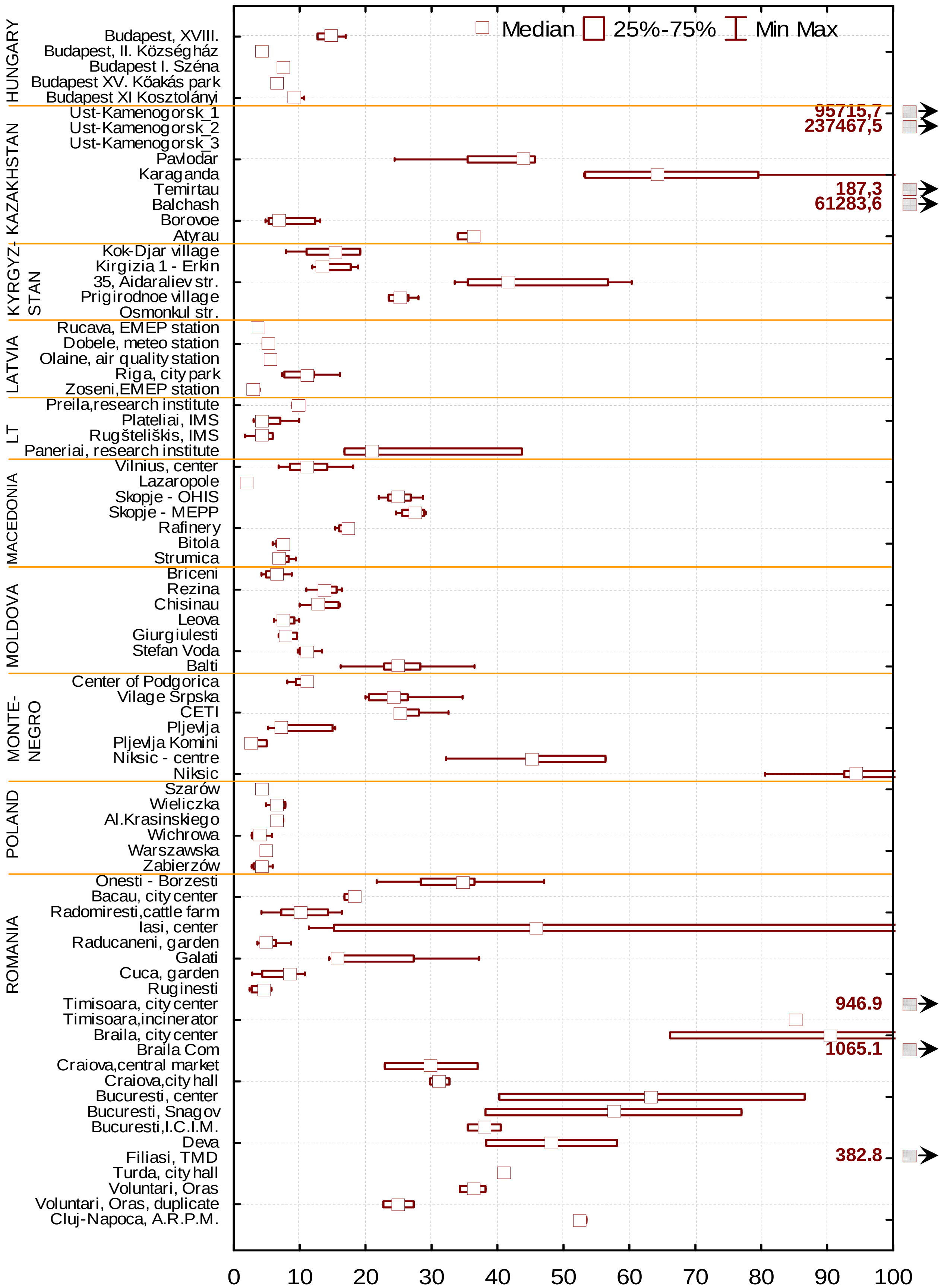


Figure 22: PCB levels (7 indicators) in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

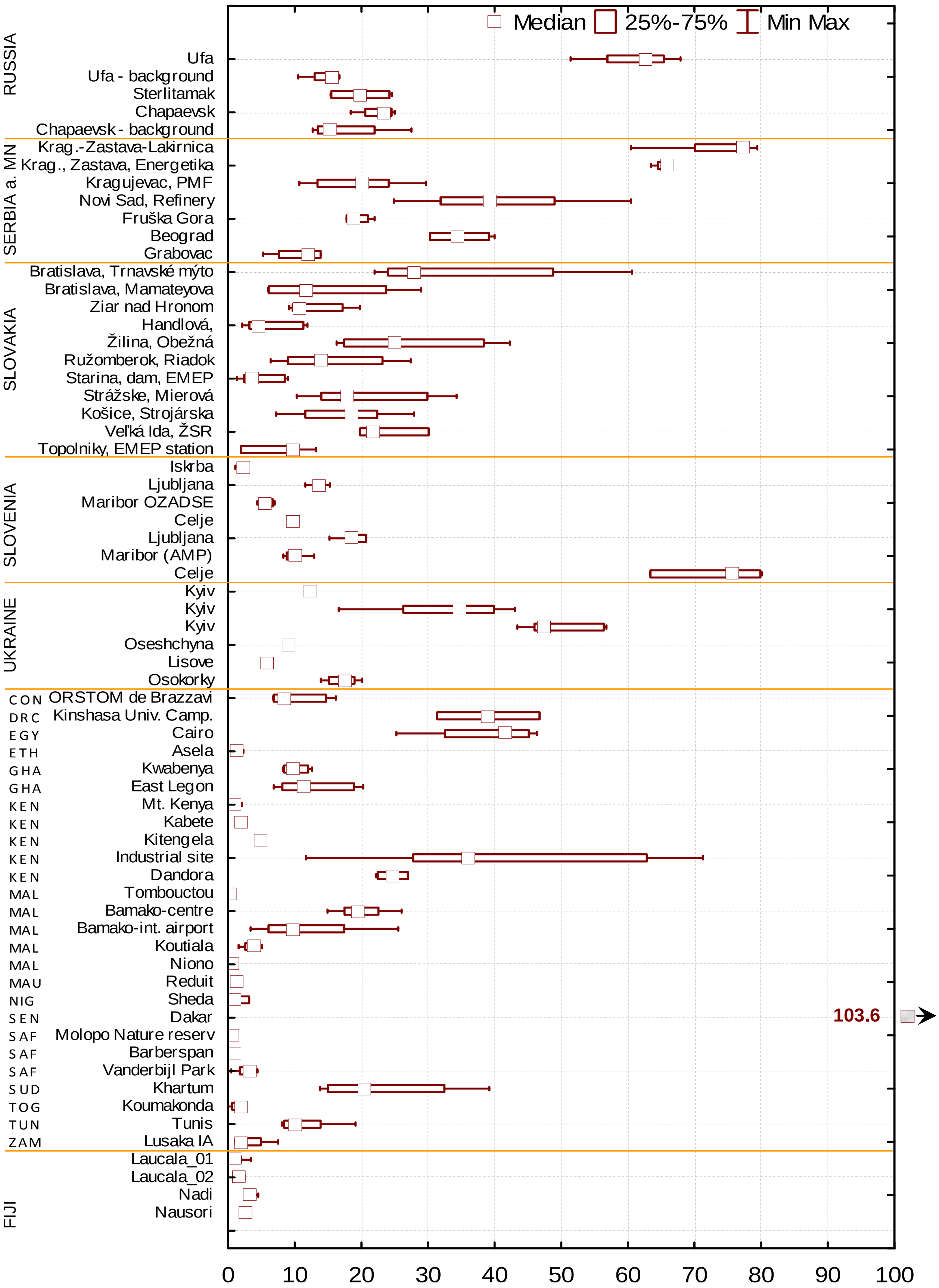


Figure 23: PCB levels (7 indicators) in ambient air (PAS, ng filter[-1]), 2004 – 2008.

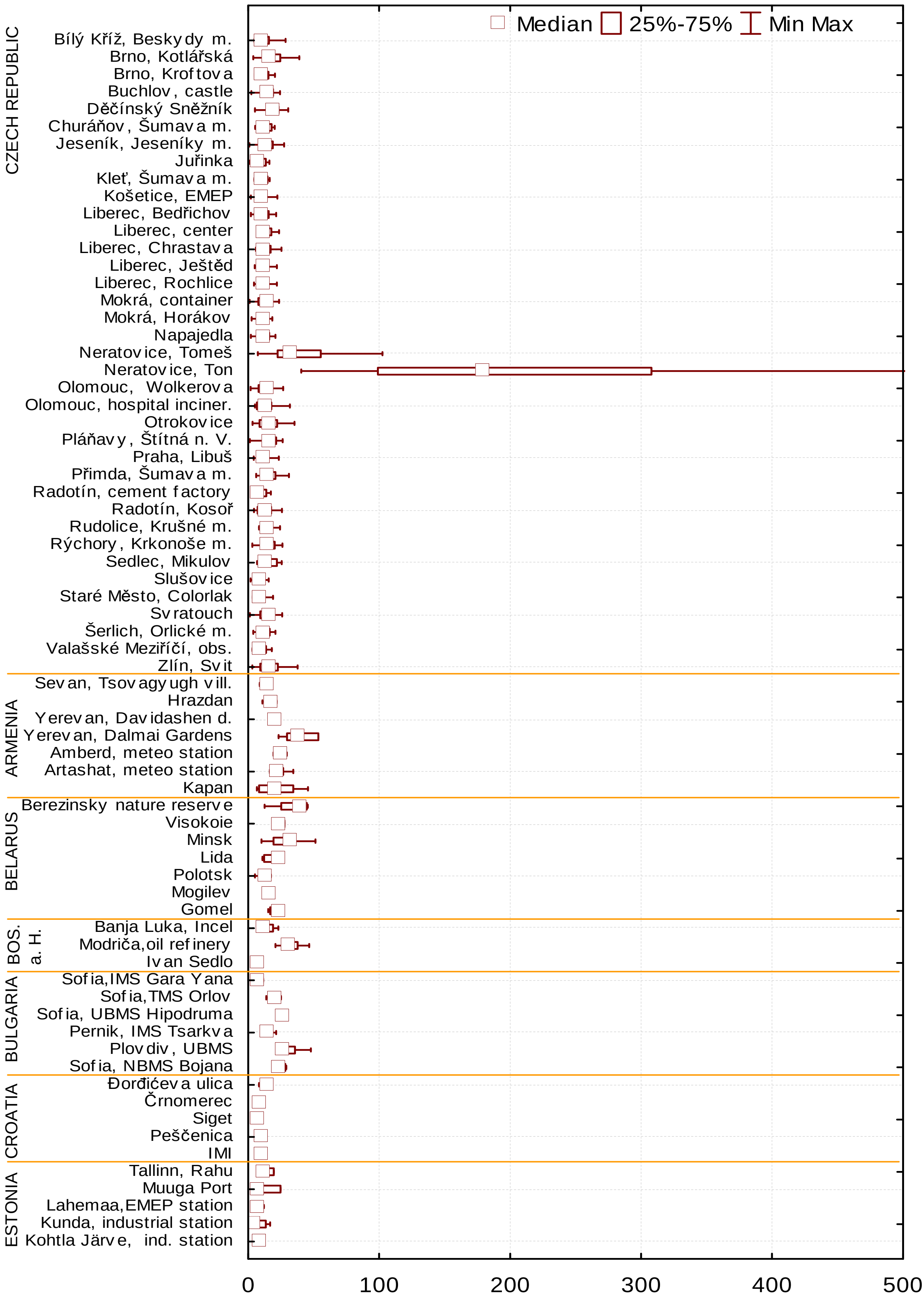


Figure 24: HCH levels (sum of α, β, γ, δ-HCH) in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

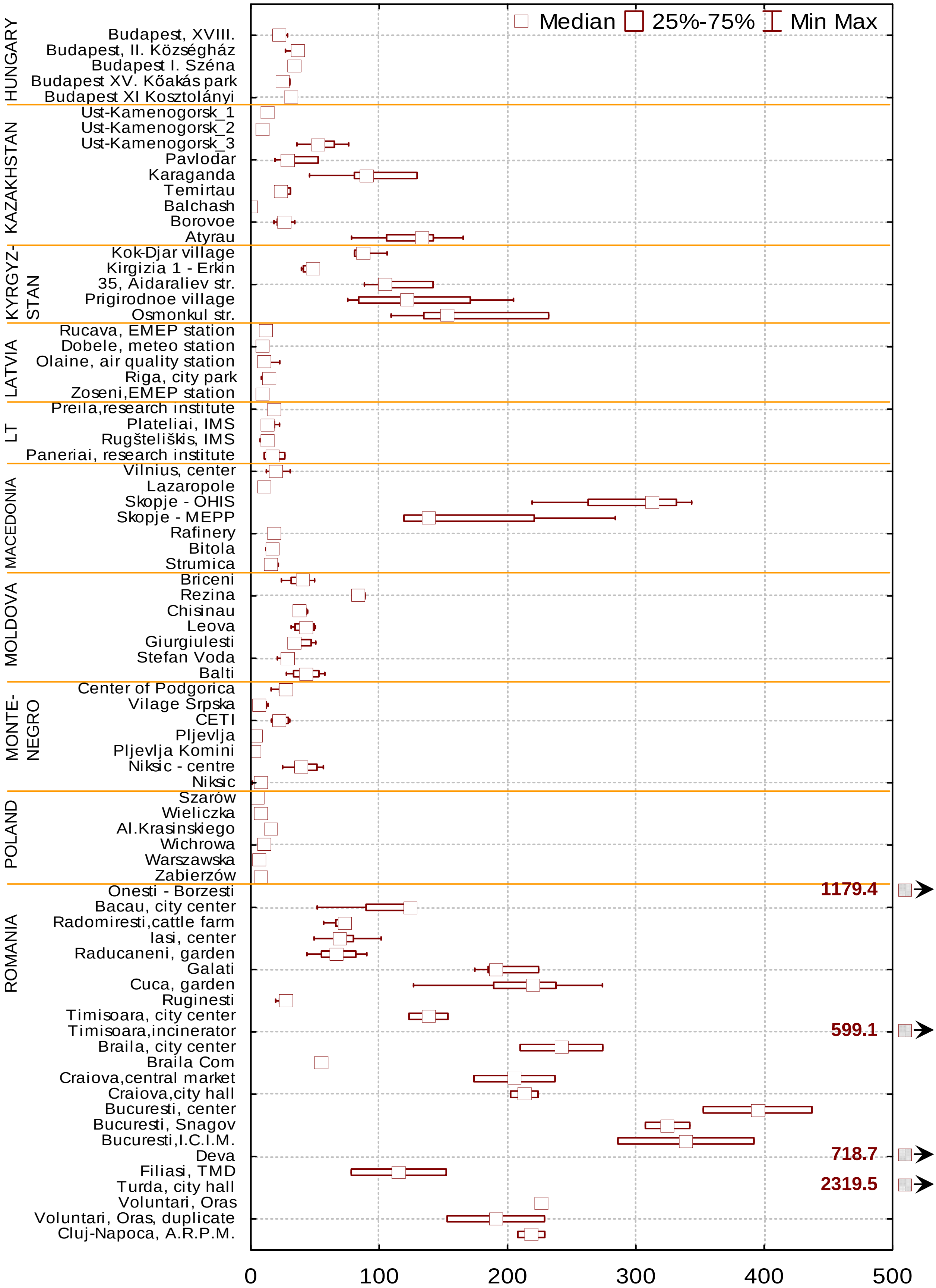


Figure 25: HCH levels (sum of α, β, γ, δ-HCH) in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

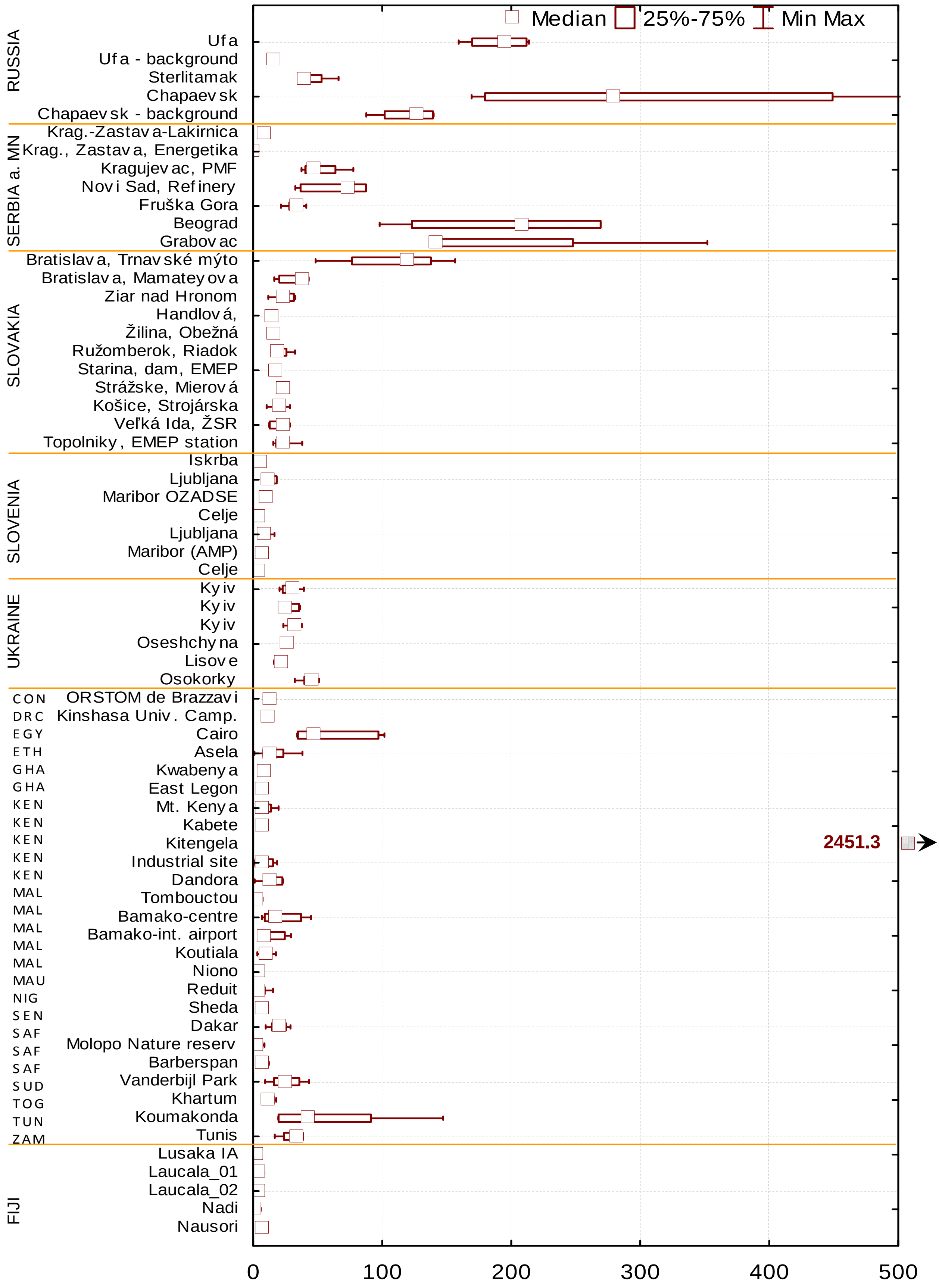


Figure 29: HCH levels (sum of α, β, γ, δ-HCH) in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

Figure 27: DDT levels (sum of o,p'- and p,p'-DDT, DDE, DDD) in ambient air (PAS, ng filter^{-1}) 2004 – 2008.

Figure 28: DDT levels (sum of o,p'- and p,p'-DDT, DDE, DDD) in ambient air (PAS, ng filter^{-1}) 2004 – 2008.

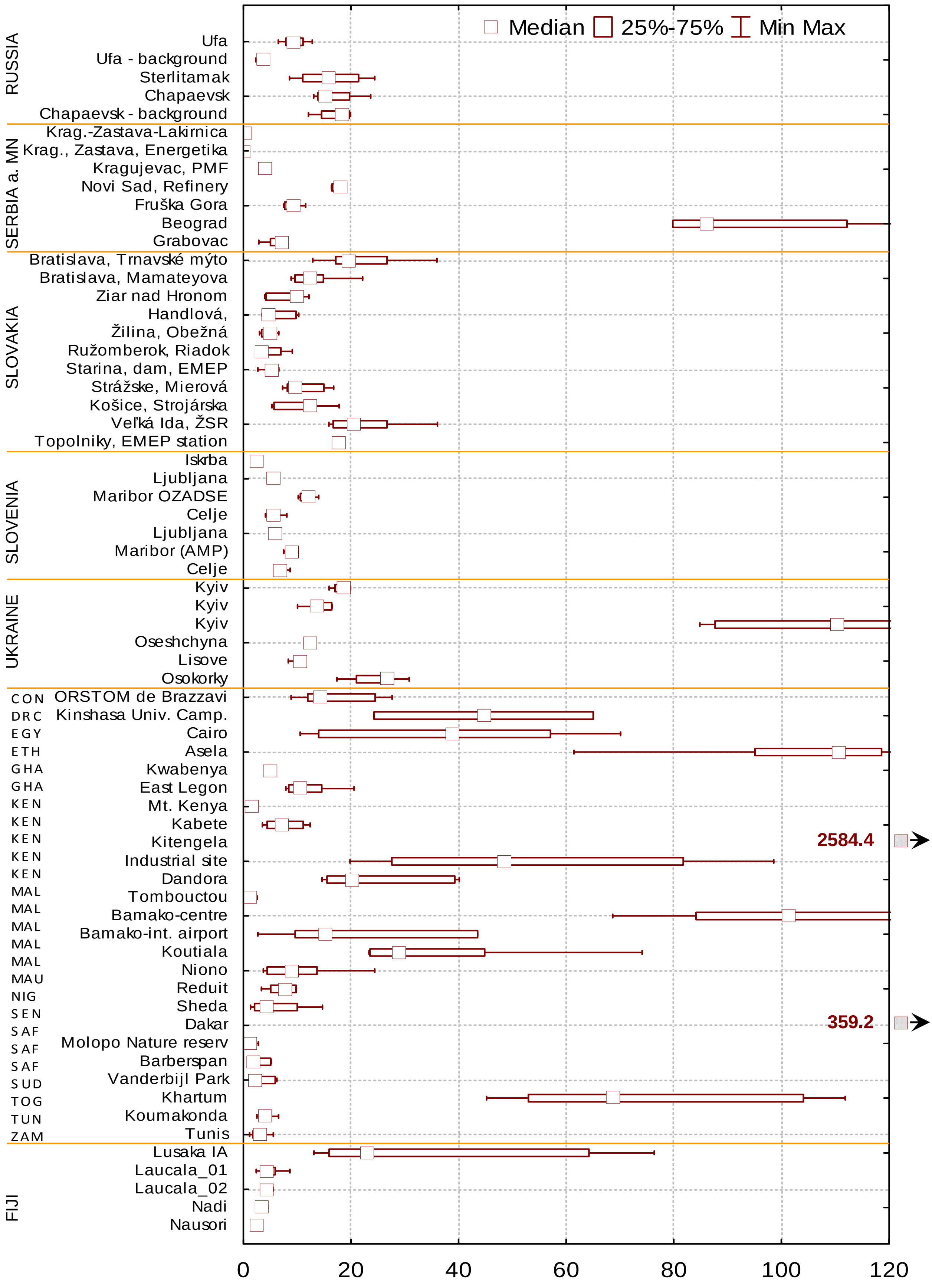


Figure 29: DDT levels (sum of o,p'- and p,p'-DDT, DDE, DDD) in ambient air (PAS, ng filter^{-1}) 2004 – 2008.

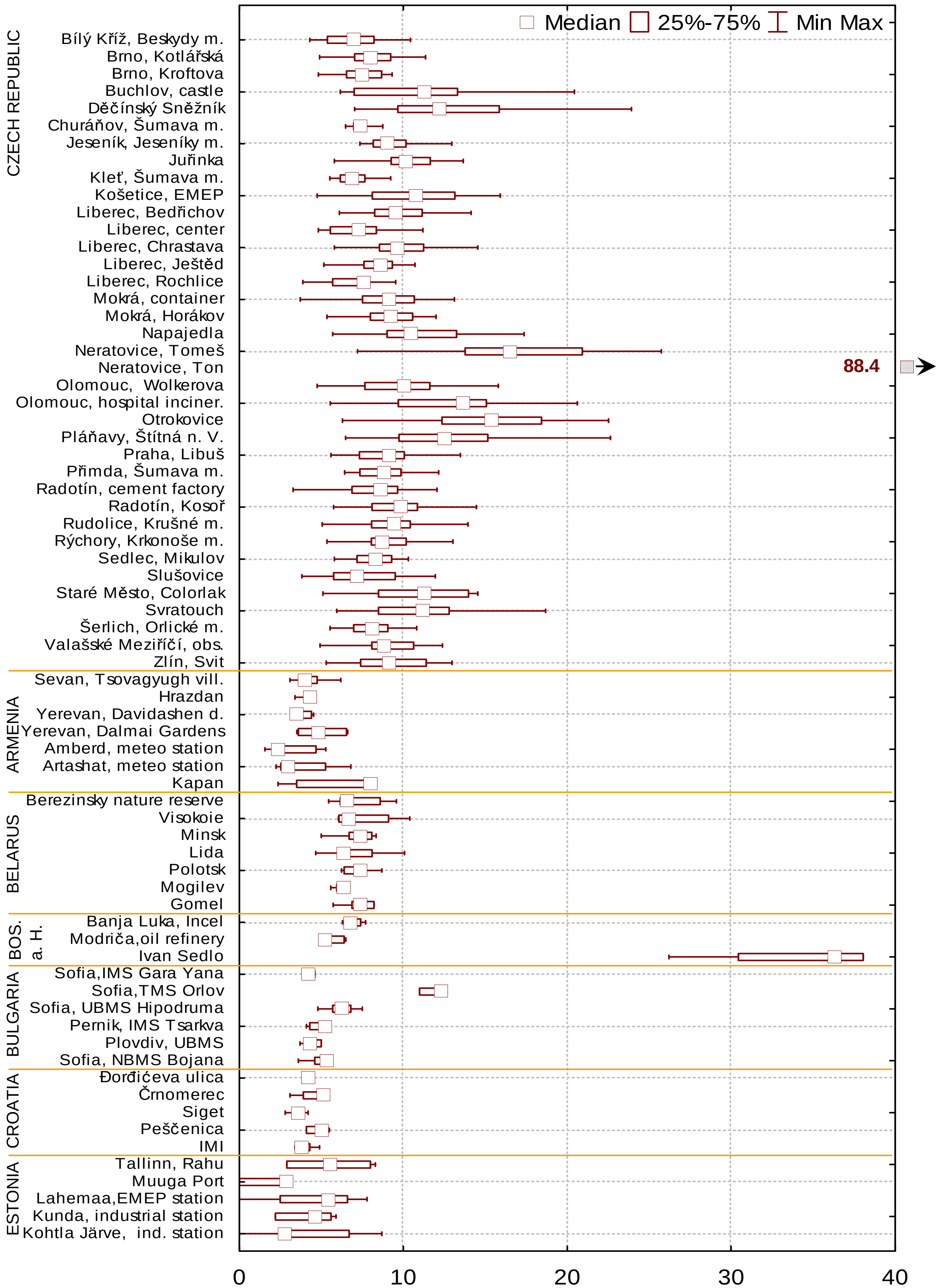


Figure 30: HCB levels in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

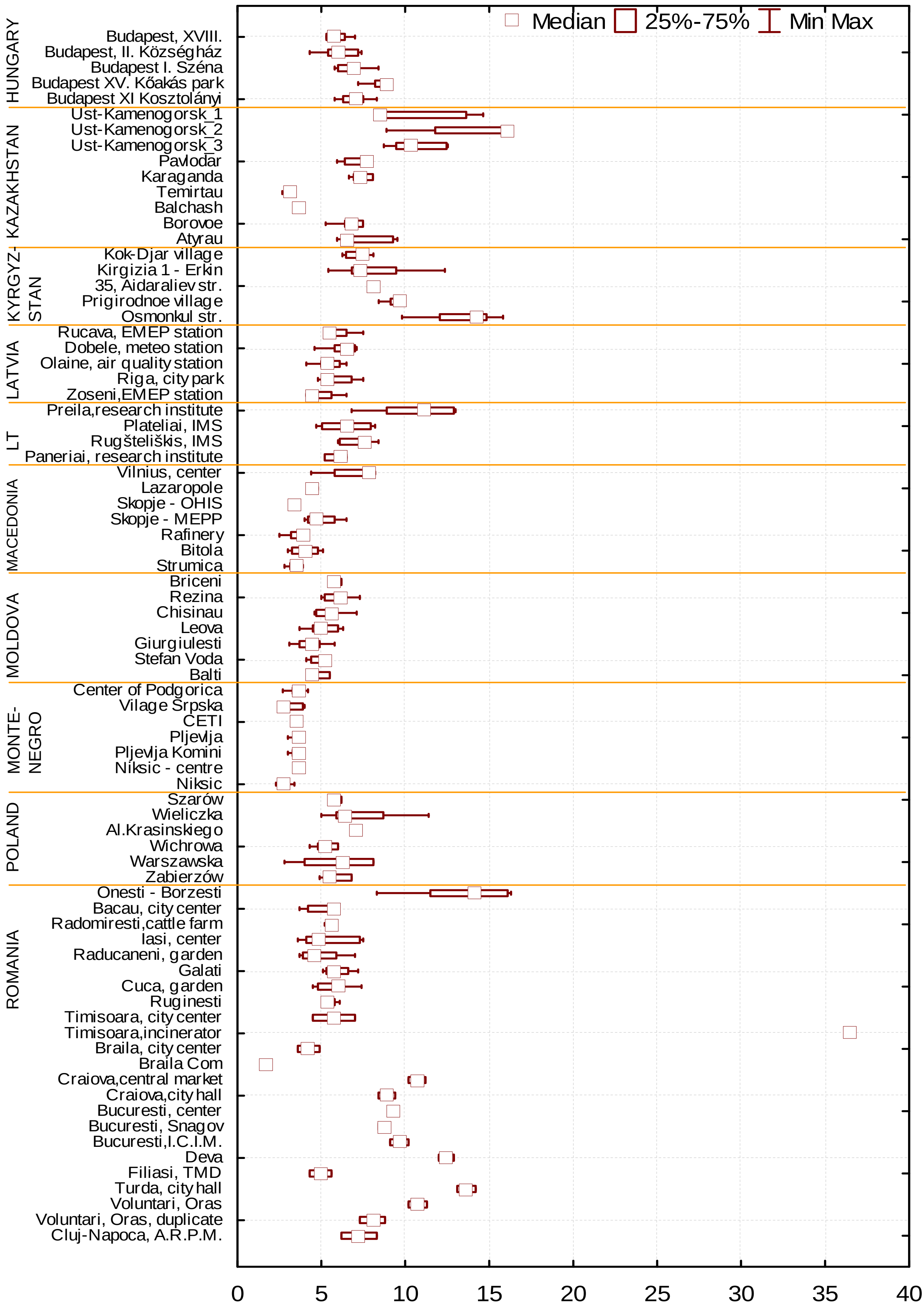


Figure 31: HCB levels in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

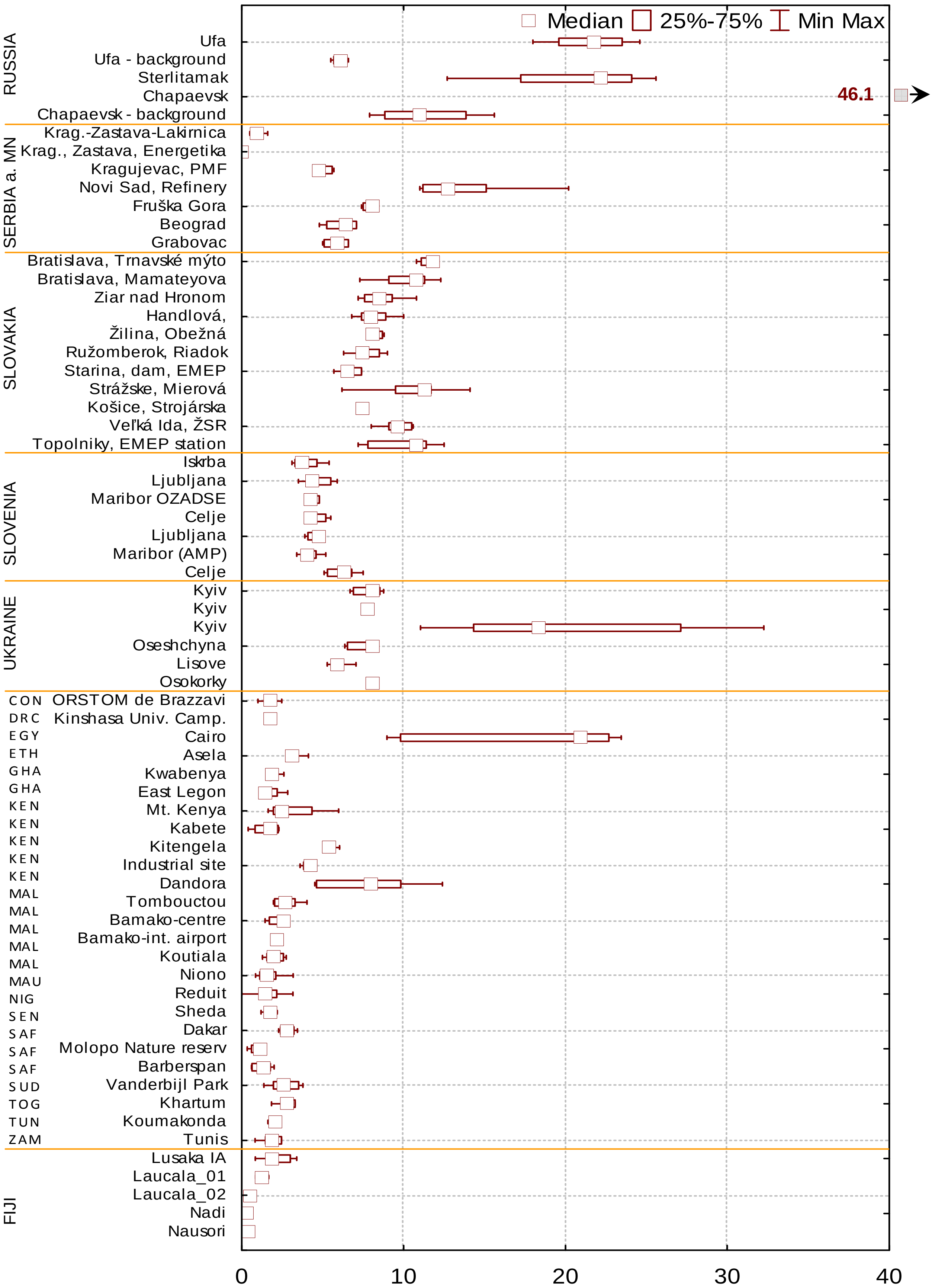


Figure 32: HCB levels in ambient air (PAS, ng filter[-1]), 2004 – 2008.

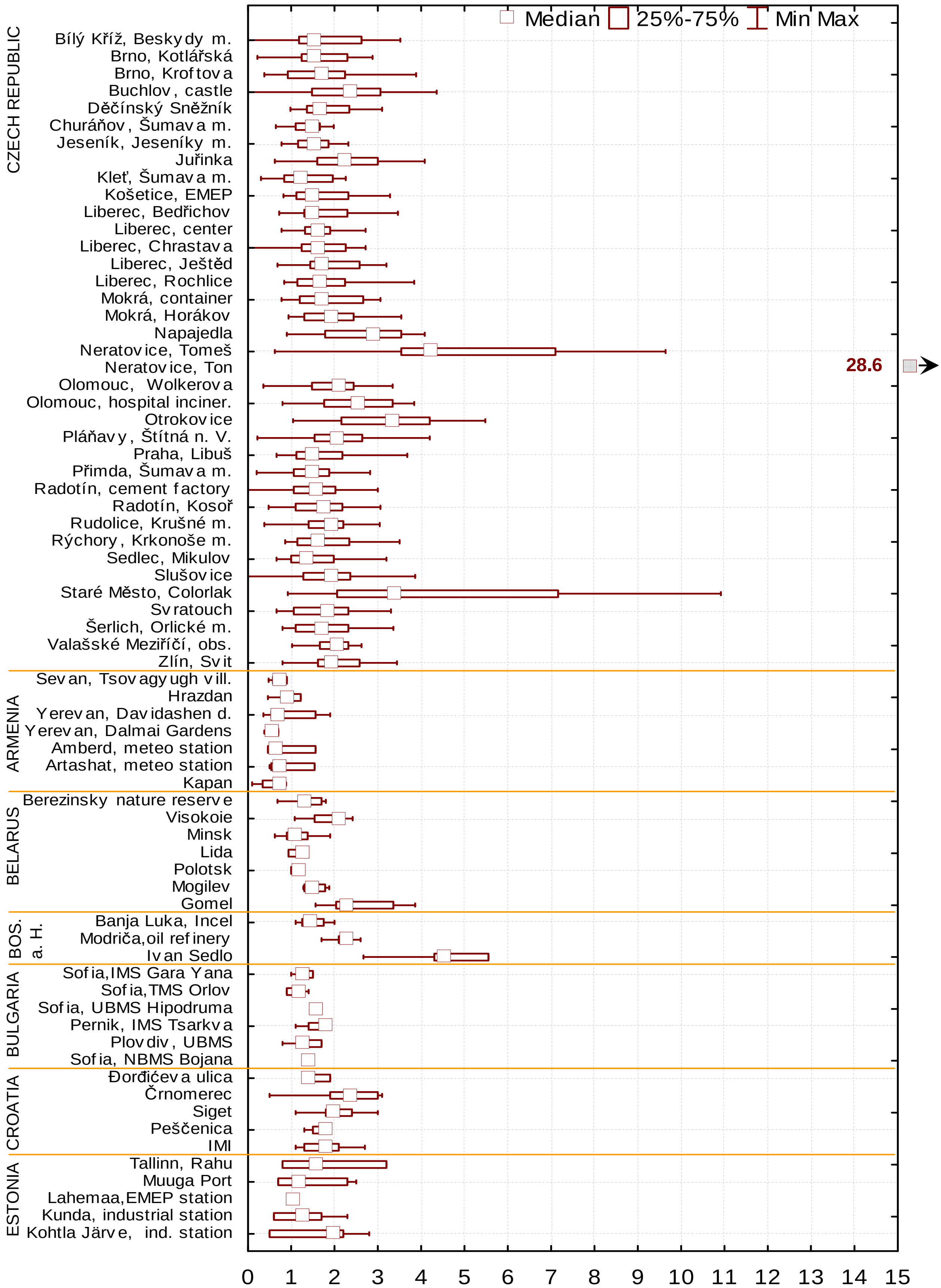


Figure 33: PeCB levels in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

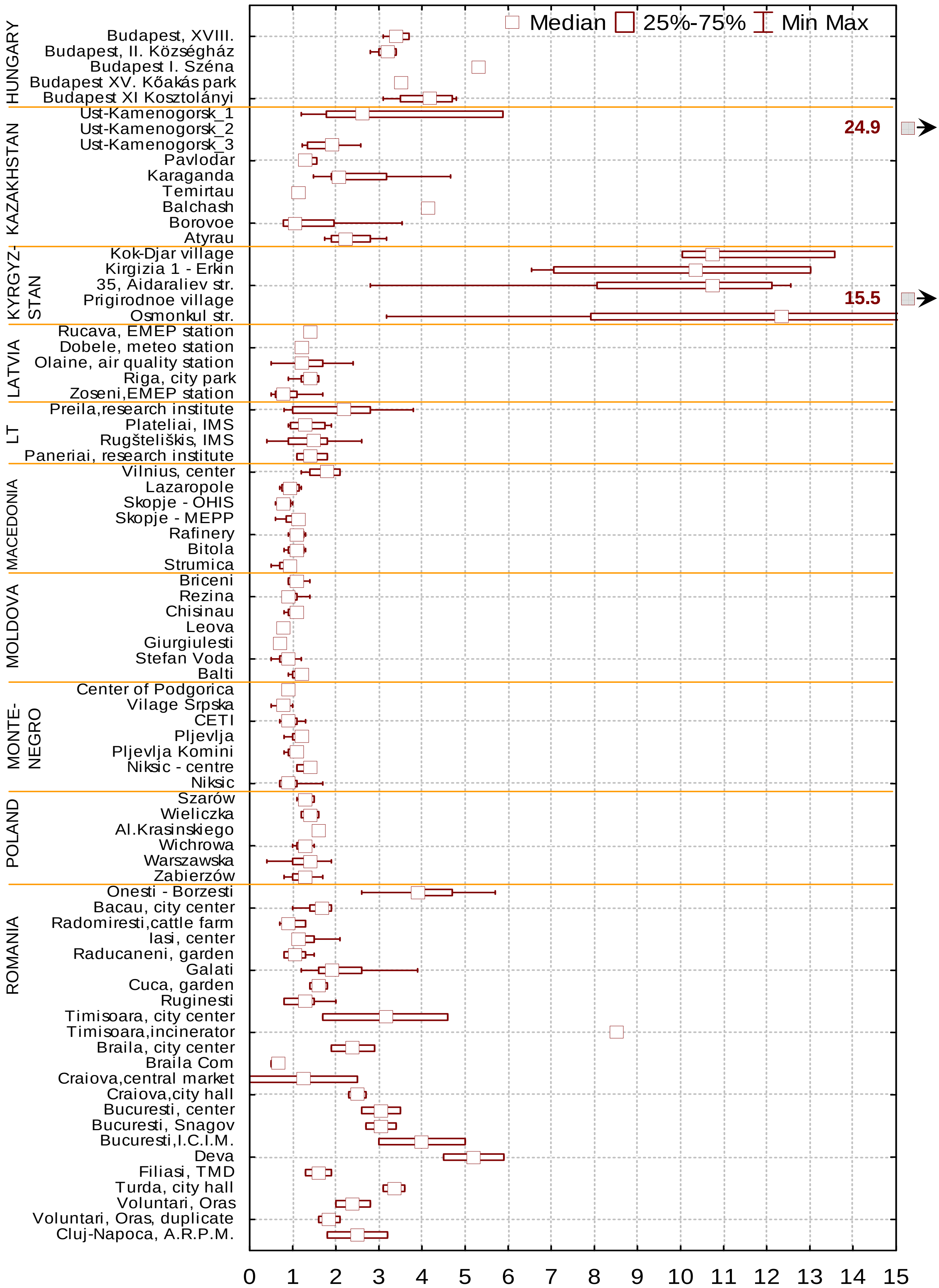


Figure 35: PeCB levels in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

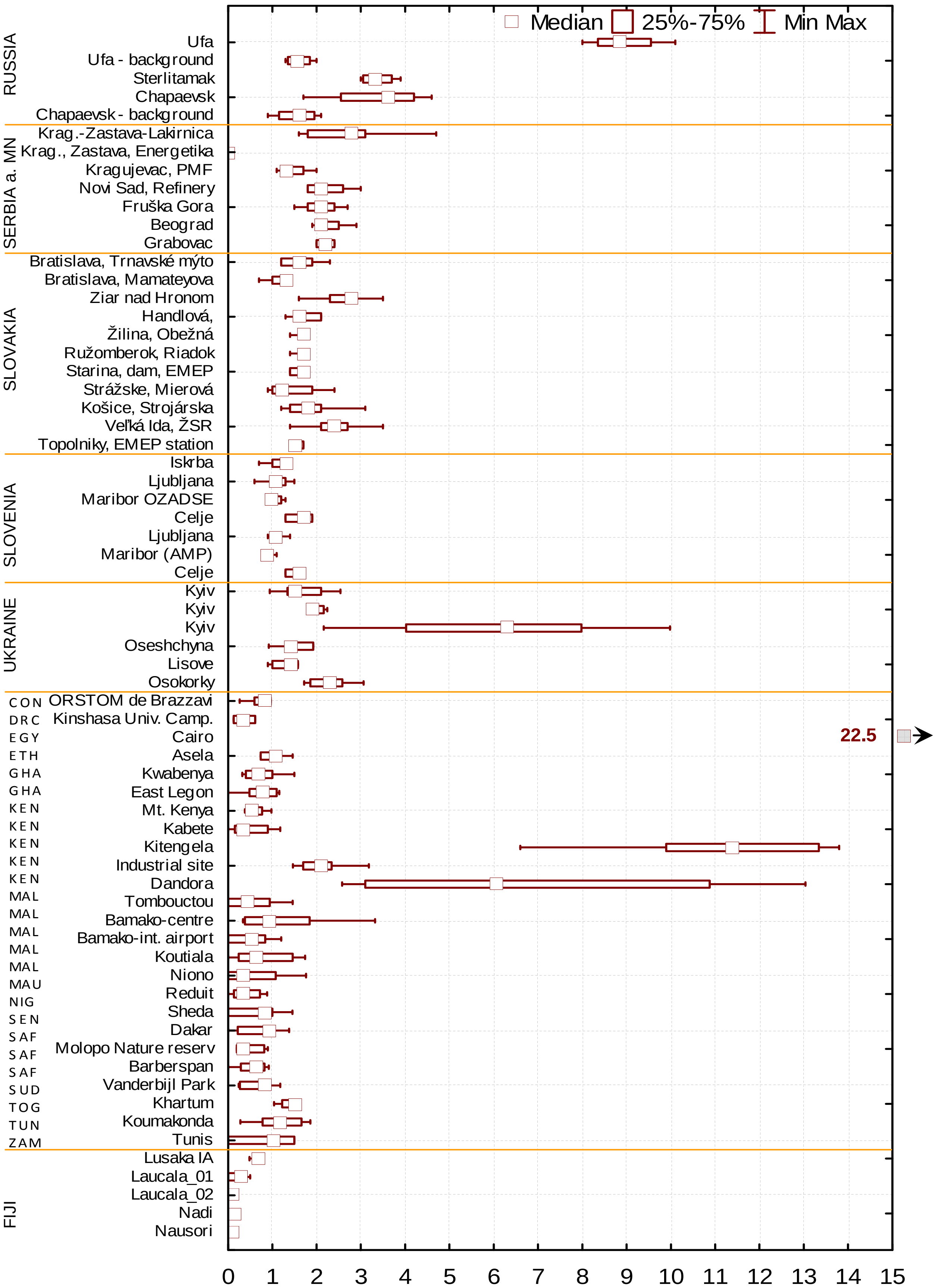


Figure 36: PeCB levels in ambient air (PAS, ng filter^{-1}), 2004 – 2008.

Previous figures demonstrated the extent of the POP contamination of ambient air in all investigated countries. For the purpose of the Global monitoring, however, only the background sites are of interest. To give an overall comparison of the background POP levels in all investigated countries, only the background sites were selected from the database based on available information and measured levels. **Each country** was represented by **one background** site. Following maps present the median background air concentrations of the POPs of interest in the regions of **Central, Southern and Eastern Europe, Central Asia, Africa, and Pacific Islands** (Fiji).

When all the impacted sites are omitted, the highest **PAH** concentrations can bee seen in Ethiopia. Also some other countries of the Central Africa (Sudan, Nigeria, Ghana) are showing the levels close to the highest median values found in Central Asia (Kyrgyzstan), Eastern (Russia) and Southern Europe (Romania, Montenegro). South Africa, on the contrary, had very low levels similar to Mount Kenya, Fiji or some Baltic sites.

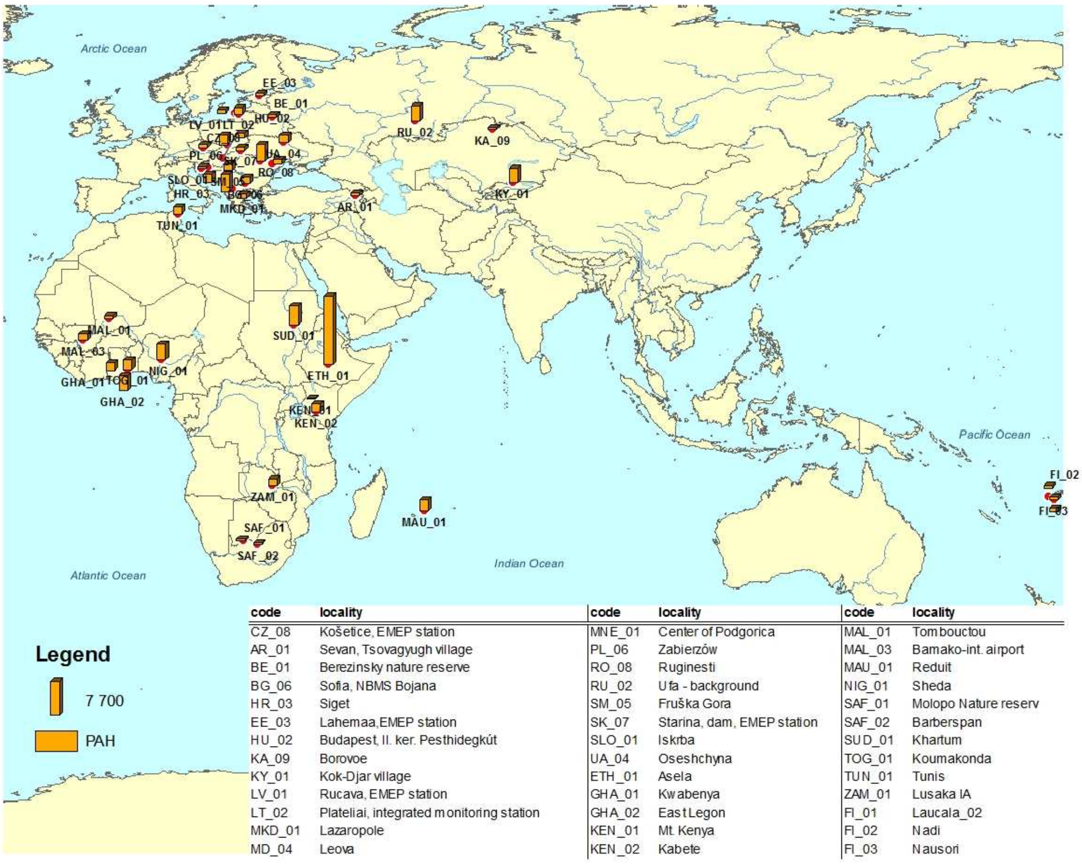
Highest median background levels of **PCBs** were measured in Sudan. Ghana and Tunisia, however, had also elevated levels similar to Kyrgyzstan, Russia, Serbia, Croatia or Montenegro (elevated levels in all former Yugoslavian countries are probably still due to the damages in the recent war conflicts). Low levels of PCBs were found along the south-eastern coast of Africa or in Fiji.

The background site in Kyrgyzstan had the highest median levels of **HCHs**, followed by the sites in Togo, Tunisia, Romania, Moldova, Ukraine and Serbia. As the background levels of HCHs are usually quite uniform, such results indicate some local sources of HCHs. South Africa and Fiji were again the cleanest sites in the project.

As expected, the highest levels of **DDTs** were determined in Central Africa, especially in Ethiopia and Sudan. High concentration, however, we also found in the South-Eastern Europe (Moldova and Romania). Zambia, Mali and Ghana were elevated, too.

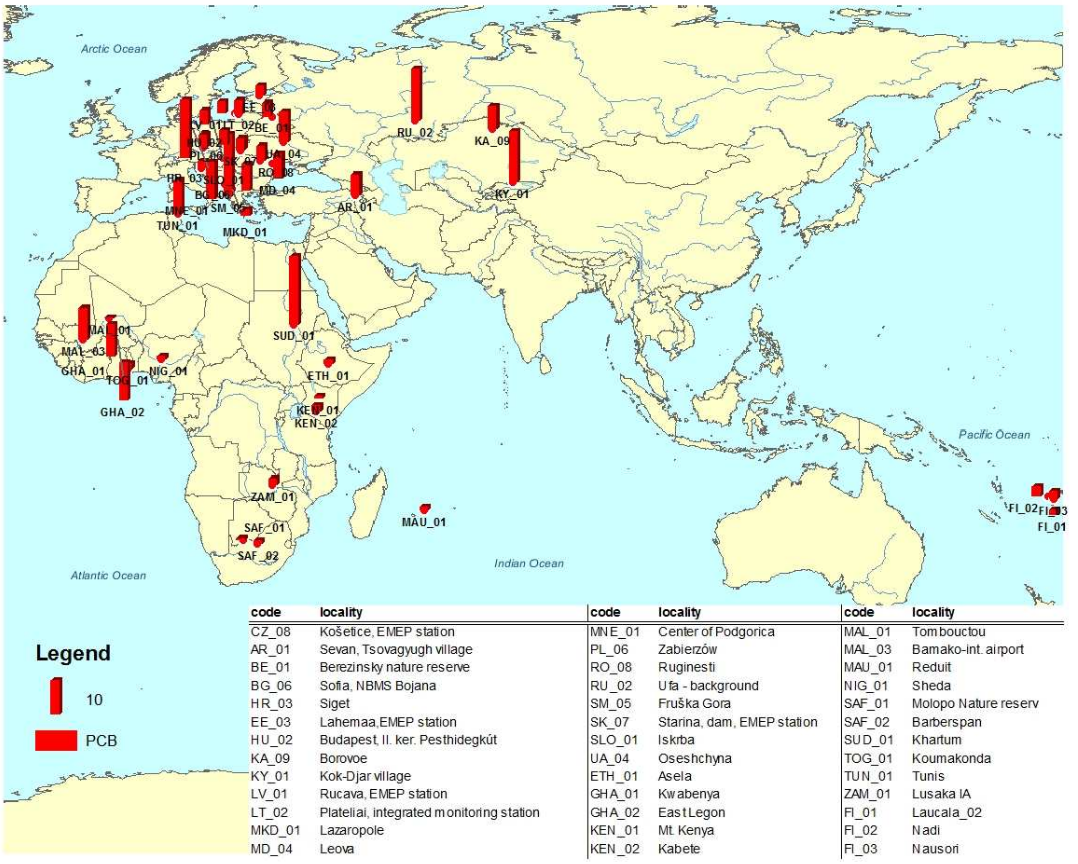
In contrast, Central Europe had the concentration of **HCB** several times higher than other regions. Even though HCB distributes very well over the large areas, we can still observe high concentration in Central Europe (Czech Republic) and Central Asia (Kyrgyzstan) when compared to the other regions (as Africa).

Situation is not so clear for **PeCB** as a degradation product of HCB. The only site with significantly higher levels of PeCB was in Kyrgyzstan.



code	locality	code	locality	code	locality
CZ_08	Košetice, EMEP station	MNE_01	Center of Podgorica	MAL_01	Tombouctou
AR_01	Sevan, Tsovagyugh village	PL_06	Zabierzów	MAL_03	Bamako-int. airport
BE_01	Berezinsky nature reserve	RO_08	Ruginesti	MAU_01	Reduit
BG_06	Sofia, NBMS Bojana	RU_02	Ufa - background	NIG_01	Sheda
HR_03	Siget	SM_05	Fruška Gora	SAF_01	Molopo Nature reserv
EE_03	Lahemaa,EMEP station	SK_07	Starina, dam, EMEP station	SAF_02	Barberspan
HU_02	Budapest, II. ker. Pesthidegkút	SLO_01	Iskrba	SUD_01	Khartum
KA_09	Borovoe	UA_04	Oseshchyna	TOG_01	Koumakonda
KY_01	Kok-Djar village	ETH_01	Asela	TUN_01	Tunis
LV_01	Rucava, EMEP station	GHA_01	Kwabenya	ZAM_01	Lusaka IA
LT_02	Plateliai, integrated monitoring station	GHA_02	East Legon	FI_01	Laucala_02
MKD_01	Lazaropole	KEN_01	Mt. Kenya	FI_02	Nadi
MD_04	Leova	KEN_02	Kabete	FI_03	Nausori

Figure 37: Central and Eastern Europe, Asia, Africa, Fiji, 2006-2008 (PAHs, ng filter^{-1}).



code	locality	code	locality	code	locality
CZ_08	Košetice, EMEP station	MNE_01	Center of Podgorica	MAL_01	Tombouctou
AR_01	Sevan, Tsovagyugh village	PL_06	Zabierzów	MAL_03	Bamako-int. airport
BE_01	Berezinsky nature reserve	RO_08	Ruginesti	MAU_01	Reduit
BG_06	Sofia, NBMS Bojana	RU_02	Ufa - background	NIG_01	Sheda
HR_03	Siget	SM_05	Fruška Gora	SAF_01	Molopo Nature reserv
EE_03	Lahemaa,EMEP station	SK_07	Starina, dam, EMEP station	SAF_02	Barberspan
HU_02	Budapest, II. ker. Pesthidegkút	SLO_01	Iskrba	SUD_01	Khartum
KA_09	Borovoe	UA_04	Oseshchyna	TOG_01	Koumakonda
KY_01	Kok-Djar village	ETH_01	Asela	TUN_01	Tunis
LV_01	Rucava, EMEP station	GHA_01	Kwabenya	ZAM_01	Lusaka IA
LT_02	Plateliai, integrated monitoring station	GHA_02	East Legon	FI_01	Laucala_02
MKD_01	Lazaropole	KEN_01	Mt. Kenya	FI_02	Nadi
MD_04	Leova	KEN_02	Kabete	FI_03	Nausori

Figure 38: Central and Eastern Europe, Asia, Africa, Fiji, 2006-2008 (PCBs, ng filter^{-1}).

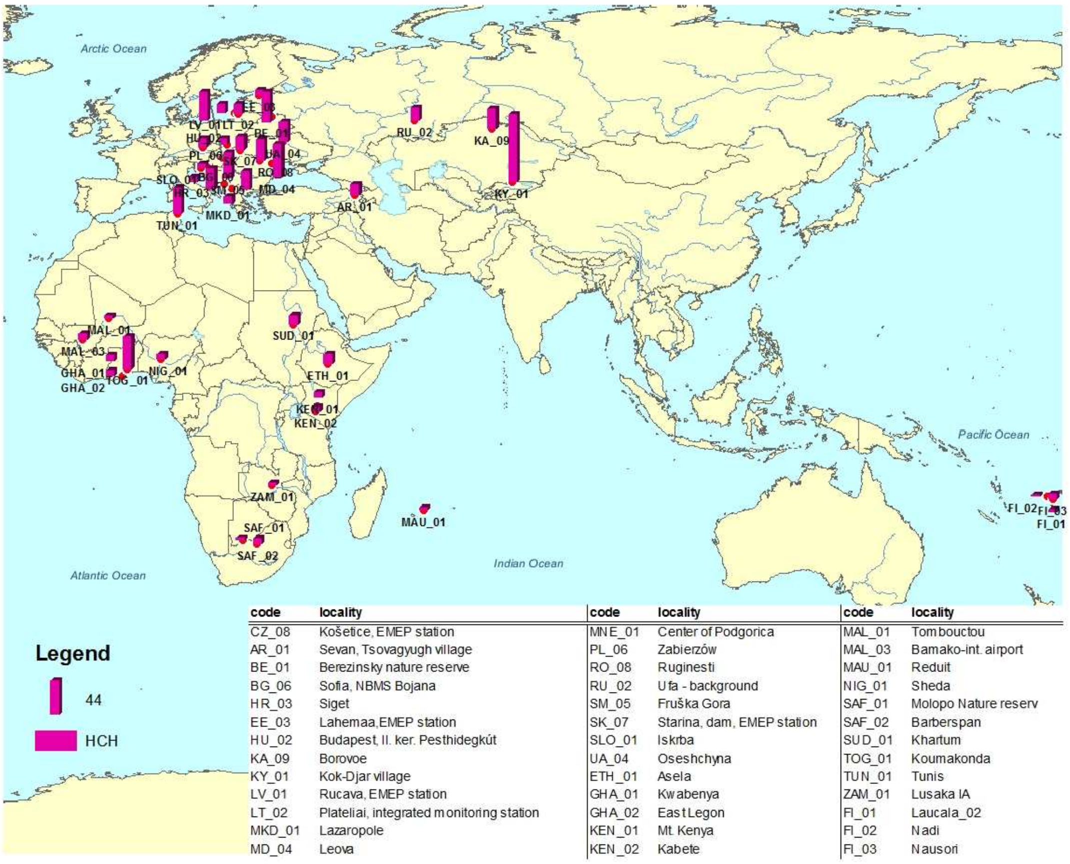


Figure 39: Central and Eastern Europe, Asia, Africa, Fiji, 2006-2008 (HCHs, ng filter^{-1}).

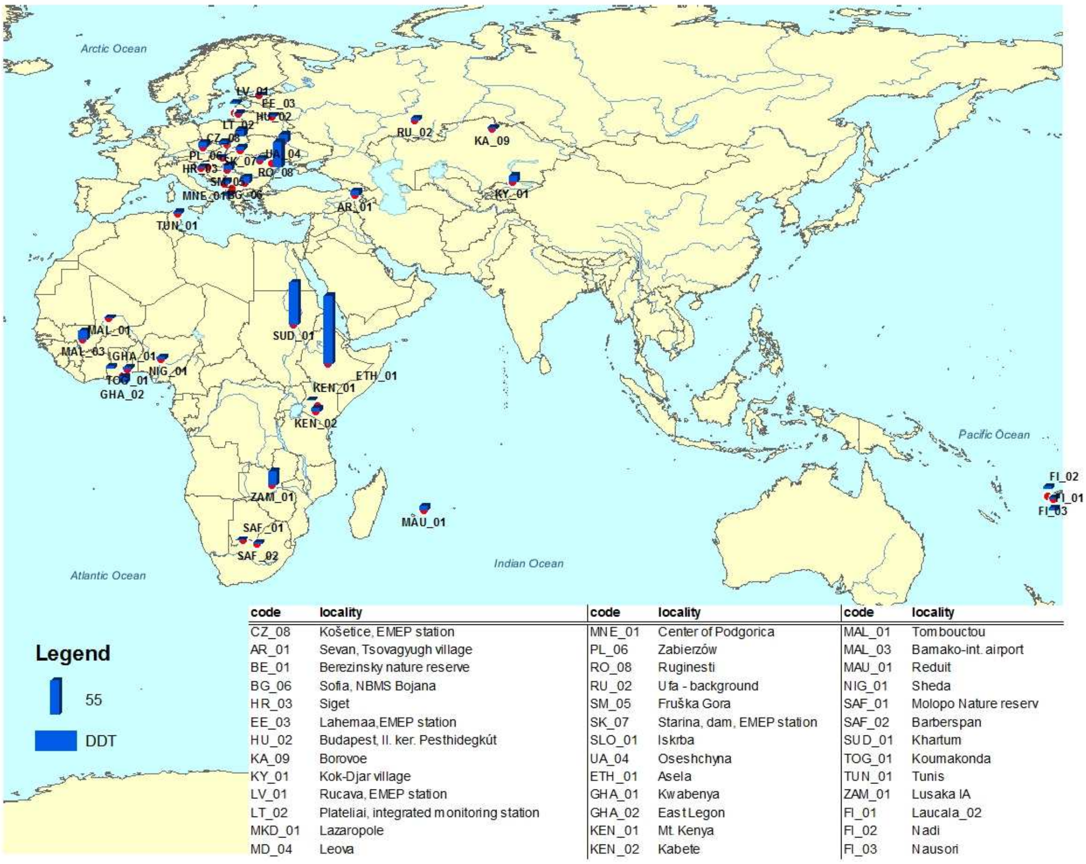


Figure 40: Central and Eastern Europe, Asia, Africa, Fiji 2006-2008 (DDTs, ng filter^{-1}).

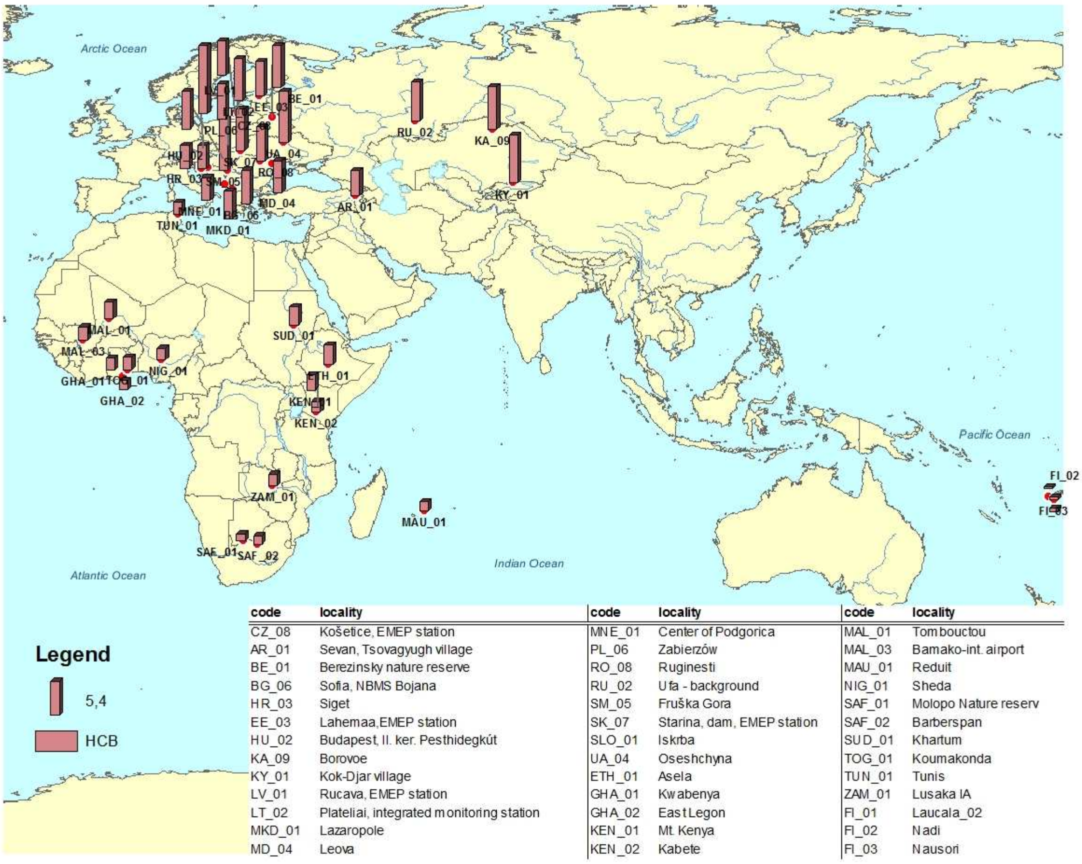


Figure 41: Central and Eastern Europe, Asia, Africa, Fiji, 2006-2008 (HCB, ng filter^{-1}).

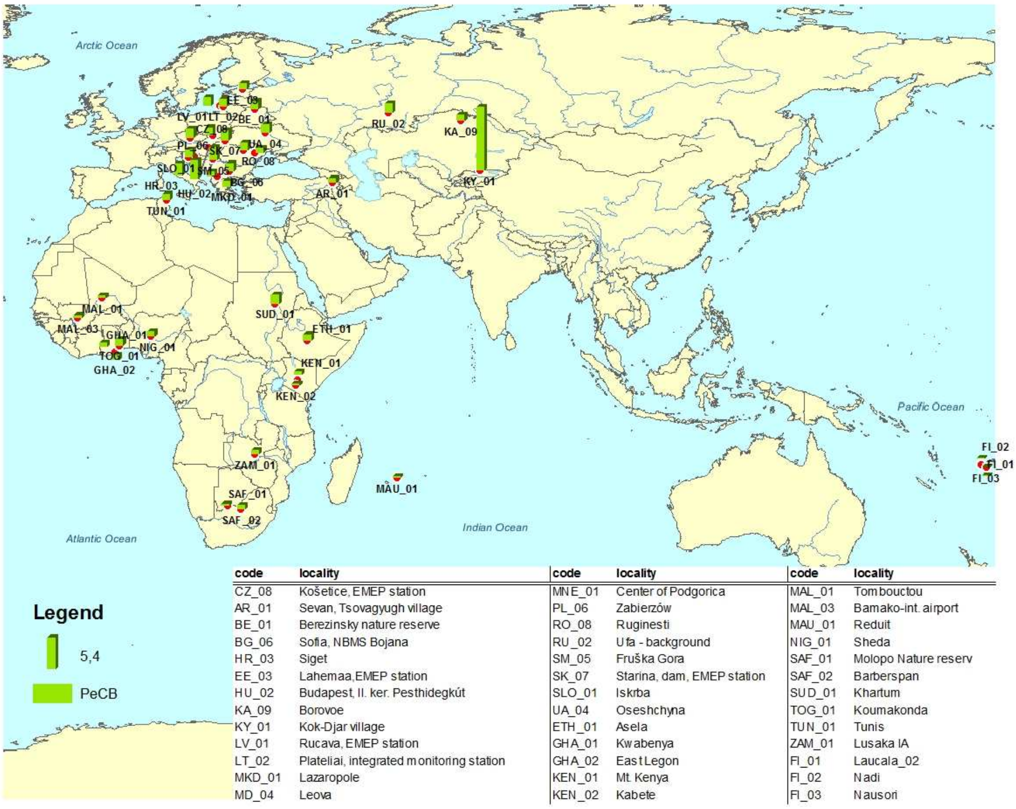


Figure 42: Central and Eastern Europe, Asia, Africa, Fiji, 2006-2008 (PeCB, ng filter^{-1}).

This report **<u>summarizes results of the ambient air monitoring activities</u>** in the Central and Eastern European region (CEEC), Central Asia, Africa and Pacific Islands driven by **RECETOX** as the **<u>nominated Regional Center of the Stockholm Convention for the region of Central and Eastern Europe</u>** under the common name of the **<u>MONET networks</u>**. For many of the participating countries these activities generated first data on the atmospheric levels of POPs. This was a reason why the background monitoring was accompanied with the screening of the extent of contamination in the individual countries. To carry these activities beyond the point of the first screening, best candidates for the background monitoring have to be selected in every region, and resources have to be sought to make the program sustainable.

In case of the CEEC, it has been recognized that knowledge on Western European POP levels would greatly improve the understanding to CEEC data. Although Western Europe is formally a part of WEOG (Western Europe and Others Group) region, and the rest of Europe is reported under the CEEC, it is **<u>desirable to harmonize the monitoring activities in both parts of Europe</u>** to gain systematic information on the levels and trends of the atmospheric pollution in this continent.

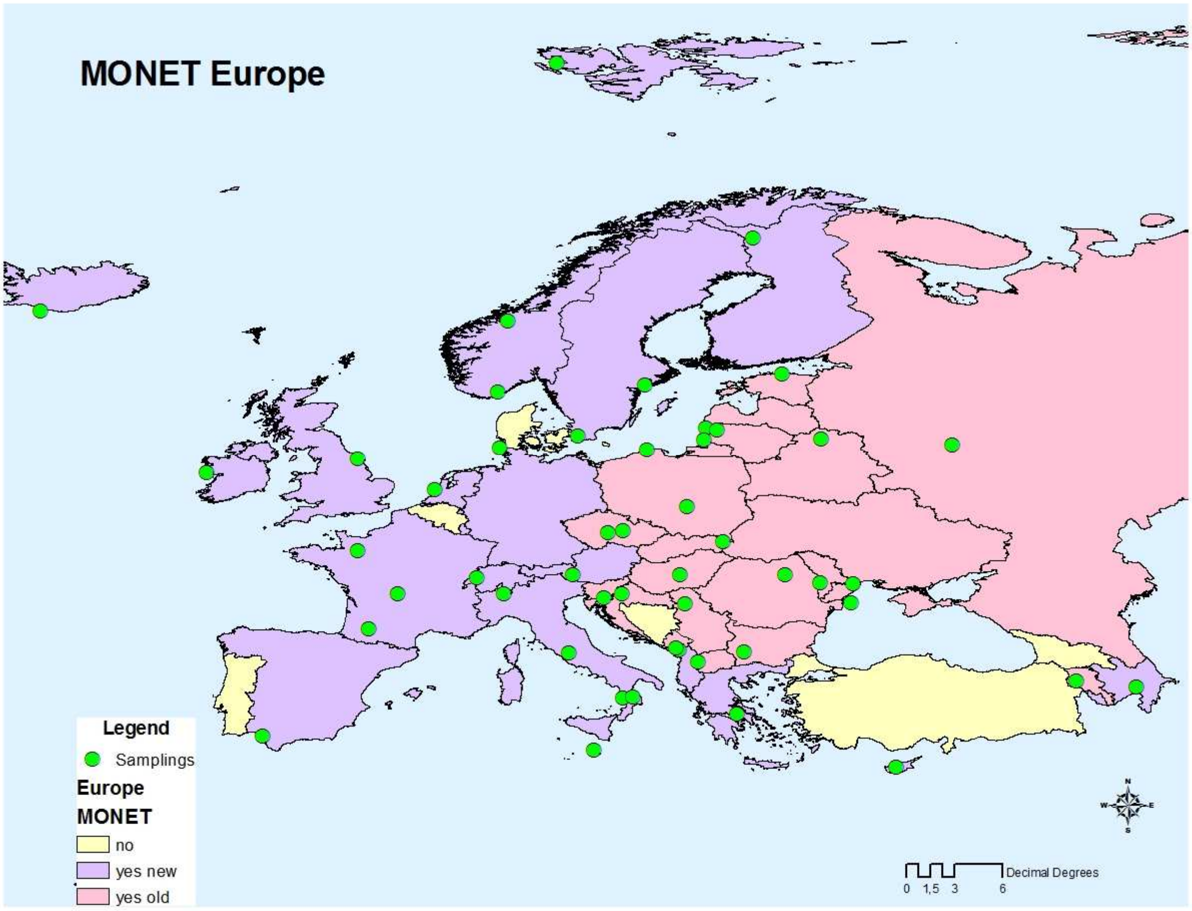


Figure 43: European passive air monitoring network.

As the EMEP stations participating in the previous MONET activities seem to be the best candidates for the long-term background monitoring in many CEE countries (Czech Republic, Estonia, Latvia, Moldova, Slovakia, Slovenia), an agreement has been made between **RECETOX and EMEP** to organize a follow-up study as a **joint activity** of these partners. MONET stations from the previous campaigns were complemented by new stations from Western Europe to provide a good geographical coverage (Fig. 43 – MONET-Europe). Local partners participating in previous campaigns are still encouraged to use this opportunity to become a part of the international network and build their own capacity. The goal is to maintain **sustainable PAS monitoring** at the majority of sites. That would greatly improve the understanding to the sources, fate and transport of POPs in Europe and provide rich information for the modeling databases. At the same time, it would create necessary **synergies between the Stockholm Convention and Convention on Long-Range Transboundary Air Pollution.**

To further develop a concept of cooperation between two conventions and between existing air monitoring programs, the workshop "**Future of Global Air Monitoring**" was held on March 31st, 2009 as a back to back event to the Task Force Hemispheric Transport of Air Pollutants Workshop, St. Petersburg, Russia. This one-day workshop was organized under the auspices of the Secretariat of the Stockholm Convention and offered a platform to the representatives of the long-term air monitoring programs from the WEOG and CEEC regions to share their experience, provide guidance, and explore potential for future cooperation (Summary of the workshop in **Annex 1**).

Substantial geographic differences currently exist in the availability of present monitoring capacity to contribute comparable data for the purpose of an effectiveness evaluation of the Stockholm Convention. Such differences in capacity within and between regions provide opportunities for regional capacity building focused to ensure a capability to detect regional trends. As the regional centers should play a role in coordination efforts, **RECETOX center is ready to extend its support to other regions**. It has been stated in the above mentioned workshop that in order to help ensure long term sustainability and comparability of results, it is recommended that new programs grow from strategic partnerships with existing programs, and benefit from their experiences. This approach has been already applied in the MONET-AFRICA and MONET-PI campaigns and RECETOX is prepared to take an active role as a strategic partner in the follow up studies. New activities of the nominated Regional Center are listed in **Annex 2**.

Capacity building has been an important aspect of the MONET networks since the very beginning. RECETOX Summer School of Environmental Chemistry and Ecotoxicology organized in cooperation with the Secretariat of the Stockholm Convention annualy since 2005 provided a platform for a training of the scientists participating in the MONET networks as well as of other interested individuals (see **Annex 3**). Capacities of the RECETOX laboratories are available for the training courses and the transfer of knowledge.

Understanding that monitoring data will only serve the purpose of effectiveness evaluation when they are available and accessible for interpretation and visualization, RECETOX has developed the **Global Environmental Assessment and Information System GENESIS** (Fig. 44). It was meant to provide a tool for collection, aggregation, processing, and visualization of environmental data as well a tool for an assessment of effects and associated risks. The aim was to build a sophisticated interactive system capable of identification of the links between the quality of the environment and the public health status. As the regional centers should assist in development and maintenance of the network of databases containing monitoring information, RECETOX offers this tool for such purpose.

GENESIS ***Global Environmental Assessment and Information System***

- Within the frame of the GENESIS project, we introduce a user-friendly system for the visualization and analysis of contamination of all environmental components by persistent organic pollutants.
- The system evaluates actual POPs contamination, its long-term trends and seasonal fluctuations.
- The GENESIS project utilizes data from national and international monitoring networks to obtain as-complete-as-possible set of information and a representative picture of environmental contamination by POPs.

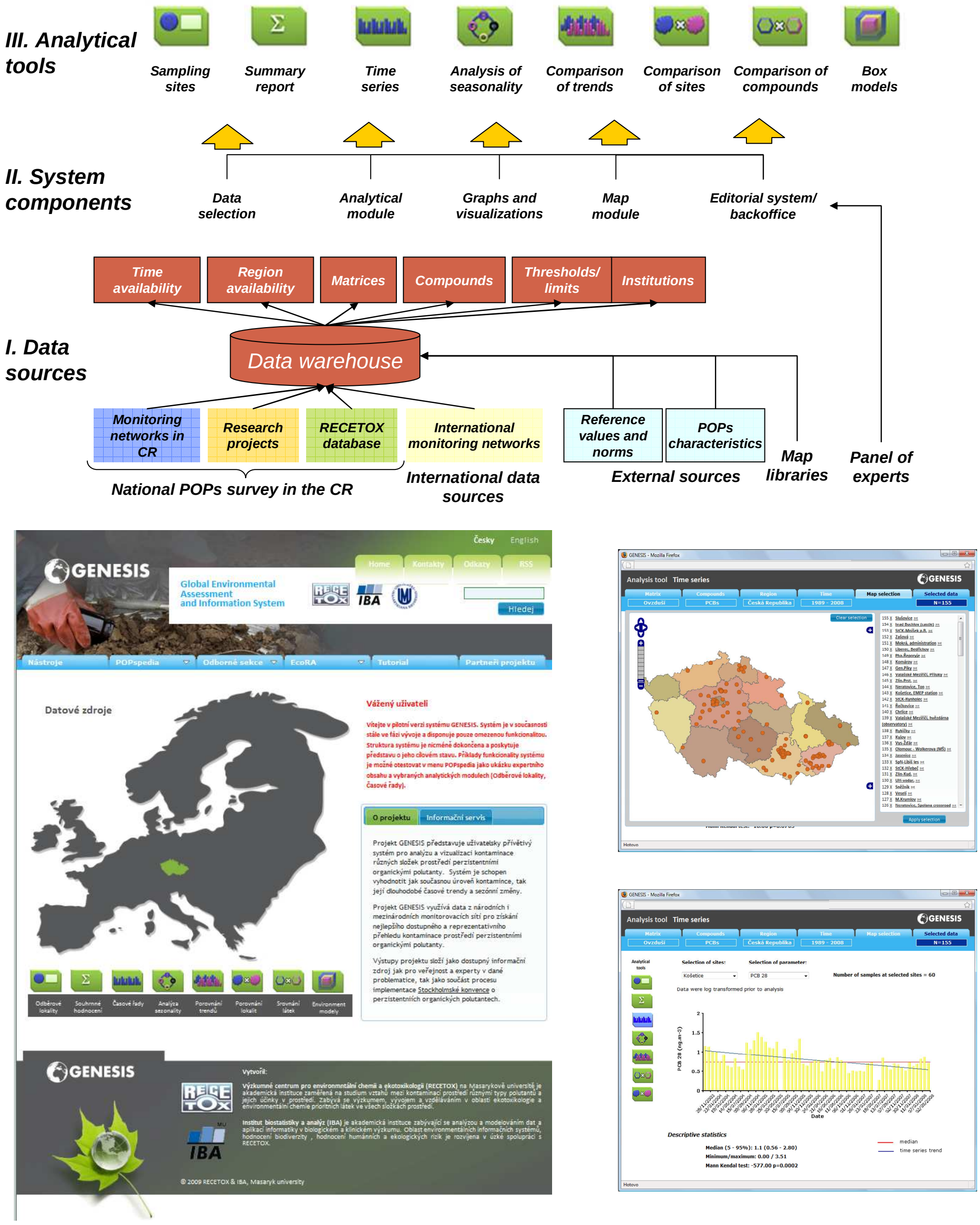


Figure 44: GENESIS - Global Environmental Assessment and Information System.

Aknowledgement

This project was supported by Ministry of Environment (SP/1b1/30/07) and Ministry of Education of the Czech Republic (MSM 0021622412) as a contribution of the Czech Republic as a country presiding over the Council of the EU to the 4th Conference of the Parties of the Stockholm Convention.
African campaign was based on the Memorandum of Understanding between UNEP (represented by the Secretariat of the Stockholm Convention) and Masaryk University, Brno, Czech Republic (represented by RECETOX). This Memorandum was signed for the purpose of implementation of the Agreement between the Swedish Chemical Agency (KEMI) and the Secretariat of the Stockholm Convention on support of the global monitoring of POPs for the evaluation of the effectiveness of the Convention.
The project would not have been possible without the support of the partners from all participating countries and cooperation with the Czech Hydrometeorological Institute.

More information on the integrated monitoring program in Kosetice station:

Holoubek, I., Klánová, J., Jarkovský, J., Kohoutek, J.: Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part I. Ambient air and wet deposition 1988-2005. *Journal of Environmental Monitoring 9 (6),* 557 – 563 (2007)

Holoubek, I., Klánová, J., Jarkovský, J., Kubík, V., Helešic, J.: Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part II. Aquatic and terrestric environments 1988-2005. *Journal of Environmental Monitoring 9 (6),* 564 – 571 (2007)

Dvorska, A.,* Lammel, G., Klanova, J., Holoubek, I.: Košetice, Czech Republic – ten years of air pollution monitoring and four years of evaluating the origin of persistent organic pollutants. *Environ. Pollut. 156 (2) (2008) 403-408*

Komprda, J., Kubošová, K., Dvorská, A., Scheringer, M., Klánová, J, and Holoubek, I.: Application of an unsteady state environmental distribution model to a decadal time series of PAH concentrations in the Central Europe. *Journal of Environmental Monitoring, 2009 (doi: 10.1039/B815719G).*

More information on the MONET networks:

Klanova, J., Cupr, P., Kohoutek, J., Holoubek, I., Application of passive sampler for monitoring of POPs in ambient air. I. Model monitoring network in the Czech Republic (MONET_CZ 2006), 2007. Masaryk Univerzity, Brno, Czech Republic. ISBN 978-80-210-4392-3

Klanova, J., Cupr, P., Holoubek, I., Application of passive sampler for monitoring of POPs in ambient air. II. Pilot study for development of the monitoring network in the Central and Eastern Europe (MONET_CEEC 2006), 2007. Masarykova Univerzita, Brno, Czech Republic. ISBN 978-80-210-4393-0

Klanova, J., Cupr, P., Borůvková, J., Kohoutek, J., Kareš, R., Přibylová, P., Prokeš, R., Holoubek, I.: Application of passive sampler for monitoring of POPs in ambient air. IV. Model monitoring network in the Czech Republic (MONET_CZ 2007), 2008. Masaryk Univerzity, Brno, Czech Republic. ISBN 978-80-210-4696-2

Klanova, J., Cupr, P., Holoubek, I., Borůvková, J., Přibylová, P., Kareš, R., Kohoutek, J.: Application of passive sampler for monitoring of POPs in ambient air. V. Pilot study for development of the monitoring network in the Central and Eastern Europe (MONET_CEEC 2007), 2008. Masarykova Univerzita, Brno, Czech Republic. ISBN 978-80-210-4697-9

Klanova, J., Cupr, P., Holoubek, I., Borůvková, J., Přibylová, P., Kareš, R., Kohoutek, J., Dvorská, A., Tomšej, T., Ocelka, T.: Application of passive sampler for monitoring of POPs in ambient air. VI. Pilot study for development of the monitoring network in the Afričan continent (MONET_AFRICA 2008), 2008. Masarykova Univerzita, Brno, Czech Republic. ISBN 978-80-210-4739-6

Klanova, J., Čupr P., Holoubek, I.: Application of passive sampler for determination of the POPs concentrations in ambient air. .Part III: Pilot study in the Southern Pacific, Fiji, 2006. RECETOX MU Brno. RECETOX_TOCOEN REPORTS No. 320. August 2007.

ANNEX 1

"Future of Global Air Monitoring" – Workshop Summary

This one-day workshop was held on March 31st, 2009 as a back to back event to the Task Force Hemispheric Transport of Air Pollutants Workshop, St. Petersburg, Russia. This one-day workshop was organized under the auspices of the Secretariat of the Stockholm Convention (SC) and offered a platform to the representatives of the long-term air monitoring programs from the WEOG and CEEC regions to share their experience, provide guidance, and explore potential for future cooperation.

The timing of the workshop coincides well with the recently completed first implementation of the Global Monitoring Plan, a mechanism for the effectiveness evaluation (EE) of the SC. The first Global Monitoring Report will be presented to delegates at the 4th Conference of the Parties (COP4) in May 2009, in Geneva. The GMP report contains recommendations for future air monitoring work and raises several important issues for consideration. These include, *inter alia*, data comparability, integration of information on long-range transport and climate variability to assess monitoring data, and issues related to the addition of new POPs to monitoring programs and the growing use of passive air samplers (PAS). These issues are relevant for future effectiveness evaluations of the SC on POPs. These topics are also relevant to the Convention on Long-Range Transboundary Air Pollution (CLRTAP).

Participants of the workshop presented overviews of their programs. Special attention was paid to sustainability of measurements and temporal trends, strengths and weaknesses of the passive sampling technique as a complementary method to high volume air sampling, deployment strategies, comparability issues, intercalibration and harmonization issues, possibilities for data reporting, and storage and modeling needs.

Expert opinion from this group on several issues that were agreed to be relevant to the future of global air monitoring is summarized below.

1. Data comparability issues. The topic of 'comparability' was addressed on several different levels.

- It was recognized that within-program comparability is crucial for producing reliable temporal trends for EE. This can be assured by adopting and maintaining proper QA/QC measures of sampling and analysis, using reference materials and through intercalibration exercises.
- The INCATPA project under the International Polar Year is now completing an international interlaboratory exercise for POPs in air that included 25 laboratories.
- EMEP will initiate an intercomparison exercise in 2009 that will be open to interested SC parties. An invitation will be sent out to known relevant laboratories during summer. EMEP will take into account the experience from the INCATPA project.
- Strategies for improving comparability between programs should also be adopted with the intention to produce a common database/dataset that can be used be end-users of data e.g. modelers. It was recognized that sources of uncertainty between different programs include a much broader scope of issues such as sampler type, frequency of sampling, sample handling and analysis, data handling, reporting and interpretation. It is unrealistic to call for a harmonization of all of these steps as this might disrupt the integrity of the valuable time series that have already been produced. A less invasive

approach to assess and improve comparability between programs could be to overlap at least one monitoring station between two or more programs. These 'overlap' stations could even be rotated (periodically move from one station to another) on an ongoing basis.

- Some comparative studies for passive air samplers (PUF-disk type) have already taken place. For instance, a study coordinated by Lancaster University showed good comparability between PAS used by Lancaster, RECETOX and GAPS (Global Atmospheric Passive Sampling) network. Similarly, collocation of PAS from GAPS and MONET program at the Kosetice station over the last 4 years showed very good agreement of the results in spite of small differences in sampler design, sampling periods and different analytical procedures. Under GAPS, co-deployment of PUF-disk (deployed on a quarterly basis) and XAD-type passive samplers (deployed for 1 year) has shown good comparability. A GAPS sampler has been co-deployed with the new passive sampling initiative in Spain that started in 2008 at 12 background (EMEP) sites. Analytical results for two campaigns (summer and fall 2008) are available for 2,3,7,8-PCDD/F, non-ortho PCBs, mono-ortho PCBs, PBDEs, HCHs, HCB and DDTs. GAPS samplers have also been co-deployed under a large scale monitoring program across China (approx. 100 sites) operated by Harbin Institute of Technology, since 2006.

<u>Passive vs active air sampling</u>

- Good comparisons between high volume and passive samplers deployed over the same period have been reported by several groups. For example, EMEP conducted a 3-month PAS study in 2006 at almost 100 sites and showed usually less than a factor of two differences between PAS and high volume at the Nordic sites for most components. Co-deployment of passive and active samplers for the past 5 years at Kosetice (MONET) resulted in similar comparability. Similar agreement was obtained from a 1-year passive sampling campaign at high volume stations operated under IADN during 2002/03.
- Further strategies should strive to co-locate passive/active at one site in each region according to the Guidance document for the GMP. It is emphasized that a proper comparison requires continuous deployment of active samplers over the same integration period.
- It would be useful to test active/passive comparability at extreme sites. The MONARPOP air monitoring sites at the Alpine summits would be suited for such a purpose since they provide continuous active air sampling, meteorological data and year-round maintenance at site.
- Several programs have already investigated, to some extent, comparisons between active and passive samplers e.g. MONET, EMEP, AMAP, NCP, GAPS and IADN. Such efforts are encouraged.
- The selection of common/comparable reporting format including the necessary metadata would promote data accessibility and comparability. For instance, the group recommends that passive data should be reported as concentrations (as opposed to amount/sampler) according to a harmonized approach. This would facilitate the use of the data by modelers.

2. Particle-bound compounds. Difficulties exist in interpreting passive sampler data for chemicals that partition between gas and particles (e.g. high molecular weight components of: PAHs, PCDD/Fs, and BFRs). So far, the air monitoring of such chemicals requires active air sampling techniques. Although some groups have begun to investigate particle-phase sampling by PAS, this is an area that requires further study.

3. New POPs. It was recognized that in the near future new POPs maybe added to the existing POPs listed under the SC on POPs and CLRTAP POPs protocol. This will add to air monitoring obligations and challenges of existing programs.

- The group agreed that it is useful to include these new POPs and relevant precursors as target analytes investigated under existing monitoring programs for air so that baselines in air can be established. It was recognized that in some instances air may not be the optimum medium (e.g. ionic compounds).
- Some studies have demonstrated the PUF disk samplers were effective at capturing several new POPs classes (e.g. chlorinated paraffins, PCNs).
- Proof of concept of SIP disk sampler has shown that it can be used to capture new POPs that are more volatile and/or polar (e.g. fluorotelomers, penta- and hexachlorobenzene). A pilot study of SIP disk samplers at a subset of 20 GAPS sites was initiated in March/April 2009 and results are expected in November 2009.

4. LRT, climate variability and meteorological variability. The group recognized that to better understand monitoring data it was essential to incorporate information of transport, and influences associated with variability in climate and meteorology.

- Understanding data is more important than just reporting levels and trends, especially for the purpose of assessing effectiveness of regulatory efforts on POPs.
- It is important to develop tools (e.g. back trajectory techniques, multimedia and transport models and investigations of meteorological and climate variability) to better interpret monitoring data. For instance EMEP demonstrated the use of seasonal plots of air masses and contribution maps to assess influences (advection) of POPs from different regions to particular sampling sites. Similar approaches were demonstrated in presentations under AMAP, GAPS, IADN, MONET, NCP and the IPY INCATPA project. The approach of MONARPOP, a separate air sampling according to the source regions of the arriving air masses on basis of daily meteorological forecasts, is also in that sense.
- Meteorological analyses are also recommended for providing information that may assist in the selection of new sites under new monitoring programs.

5. Existing and new air programs.

- To help ensure long term sustainability and comparability of results, it is recommended that new programs grow from strategic partnerships with existing programs, and benefit from their experiences. Training visits for the purpose of capacity building/technology transfer are encouraged and should be supported.
- A summer school in environmental monitoring operated by RECETOX since 2005 has been used for this purpose.
- Newly established passive air monitoring programs are encouraged to overlap (at least at 1 site) with an existing established program (e.g. GAPS, MONET) to promote comparability.
- EMEP has recently developed a new strategy for air monitoring and capacity building and welcome feedback on this plan. This can be located at: www.tarantula.nilu.no/projects/ccc/rev_monitoring_strategy.
- AMAP will evaluate its ongoing air monitoring program and explore the use of PAS to fill gaps.

5. Data Availability. The group agreed that better access to data would be useful for several purposes e.g. model development.

- Existing and new programs are strongly encouraged to incorporate data management in their programs, i.e. employ sustainable databases.

- Consideration should be given to the most suitable format and interface for end users of the data e.g. modelers.
- There are many benefits to including data management tools (e.g. graphing, mapping, and statistical analysis) as part of the data storage applications.
- NILU already maintains a database that is used by several air monitoring programs (e.g EMEP, AMAP, CAMP, HELCOM, WMO/GAW) and research projects, and is open to new datasets. Visit ebas.nilu.no.
- GENESIS database at RECETOX contains all MONET and EMEP Kosetice results and will be publicly available. It has been offered to the Secretariat of the SC for management, analysis, interpretation and presentation of GMP data.

6. Air programs. Several program coordinators indicated that it would be beneficial to be better informed on data needs and timing for proposed new POPs and associated reporting requirements and deadlines.

7. The group agreed that a **future meeting** of the program representatives (including regions not represented at the St. Petersburg workshop) is required to further develop a comprehensive global air monitoring strategy and related needs.

ANNEX 2

RECETOX Initiative

In response to the points raised in "Expert Advice on Future of Global Air Monitoring" coming from discussion at the "Future of Global Air Monitoring" Workshop held as a back to back event of the TF HTAP Workshop on March, 31^{st}, 2009, in St. Petersburg, Russia,

RECETOX (Research Centre for Environmental Chemistry and Ecotoxicology) nominated as the Stockholm Convention Regional Centre for Central and Eastern European region in the co-operation with the Czech Hydrometeorological Institute, Prague, CR and EMEP Meteorological Synthesizing Centre East, Moscow, Russian Federation present their new activities supporting Global Monitoring Plan for Effectiveness Evaluation of the Convention measures:

1) A fact that the EMEP Central European background station in Kosetice has a history of 20 years of high volume measurements of POPs in ambient air, out of which MONET and GAPS programs passive air samplers have been collocated for 5 and 4 years, respectively, makes it a good candidate for the "calibration station" of active and passive air sampling methods serving both~~,~~ programs. Continuous active sampling will be initiated at this station in addition to on-going 24-hour-per-week sampling.

2) In addition to PCBs, HCB and DDT and metabolites as the SC target compounds, HCHs and pentachlorobenzene from the candidate list are already being monitored together with PAHs. Selection will be further extended in order to cover some of new POPs as brominated flame retardants.

3) Long-term data from this station comparing passive and active data will be exploited in order to provide preliminary estimation of the compound- and season-specific sampling rates of the particle-bound compounds.

4) RECETOX GENESIS expert system developed as an advanced tool for the purpose of evaluation, interpretation and presentation of environmental monitoring data is currently being used for MONET. It has been offered to SSC as a joint database supporting interpretation of GMP data.

5) RECETOX as the nominated Regional Centre for CEEC region extends it's offer for the strategic partnership in the field of the air monitoring beyond the region to all parties that are currently not covered by other centres.

6) RECETOX Summer school of Environmental Chemistry and Ecotoxicology organized annually since 2005 will continue to offer one class focused on the practical training for environmental monitoring as a tool for the capacity building in regions developing the monitoring strategies.

ANNEX 3

RECETOX - *Research Centre for Environmental Chemistry and Ecotoxicology*

EU-DG Research Centre of Excellence for Environmental Chemistry and Ecotoxicology

5th Summer School of Environmental Chemistry and Ecotoxicology

Date:

6.-11.7.2009

Venue:

RECETOX
Masaryk University
Brno
Czech Republic

Field observatory
Košetice
Czech Republic

Studies of relationships between environmental levels of chemicals and their biological effects with special attention to persistent and toxic substances

The basic goal of the 5th Summer School is integrated monitoring/modeling in the research of environmental contamination by persistent toxic substances (PTS) and other emerging pollutants.

The Summer School will be organized in two groups (classes):

A) Environmental chemistry and ecotoxicology of PTS
- laboratory and field studies

B) Sampling, analysis and monitoring of PTS (co-organized with the Secretariat of the Stockholm Convention, UNEP)

The special attention of the 5th Summer School will be focused on field studies and experimental methods in environmental sampling and analytics, studies of environmental processes and their modeling, ecotoxicology, data collection, evaluation and use in the risk assessment.

Topics:

- ✓ Fate of PTS, environmental processes
- ✓ Monitoring and analyses of PTS
- ✓ Modelling of PTS in the environment
- ✓ Ecotoxicology & effects in ecosystems
- ✓ Risk assessment, data evaluation

RECETOX lecturers:

Prof. I. Holoubek, Prof. J. Klánová, Prof. Z. Šimek, Prof. B. Maršálek, Prof. L. Bláha, Dr. K. Hilscherová, Prof. L. Dušek, Dr. K. Brabec, Dr. P. Čupr, Dr. J. Jarkovský, Dr. A. Dvorská

Invited speakers:

Prof. P. Garrigues, University of Bordeaux, France
Dr. K. Semple, University of Lancaster, UK
Dr. M. Scheringer, Swiss Federal Inst. of Technology
Dr. A. Kočan, Inst. of Prev. and Clinical Medicine, SK
Prof. V. Shatalov, EMEP MSC-East, Russia
Prof. H. Hollert, University of Heidelberg, Germany
Prof. R. Triebskorn, University of Tuebingen, Germany
Dr. E. Fries, University of Osnabrück, Germany

More information:

Please visit the RECETOX web pages: http://www.recetox.muni.cz/5SS

Contact to organizers: kostrhounova@recetox.muni.cz, holoubek@recetox.muni.cz

Registration fee 350 € (lectures and practical exercises, background materials, field trip, accomodation, lunches). Participants cover their travel expences.

Towards the Global Monitoring of POPs
Contribution of the MONET Networks

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