

SUMMARY REPORT

Objectives

During the Balkan wars and Allied Forces operation in the spring of 1999, the burning or damaging of industrial and military targets in the former Republic of Yugoslavia resulted in the release of large amounts of various persistent organic pollutants (POPs). There is evidence that significant quantities of polychlorinated biphenyls (PCBs); various flame retardants and explosives, among other substances, were released into the environment. The objective of this project was to investigate the levels of POPs (with special attention to PCBs) in various environmental matrices, their atmospheric and hydrogeological fate, human intake and the ecotoxicological consequences of the exposure of living organisms to POPs in several regions of Croatia, Serbia and Montenegro, Bosnia and Herzegovina, and Kosovo affected by the war. The main goals also included the identification of hot spots, laboratory and field PCB biotransformation studies, and suggestions for the remediation of contaminated soils.

Activities

- 1) The intercalibration exercise was organized by RECETOX in two phases for all the participating labs to assure the quality of the results. Harmonization of the operational procedures, sampling and analytical methods were performed in the second workshop. Good laboratory practice and quality assurance/quality control procedures were introduced by UMB. Training of less experienced colleagues took place in analytical laboratories at RBIZ.CMR, UMASA.RECETOX and IPHSI.EP.HSA.
- 2) Data on suspected sources of POPs pollution and the soil and water contamination of various sites in continental Croatia, Bosnia and Herzegovina, Serbia and Kosovo were collected by RBIZ.CMR, UNS.FS.IC and GEOSURV.
- 3) The levels and fate of POPs, especially PCBs, in the soil or other parts of the significantly polluted ecosystem in Croatia, Bosnia and Herzegovina, Serbia and Montenegro, and Kosovo were investigated. Collection of samples and POPs analysis were performed by RBIZ.CMR and the subcontractors IPHZ.HED and UNIPRIS.FS.DC for soil, sea and river sediment, and for biota samples in Croatia and Kosovo. Collection of samples and analysis of POPs were performed by RBIZ.CMR and GEOSURV for soil and river sediment samples in Bosnia and Herzegovina. Collection and analysis of sediment samples in Bosnia and Herzegovina were performed by GEOSERV and IPHSI.EP.HSA. Collection and analysis of soil samples in Croatia, Bosnia and Herzegovina and Serbia and Montenegro were performed by UMASA.RECETOX. Collection and analysis of soil, sediment and biota samples in Serbia and Montenegro and Bosnia and Herzegovina (Republic Srpska) were performed by UNS.FS.IC, UBEG.FMG.IH, UMASA.RECETOX and IPHSI.EP.HSA.
- 4) A detailed study of the geochemical properties, behavior of PCBs and other contaminants in soil, the unsaturated and saturated zones of the karst aquifer, and the soils and the karstic aquifer off the Zadar area in Croatia was performed by RBIZ.CMR, UMB and IGEO.DHG.
- 5) A study of the geochemical properties, behavior of PCB and other contaminants in soil, and the unsaturated and the saturated zones of the alluvial aquifer of several rivers and lakes in Serbia and Montenegro was performed by UNS.FS.IC, UMASA.RECETOX and UBEG.FMG.IH.
- 6) High volume and passive air ambient sampling was performed in Croatia, Serbia, Bosnia and Herzegovina, and Kosovo by RECETOX, in cooperation with RBIZ.CMR and IPHZ.HED in Croatia; GEOSURV in Bosnia and Herzegovina and UNS.FS.IC in Serbia and Montenegro. Air samples were analyzed by UMASA.RECETOX. A passive air-sampling network was established in the Czech Republic as a reference region (UMASA.RECETOX).
- 7) A mathematical model of the human intake of POPs for the ecological and social conditions of the investigated region was developed and applied. Investigations of the correlation between the level of environmental contamination with the investigated POPs and the biological response of living organisms were conducted. These investigations were performed in cooperation with the partners UNIPRIS.FS.DC and UMASA.RECETOX.

- 8) The collection of data on professional and recreational fishermen and their families from the Zadar region in order to gain insight into their consumption of fish caught in the coastal waters of Zadar was performed by RBIZ.CMR and IPHZ.HED.
- 9) The selection of the most efficient microbial cultures in the transformation of target PCBs and the preparation of seed cultures for field biotransformation experiments were performed. Laboratory and field PCB biotransformation studies with evaluation of the efficacy of the proposed remediation method at the investigated small-scale field site were performed by RBIZ.CMR and the subcontractor IPHZ.HED, and IPHSI.EP.HSA.

Results achieved

Ad 1)

In the first intercalibration test in the autumn of 2002, four out of six laboratories provided reasonable results for the PCB standard solution and soil sample. Two laboratories faced more serious problems, and improvement in their methods was obviously necessary. There were several study visits by the Project participants organized in the RECETOX laboratories to improve the QA/QC level at the laboratories with problems. Unfortunately, these two laboratories never met the expected standards and could not perform the analyses planned in the Project.

In the laboratory of Partner 005, two young assistants from Pristina University spent a total of 8 months in training. Despite this relatively short training period, both of them became acceptably adept in laboratory work for the analysis of PCBs and DDTs in soil and river sediment samples. Also, the laboratory in Maribor helped improve the skills of a young assistant from Novi Sad University in analyzing POPs in environmental samples.

Additional attention and financial support should be provided for the development of the regional laboratories. While some of the partners demonstrated the ability to produce high quality results, some were not able to perform trace analysis, even with the assistance of the Project and other partners. To ensure the continuation of the independent research projects and the establishment of some kind of monitoring networks, improvement of the local laboratories is needed.

Ad 2)

Particular attention has been devoted to the collection of data on possible PCB spills into the environment in the countries of the former Yugoslavia, especially the vulnerable karstic areas in the Bosnian highlands where military communication relays were damaged or destroyed and all the other places where electrical transformer stations and capacitor batteries were damaged or destroyed. About 500 electrical transformer stations and capacitors in Bosnia and Herzegovina, mostly within the Federation, were damaged or destroyed during the war, 1992–1995.

Ad 3)

At the Zadar Electrical Transformer Station in Croatia, one condenser battery was damaged in 1991 during the war. This was the reason for a more detailed investigation of the PCB levels in the surroundings. Investigations of PCB pollution was performed by analyzing more than 50 soil samples collected several times and wipe samples of the polluted asphalt-concrete surfaces under the condensers. The dispersion of the PCB levels in the soil samples around the damaged condenser showed a significant decrease in the PCB levels only a few meters from the pollution hot-spot. Two research holes in the area of the Zadar E.T.S. were excavated. One was excavated inside the asphalt-covered base and the second outside the asphalt-covered base around the damaged condenser battery. The PCB levels in the top layers of the outer hole were markedly high while the levels were very low in all the layers of the inner hole. Therefore, it has been concluded that the asphalt-covered base effectively protected the soil below from more serious PCB penetration.

In February 2005, employees of HEP Croatia cleared and burned all the pine trees around the Zadar substation. Partner 005 collected 2 samples of ash remaining from the burned pine needles and sent them to Partner 008 for analysis. The observed PCB-TEQ total values were 1.5 and 3.7 pg WHO-TEQ/g d.w., and 0.8 and 4.9 pg WHO-TEQ/g d.w. of PCDD/F. It is evident that the TEQ PCB values are 2 times higher than the WHO-PCDD/F-TEQ values. PCB levels have also been investigated at several localities in the city of Zadar. Another serious potential source of PCB contamination has been discovered in the area of the former textile factory, TIZ.

Due to the significant PCB levels observed in sediments and some organisms from the Zadar coast in previous research, investigations of these pollutants have intensified in the last few years within the APOPSBAL project. During this investigation, over sixty sediment samples (at two depths) and fish samples were collected and analyzed at 22 stations off the Zadar coast. Comparison of the distribution of PCB congeners in the sediments indicated that the Jazine area was highly contaminated. The finding of high PCB levels in deep sediment layers in this area indicates the deposition and accumulation of pollutants over a period of several years. Analysis of the relative distribution of PCB levels in samples of annular sea breams (*Diplodus annularis* L.) and other fishes caught off the Zadar coast also demonstrates that the highest PCB levels were found in the Jazine area (maximum of 1198 ngg⁻¹ of the total PCBs).

During the warfare in the Rijeka Dubravačka area, the Komolac Electrical Transformer Station was heavily damaged and there was suspected PCB contamination of this area. From the results, it was evident that the PCB levels in the soil, sediment and biota samples collected near the damaged E.T.S. were not high. Through interviews of the local people, it was learned that some of the waste construction material from the destroyed Komolac E.T.S. was transported to the sea coast around Sustjepan. After sampling sediments at 11 stations along Rijeka Dubravačka, significant PCB levels were found at the station near Sustjepan, 2594 ngg⁻¹. It is suspected that the high PCB levels in the sediment are due to the deposition of waste material from the Komolac E.T.S. in this location.

PCB analysis of soil samples in the former war zone of western Slavonia in Croatia showed exceptionally high total PCB levels in a few locations, from 442 000 to 1 784 000 ngg⁻¹ d.w. In the future, it will be necessary to investigate the levels of PCBs in this area more thoroughly, especially in the aquatic ecosystem, in order to make a realistic assessment of the input of these pollutants to the anthropogenic system.

From PCB analysis of soil samples collected in Bosnia and Herzegovina, it could be concluded that there is a great range in the total observed PCB levels, from 50 to over 100 000 000 ngg⁻¹ d.w. Exceptionally high total PCB levels have been observed in soil samples from the Tuzla area (96 178 000 ngg⁻¹ d.w.) and Tešanj (178 954 000 ngg⁻¹ d.w.). These enormously high PCB levels were registered at sites where damaged capacitors were located. The terrain is constructed of alluvial sediments and the oil could run off through the alluvium to the Usora River and from there to the alluvial aquifers on the opposite left bank of the river. There are wells built for the water supply of the majority of the inhabitants of the municipality of Tešanj and also wells in numerous places further downstream to the Bosna River.

High PCB content was also found in the former military tunnel of Željjava near Bihać, 164 000 and 106 000 ngg⁻¹ d.w. This indicates that the spilt oil with pyralene was from facilities inside the tunnel and not from the outside. From there, pyralene can infiltrate through karstic rock masses and then appear in the strong karstic springs around Bihać and after that to the Una River. It can be concluded that further sampling of the soil in the deep tunnels and rooms of these underground facilities is needed.

The observed levels of the sum of the 7 key PCBs in sediments from Bosnia and Herzegovina ranged widely, from less than 0.35 (below the sensitivity of the method) to 2691 ngg⁻¹ d.w. In a few locations in Bosnia and Herzegovina, exceptionally high levels of the sum of the 7 key PCBs were determined: the Miljacka River 929 ngg⁻¹ and the Zujevina River 2691 ngg⁻¹ d.w. in the Sarajevo area; the fishpond Klokot 2 near Bihać 361 ngg⁻¹; and in the rivers of the Tuzla area: Gostilja (Han Nevrenča) 377 ngg⁻¹ and Spreča (Puračić) 483 ngg⁻¹ d.w. The analysis of 6 fish from Klokot 2 fishpond did not show increased PCB content in the muscle tissue, ranging from 12 to 73 ngg⁻¹ d.w. of PCBs.

There was a pilot study performed for another probable hot spot, Banja Luka in Bosnia and Herzegovina. The PCB levels at several sampling sites in Banja Luka were as high as 400 000 ngg⁻¹ d.w, i.e. two orders of magnitude higher than at any other site investigated by UMASA.RECETOX.

Only 8 sediment and 4 soil samples were analyzed in Kosovo. In all the soil samples, the PCB levels were less than 1000 ngg⁻¹ d.w. The obtained PCB range as the sum of the 7 key PCBs in sediments was from 5 to 208 ngg⁻¹ d.w.

Soil samples were collected at three hot spots in Serbia: near the Zastava auto factory and in the surroundings of Kragujevac, Kormansko Polje; on the territory of the Novi Sad oil refinery; and in the territory of Pančevo in the oil refinery and petrochemical plant. High levels of PCBs were found in the painting hall of the Zastava auto factory in Kragujevac and in one sample at the petrochemical plant in Pančevo.

Topsoil samples were taken at sampling sites of high volume and passive air sampling campaigns near damaged industrial objects in Serbia and Montenegro. The results of the analysis of the polychlorinated biphenyls, pesticides and PAHs in these soils correlated very well with the data on atmospheric pollution. Since the sampling sites on the grounds of the Zastava factory in Kragujevac provided the most contaminated air samples, additional soil and sediment sampling was recommended to determine the sources of air pollution. It is likely that the atmospheric contamination comes partially from secondary sources (contaminated land) and partially from primary sources (PCB-filled transformers still in operation). Sediment samples were collected in the surroundings of Kragujevac, including the rivers Zdraljica, Lepenica and Morava. Danube sediments were also collected on the territory of Novi Sad. The results revealed very high PCB levels in the sediment samples from the Zdraljica River, while PCB levels were considerably lower in the sediment samples from the rivers Velika Morava and Lepenica.

Ad 4)

Bulk mineralogical analysis of soil samples collected from the Zadar E.T.S. showed a predominance of quartz and calcite. The organic carbon content of the soil samples shows values between about 1% and 10%. However, some samples show exceptionally high values (up to 26%). In the sediment sample from the Jazine area, which was split according to various grading fractions, the contents of the total inorganic carbons in lower sediment fractions were higher in comparison to fractions of larger granularity. The total organic carbon was completely reversed. The maximum level of the sum of the 7 key PCBs was found in the fraction between 0.2 to 0.63 mm. It is interesting that the PCB levels in fractions lower than 0.063 mm were significantly lower in comparison to fractions of larger granularity.

Due to the requirements of the hydrogeologic intrinsic vulnerability and specific vulnerability assessment of the Zadar municipal area, relevant data suitable for further modeling and evaluation were incorporated into the GIS form. The hazard mapping and database structuring performed in the area of the city of Zadar followed the hazard inventory proposed by COST Action 620. In the city area, 28 types of hazards were identified, 13 polygonal, 12 point and 3 line sources of hazard. A specific vulnerability map was prepared for PCBs. We considered the specific attenuation of cover deposits regarding PCBs and its combination with the vulnerability map by the COP method. Combination of the maps of a particular layer within each model was also performed using the GIS tools, ESRI ArcMap ArcView 8.3 with extensions 3D Analyst and Spatial Analyst.

Ad 5)

In the Kragujevac area, research was carried out at three locations: TS-305 - additional research at specific spots, painting hall - research drilling, groundwater level monitoring; and lower flow sections of the rivers Zdraljica, Lepenica and Velika Morava - sampling of river sediment and recently flooded nearby terrain (Kormansko Polje). The presence of alluvial sediments was registered on the basis of drilling data. The alluvial sediments consist of underlying gravel with sand, up to 1 m in thickness. Pure clay and clay with sand, which is 1-6 m thick, are layered alternately above. The cover deposits consist of artificially deposited building material (3.8 m thick). Since the PCB levels in soil samples from the factory area are relatively low, the residual quantities of contaminants do not pose a threat to the environment. Further investigation was therefore expanded to Kormansko Polje, nearby flooded terrain up to the Lepenica River. The presence of PCBs in the riverbeds of the Zdraljica, Lepenica and Velika Morava proves that significant quantities of this contaminant were transported through the rain drainage system in the above-mentioned rivers after the flood of 1999 and were present in the flooded parts of the terrain.

Ad 6)

The first systematic ambient air sampling campaigns for POP analyses were performed in Croatia, Serbia, and Bosnia and Herzegovina. The data will provide a useful contribution not only to this project but also for ongoing national POPs inventories as a part of the implementation of the Stockholm convention. The concentrations of PCB congeners, OCPs and PAHs in the gaseous and particulate phases of the air samples were determined. During the ambient air sampling campaign, samples of surface soil were collected close to the sites of the atmospheric sample collectors. It was obvious that the PCB levels in the atmosphere of the Zadar Electrical Transformer Station, the Tuzla E.T.S. and the Elektrodistribucija fire station were significantly higher in comparison to the other Croatian and Bosnian localities. However, the PCB levels in the atmosphere of the Zastava factory in Kragujevac, Serbia, were at least another order of magnitude higher (the highest among all the sites investigated during the course of the project in Serbia, Croatia, and Bosnia and Herzegovina). PCB levels measured in the air samples correspond well with the levels determined in the soil samples.

An additional passive air sampling campaign was performed in 2004 at 34 sampling sites. The results of the passive air sampling campaign were in very good agreement with the previous high volume measurements. The amounts of PCBs sequestered by PAS filters were as high as 7 µg of the sum of the 7 indicator congeners (2 µg for the individual congeners) at the Zastava factory sampling site, while remaining in the range of hundreds of nanograms for most of the other industrial sites, and in the range of tens of nanograms for residential areas. PCB congener pattern was also investigated. While PCB 28 was the most abundant in both the active and passive sampling results at the Zadar transformer station, PCB 52 and PCB 101 were most abundant at the highly contaminated sites at the Tuzla fire station and the Zastava factory in Kragujevac, indicating different sources of contamination. Again, passive and active samplings provided very similar information about the congener distribution. The decreasing trend in the levels of PCB and OCP air contamination from July to December corresponds to decreasing temperatures and indicates enhanced evaporation from secondary sources during the warm season. Significant correlation between the PCB levels in the atmosphere and in the soil surface, and between the congener distribution in the air and soil, was noted. An additional twenty sampling sites in the Czech Republic were selected to serve as a reference region, including the background sampling of the Kosetice observatory used as an EMEP monitoring station. Results of the study showed a highly uneven distribution of PCBs and other POPs in the atmosphere of the countries of the former Yugoslavia, indicating the presence of strong point sources of pollution. All the sites originally suggested for investigation due to damage from warfare were confirmed to be sources of considerable air pollution. However, the PCB levels in the residential and background areas are comparable to the levels in the Czech Republic as a reference region.

Ad 7)

In this study, we also attempted to detect the genotoxic effects of the cumulative air samples collected at sampling sites in Zadar, Sarajevo and Tuzla. The samples were tested separately for organic pollutants in gas and solid phases in the air. The SOS chromo test was used as the system to detect genotoxic potency. Samples were also tested with the addition of metabolic activation (S9 fraction of an extract of rat liver cells), facilitating the detection of the effects of progenotoxic compounds. The genotoxic potency was then quantified as a value of the induction factor. While none of the Croatian samples induced any significant response in the test, with or without metabolic activation, increased response was detected in air samples from Bosnia and Herzegovina in the test with metabolic activation. The pollutants with genotoxic activity were mainly bound in particulate matter.

Partner 006 developed and used a mathematical model for human dietary exposure to POPs based on the calculation of human exposure factors (HEF) to POPs via various members of the terrestrial food chain, where the total human exposure depends on exposure factors and POP concentrations in the atmosphere and soil. Comparison of the calculated values obtained through the application of the proposed mathematical model and experimentally determined concentrations of contaminants in vegetation shows that the correlation between them is excellent. On the basis of the concentration of POPs in the foodstuffs, atmosphere and soil in Novi Sad and its surroundings, it was calculated that an adult in Novi Sad of average weight (70 kg) consumes 24.58 µg DDT (1.50% ADI); 2.46 µg HCH (0.83% ADI); 0.07 µg endosulfan (0.02% ADI) and 0.79 µg PCB (1.1% ADI) daily. Investigation of the oxidative metabolism of PCBs and other organochlorine compounds involves the induction of cytochrome P450 enzymes, yielding either activated or inactivated metabolites. It also provokes oxidative stress leading to disturbance of the antioxidative defense system. The extent of the adverse effects can be assessed via a lipid peroxidation system model. It was demonstrated that in a mixture with laurel poppies, Ascarel and Pyralene showed no prooxidative properties and did not stimulate the production of OH radicals. The results confirm that an increase in the pyralene oil concentration leads to a decrease in lipid peroxidation intensity in comparison to control values (or even lower), which could be explained by their negative synergism with radicals produced during the lipid peroxidation of liposomes.

Ad 8)

In 2003, an investigation was conducted among fishermen and their families from the Zadar area in order to define the precise daily intake of PCBs by this "critical" group. Fifty families with a total of 200 family members were interviewed about the amount of fish consumed per month from total Zadar coastal area and the closest urban area. Estimated total PCB consumption was established on the basis of the PCB levels in the fish species most frequently consumed by the investigated families. The estimated distribution of the daily intake of PCBs by fishermen's families from the Zadar area regarding the consumption of sea bream, which has a mean PCB level like those, collected in 2004 from the Zadar coastal area, shows that the daily intake of PCBs is higher than the ADI in more than 10 cases.

Ad 9)

Comparative PCB transformation studies performed with pure Z6 culture confirmed its substantial activity in the presence of biphenyl and demonstrated an enhancing effect on the kinetics of PCB transformation in the presence of natural compounds (xylose, carvone and soya lecithin) when compared to the control experiment. To further verify the effectiveness of the selected cultures in PCB transformation, microcosm biodegradation experiments with artificially contaminated soil were performed using soil originating from the Zadar E.T.S. These experiments confirmed significant PCB transformation activity of pure Z6 culture in the presence of selected natural compounds (carvone, xylose and soya lecithin). Based on the results of laboratory biodegradation experiments, laboratory model field experiments were established and 3-month bioaugmentation treatment showed a gradual decrease in the PCB mass fractions in the soil.

Natural soil contaminated with PCBs, excavated from the area around the damaged capacitor of the Zadar Electrical Transformer Station, was used in a small-scale field experiment. This study investigated the effects of various plant species and natural attenuation on the dissipation of PCBs in the soil. A lysimeter experiment conducted for 1 year under natural climatic conditions was designed to measure the concentration of PCBs in the soil and leachates. The research field was composed of four plots located near the E.T.S. Three lysimeters were set up on each plot. The plots were planted in September 2004. Plot No. 1 was sowed with legume alfalfa (*Medicago sativa* L.) seeds, plot No. 2 with a commercial grass seed mixture suitable for the arid Adriatic region and plot No. 3 was sowed with *Arabidopsis thaliana* (Heynh L.) seeds. Plot No. 4 was a control plot that was left to grow wild. After 12 months of experiments (including twelve periods of rainfall events), negligible quantities of Aroclor 1248 (an average of 0.024%) and $\Sigma 7$ key (an average of 0.032%) were leached from the soils. The first soil sampling was performed in June 2004 (before planting) and the second soil sampling was in June 2005 (after planting). Soil samples were taken at three depths from each lysimeter (surface layer, middle layer and deep layer) and soil around the plant root. After the 12-month experiment, only soil from plot No. 1 had significantly lower levels of Aroclor 1248 compared to the initial concentration. The initial amount of $\Sigma 7$ key was significantly decreased in the surface soil layer (by about 47.6%). Correlation between the PCB 28 loss and deep soil indicates that in the deeper soil layer we have a lower decrease of PCB 28 (except in the soil of plot No 2). These results may be related to the opinion that PCB 28 (as more volatile) evaporates into the atmosphere. The results generally present an accumulation of PCBs in the deepest soil layer, probably due to vertical transfer and a lack of volatilization. Taking all these facts into consideration, future pilot studies will determine the levels of PCB retention in soil layers mixed with specific ratios of substances for PCB retention as well as the retention of PCB in the runoff water. Based on these investigations, a pool will be constructed in for the deposit of the contaminated soil and the more significantly contaminated parts of the asphalt cover of the Zadar Electrical Transformer Station. In this manner, a combination of the phytoremediation of the surface soil layer and the retention of PCB in the lower layers with its degradation by aerobic and anaerobic processes would prevent the penetration of PCBs into the water ecosystem of this karstic terrain.

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Conclusions

The main goal of the APOPSBAL project was to investigate the extent of POPs contamination in the countries of the former Yugoslavia due to warfare as well as to foster the development and collaboration of the local laboratories engaged in the trace analysis of POPs.

In the first intercalibration test performed in the fall of 2002, four out of six laboratories provided reasonable results for the PCB standard solution and the soil sample. A very important task of the more experienced laboratories taking part in the APOPSBAL project has been the training of young scientists from laboratories with less experience in POP analysis in environment samples. Additional attention and financial support should be given to the development of the regional laboratories. While some of the partners demonstrated the ability to produce high quality results, some were not able to perform trace analysis, even with the help of the Project and other partners. To ensure the continuation of the independent research projects and the establishment of some kind of monitoring networks, improvement in the local laboratories is needed.

Dispersion of the PCB levels in the soil samples around the damaged condenser in E:T:S: Zadar has shown a significant decrease in the PCB levels only a few meters from the pollution hot-spot. It was also found that the asphalt base protected the soil below from more serious PCB penetration into the soil.

Generally, in the Jazine area in Zadar, Croatia, higher PCB levels have been observed in the deeper layer of sediment (2–5 cm) than in the surface layer (0–2 cm), which indicates the depositing and several years of the accumulation of pollutants in the Jazine sediment.

There is the suspicion that higher levels of PCBs in the sediment samples in Rijeka Dubrovačka near Sustjepan are due to the deposit of waste material from the damaged substation in Komolac on the coast near Sustjepan.

In several soil samples in the war-afflicted area of western Slavonia in Croatia, exceptionally high levels of total PCBs have been determined. It will be necessary in the future to investigate the levels of PCBs in this area more intensively, especially in the aquatic ecosystem (rivers, lakes and fish ponds) for a realistic estimation of the input of these very dangerous pollutants into the anthropogeologic system.

In most of the soil samples from Bosnia and Herzegovina, the PCB concentrations found were less than 10 000 ngg⁻¹ d.w. Exceptionally high total PCB levels have been observed in soil samples from the Tuzla area (96 178

000 ngg⁻¹ d.w.) and Tešanj (178 954 000 ngg⁻¹ d.w.). The PCB levels at several sampling sites in Banja Luka were as high as 400 000 ngg⁻¹ d.w.

High levels of PCBs were also found in the painting hall of the Zastava auto factory in Kragujevac, and extremely high levels in one sample from the petrochemical plant in Pančevo, Serbia and Montenegro. These sites should be the center of attention for the following studies together with all other hot spots in Croatia, Bosnia and Herzegovina, and Serbia and Montenegro.

The city of Zadar is mainly situated on very permeable karstic limestone. The expected results from the hydrogeological study performed were to provide necessary information about the geometric, structural and hydrogeological relations of the investigated area, mainly about preferential flow paths and outflow locations into the sea, land use and hazard points, all what can identify possible PCB pathways into the groundwater and finally into the sea. In the area of the city, 28 types of hazards were identified: 13 polygonal, 12 point and 3 line sources of hazard. A specific vulnerability map was prepared for PCB groups of contaminants that are already present at several marine and inland locations of the area studied. For vulnerability and risk modeling with the models, procedures included overlaying obtained polygonal layers or raster calculation of obtained grids with cell values. For the purpose of this project, 10 GIS maps were completed.

High volume and additional passive air sampling were successfully performed above the project frames. Samples were analyzed and results evaluated, on the basis of which several sites were selected as targets for more detailed study, continuous monitoring or remediation. New hot spots not initially included in the project were determined and further monitoring activities suggested estimating the extent of the damage. Additional funding to support these activities is recommended. The applicability of passive air sampling for air quality monitoring as a cheap, versatile and effective alternative to conventional high volume sampling was confirmed. In this study, we also attempted to determine the genotoxic effects of the cumulative air samples collected at sampling sites in Zadar, Sarajevo and Tuzla. While none of the Zadar samples induced any significant response, both in and out of the test, increased response was detected in air samples from Bosnia and Herzegovina by the test with metabolic activation. The pollutants with genotoxic activity were mainly bound to particulate matter.

It was shown that in a mixture with laurel poppies, Ascarel and Pyralene showed no prooxidative properties and did not stimulate the production of OH radicals. The results confirm that an increase of the pyralene oil concentration leads to a decrease in lipid peroxidation intensity to control values (or even lower), which could be explained by their negative synergism with radicals produced during the lipid peroxidation of liposomes.

A mathematical model for human dietary exposure to POPs, based on the calculation of human exposure factors (HEF) to POPs via various members of the terrestrial food chain, where the total human exposure depends on exposure factors and the POP concentration in the atmosphere and soil, was developed and applied. On the basis of the concentrations of POPs in the foodstuffs, atmosphere and soil in Novi Sad and its surroundings, it was calculated that an adult in Novi Sad of average weight (70 kg) consumes 0.79 µg PCB (1.1% ADI) daily.

The estimated distribution of the daily PCB intake by fishermen's families from the Zadar area in the case of consuming sea breams, which have the same mean PCB level as fish collected in 2004 from the Zadar coastal area, shows that in more than 10 cases the daily PCB intake is higher than the ADI. On the basis of the PCB levels in fish sampled from markets in Zadar (2003), Rijeka (2004), Pula (2003) and Poreč (2003), the daily intake of PCBs by the "critical" group of people from these areas was estimated. In only several cases the "critical" group consuming fish from the Rijeka market would consume more PCBs than the acceptable value.

Microcosmos biodegradation experiments with artificially contaminated soil confirmed significant PCB transformation activity by pure Z6 culture in the presence of selected natural compounds (carvone, xylose and soya lecithin). Based on the results of laboratory biodegradation experiments, laboratory model field experiments were established and the results of an experiment during a 3-month bioaugmentation treatment showed a gradual decrease in PCB mass fractions in the soil.

Natural soil contaminated with PCBs, excavated from an area around a damaged capacitor of the Zadar Electrical Transformer Station, was used in a small scale field experiment. This study examined the effects of various plant species and natural attenuation on the dissipation of PCBs in the soil. No statistically significant difference in the impact from the tested types of plant cover on the success of the bioremediation of the relatively thin layer of contaminated soil was observed. After 12 months of experiments (including twelve periods of rainfall events), negligible quantities of Aroclor 1248 (an average of 0.024%) and Σ7 key (an average of 0.032%) were leached from the soils. Taking all these facts into consideration, future pilot studies will determine the

levels of PCB retention in soil layers mixed with specific ratios of substances for PCB retention as well as the retention of PCB in runoff water. Based on these investigations, a pool will be constructed for the deposit of the contaminated soil and the more significantly contaminated parts of the asphalt cover of the Zadar Electrical Transformer Station. In this manner, a combination of the phytoremediation of the surface soil layer and PCB retention in the lower layers with degradation by aerobic and anaerobic processes could prevent the penetration of PCBs into the water ecosystem of this karstic terrain.

The APOPSBAL project was highly successful in meeting both its goals - gaining new information as well as promoting scientific cooperation and improving the level of environmental analysis. The data will be a useful contribution not only to this project but also to ongoing national POP inventories as part of the implementation of the Stockholm convention.