PASSIVE AIR SAMPLING MONITORING OF POPs IN SOUTHEASTERN EUROPE AT HIGH MOUNTAIN STATION BEO - MOUSSALA, BULGARIA

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ABSTRACT

The aim of this study was to investigate the behaviour trends of the harmful to human health persistent organic pollutants in the Rila Mountains' atmosphere. Passive air monitoring was carried out at Basic Ecological Observatory - Moussala, Bulgaria, during the period of three years. PAHs - naphthalene (1482.99 ng sample^{-1}), biphenyl (533.14 ng sample^{-1}), phenantrene (384.10 ng sample^{-1}) and fluorene (293.04 ng sample^{-1}) have highest concentrations, followed by organochlorine pesticides (DDTs, HCHs) and PCBs. A mathematical model of the data set was made using an artificial neural network. Clear positive correlation in PCB 118, PCB 138, PCB 180 and o,p'-DDT, d-HCH, PER, p,p'-DDT, p,p'-DDD as well as HCB behavior was observed. The variation in atmospheric load with POPs during identical time periods of two consecutive years could be attributed to significant differences in advection during the both selected time intervals.

Keywords: POPs, passive air sampling, ambient air, pollutants long-range transport, SOM.

INTRODUCTION

Persistent organic pollutants (POPs) are among the most dangerous anthropogenic pollutants, because they remain in the atmosphere for a long period of time and become toxic under certain conditions. Because of their accumulation in living organism's tissue they reach the humans through the food chain and cause the development of various diseases, striking the nervous and immune system. They are introduced into the environment as insecticides, fungicides and pesticides as well as products of the incomplete combustion.

There is a group of 12 POPs in three categories, so called "a dirty dozen", consisted of pesticides (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene), industrial chemicals (polychlorinated biphenyls (PCBs)) and by-products (polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF)). These substances are extremely toxic and therefore they are under the strict control of the Stockholm Convention on POPs [1, 2]. According to Lohmann, POPs can be classified into several groups - flyers, multi- and single hoppers, as well as swimmers [3]. The atmospheric transport is the main dispersion mechanism for most of the POPs and it is related to their physicochemical properties. This distribution is based on the fundamental chemicals transport behaviour globally in accordance with their specific properties [4 - 6]. For the first time, in 1974, was mentioned that fallen into the atmosphere POPs can migrate as gases and aerosols and when reach to the areas with lower temperatures they condense. Wania and Mackay suggested that the POPs are accumulated in different geographic areas as a result of their atmospheric transport to the North and South Pole [7]. They have proven that the most of POPs are volatile under normal temperature conditions and evaporate with subsequent precipitation. The low temperatures in the high mountain regions favour their deposition from the atmosphere on the soil and water surface. The high temperatures contribute the evaporation process from the earth's surface in tropical and subtropical areas [8]. The pollutants can migrate in air from areas with tropical climate to lower-temperature areas such as the Arctic high mountain ecosystems. With temperature decreasing, the POPs condense, fall down on the earth surface and thus they are captured. This is so-called cold trapping or grasshopper-effect [9 - 12]. Depending on the chemicals properties and environmental conditions (seasonal temperature, wind speed and direction), the chemicals may evaporate and condense one or more times [6, 8, 13]. This results in a pronounced POPs spreading cycle into the air, water and soil. With temperature decreasing or increasing altitude the organic pollutants are accumulated into the environment (global distillation). This is due to the particles (raindrops, snowflakes) transition into the gas phase as well as the temperature changes associated with the geographical location. The global distillation explains the presence of PCBs, DDTs and other organochlorine pesticides in Polar Regions of Earth where have no local sources of these kind of pollutants.

Passive monitoring network, created in 2004 in the Czech Republic [14, 15], was extended in 2006 to the rest of Central and Eastern Europe for POPs in ambient air Global Monitoring Plan purposes. A regional database was created to collect representative information on each POPs polluted area. The collected data serves to increase the competence related to the POPs spatial and temporal variability in the region of Central and Eastern Europe, as well as to harmonize the collection and interpretation techniques [16]. The European monitoring network includes 37 high-mountain observatories and one of them is the Basic Environmental Observatory (BEO) - Moussala.

BEO - Moussala is located in the Rila National Park on the highest peak of the mountain and the Balkan Peninsula. Moussala peak is the sixth highest in Europe. The observatory is located on the way of the air flows coming from Central Europe and Mediterranean basin. The area has typical alpine climate characterized by low atmospheric pressure and temperature with insignificant temperature amplitude, high relative humidity, intensive solar radiation and frequent mountain-valley winds. Rila Mountain is located on the border between the continental and the transitional Mediterranean climates. There the winds have western and southwestern direction. About 80 % of annual rainfalls are of snow. The negative temperatures are kept for about 9 months. The snow cover is kept for about 200 - 220 days per year. A steady temperature increase is observed in the middle and the end of July. Over 2000 m above the sea level, the snow cover is the thickest during March (70-80 cm). In the highest zones, the maximum thickness of the snow cover reaches 200-240 cm. Winds with speed of 30 - 40 $m\ s^{-1}$ (over 100 $km\ h^{-1}$) and with predominantly southwestern and western orientation, are not exceptions. The northwest and northeast winds are more moderate. The average monthly wind speed on the highest Rila mountain peaks reaches 11 - 12 $m\ s^{-1}$. Thus the results obtained from long-time environmental monitoring are representative for a large region, where the BEO - Moussala is the only environmental observatory at this height. Located in the protected area, the station is favoured by minor anthropogenic influence and pollution sources with primarily cross-border origin [17].

The aim of this study was to complete the pattern of the long-range atmospheric transport on the basis of the newest PCBs, polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (dichlorodiphenyltrichloroethane and metabolites (DDXs), and hexachlorocyclohexanes (HCHs)) concentrations in the free troposphere (FT) and to determine the time period during which these substances remain active.

EXPERIMENTAL

Sampling campaign

A passive sampling method, suitable for validating of the data obtained from the active methods, was used for the purpose of this study [18, 19]. The sampling was performed using a passive air sampler with polyurethane foam (PUF) disks. PUF disks (diameter 150 mm, thickness 15 mm, density 0.030 g cm^{-3}), from Breclav, Czech Republic, were pre-cleaned using acetone and dichloromethane. After cleaning, the PUF disks were dried and placed into the sampler.

After the sampling was completed, the filters were wrapped in two layers of aluminium foil, labeled (date, place and number of samples) and transported in a refrigerated box to the laboratory, where they were stored in a polyethylene packs at - 18°C. The sampling frequency, which is established by empirical measurements, varies between 3 - 5 m^3 per day. This is approximately 100 - 200 m^3 for a 28-day sampling cycle (March 2009 - February 2013).

Sample analysis

The samples were analyzed for PCBs, PAHs, DDXs, HCHs in Research Centre for Toxic Compounds in the Environment - RECETOX, Brno, Czech Republic.

Data analysis

The monitoring data were analyzed using Kohonen's Self-Organizing Map (SOM) [20 - 24]. These maps classify the incoming data by similarity and allow clusters formation where values with many similar characteristics are concentrated. On the basis of such structured results, conclusions for patterns of POPs behaviour can be drawn.

RESULTS AND DISCUSSION

The POPs concentrations in ambient air were measured at altitudes of 2925 m (BEO - Moussala). As a result of ambient air monitoring, data for following persistent organic pollutants were collected: PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180); PAHs (Pentachlorobenzene (PECB), Hexachlorobenzene (HCB), Anthracene (ANT), Benzo(a)anthracene (BAA), Benzo(b)fluoranthene (BBFLA), Benzo(k)fluoranthene (BKFLA), Benzo(a)pyrene (BAP), Indeno(123cd)pyrene (IP), Dibenz(ah)anthracene (DBAHA), Benzo(ghi)perylene (BGP), Benzo(b)fluorene (BBFLU), Benzo-naphto-thiophene (BNT), Benzo(ghi)fluoranthene (BGFLA), Cyclopenta(cd)pyrene (CPCDP), Triphenylene (TPH), Benzo(j)fluoranthene (BJFLA), Benzo(e)pyrene (BEP), Perylene (PER), Dibenz(ac)anthracene (DBACA), Anthanthrene (ANTT), Coronene (COR), Naphthalene (NAP), Acenaphtylene (ACY), Acenaphtene (ACE), Fluorene (FLU), Phenantrene (PHE), Fluoranthene (FLA), Pyrene (PYR), Chrysene (CHRY), Biphenyl (BIPH), Retene (RET)); HCHs (a-HCH, b-HCH, g-HCH, d-HCH), Dichlorodiphenyltrichloroethane (o,p'-DDT, p,p'-DDT) and its metabolites (dichlorodiphenyldichloroethane (o,p'-DDD, p,p'-DDD,) and dichlorodiphenyldichloroethylene (o,p'-DDE, p,p'-DDE)). For the concentrations determination of each pollutants group, their medians were calculated, as well as the minimum and maximum values.

The lowest concentrations measured for the PCBs, PAHs and HCHs groups are in the range of 0.02 to 83.74 ng $sample^{-1}$, and the highest concentrations measured in the same groups are in the range of 0.42 to 1482.99 ng $sample^{-1}$.

The PCBs concentrations vary from 0.02 to 3.85 ng $sample^{-1}$ (Fig. 1). Virtually all of PCBs have similar concentrations, as the lowest values for PCB 180, PCB 153 and the PCB 138 were observed, and the highest - for PCB 28. The maximum concentrations for this pollutants class were recorded during 2011 (July and September). It

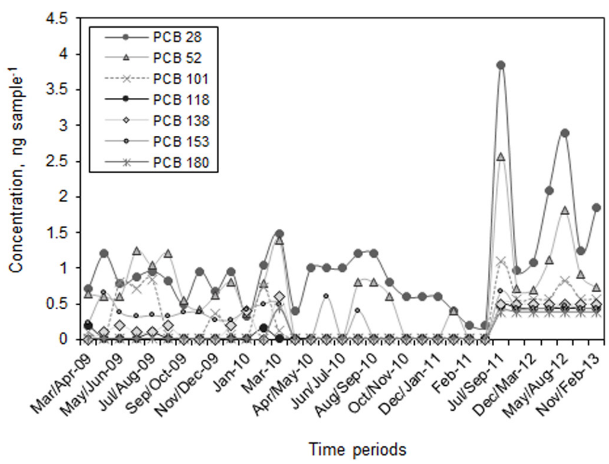

Fig. 1. PCBs concentration comparison.

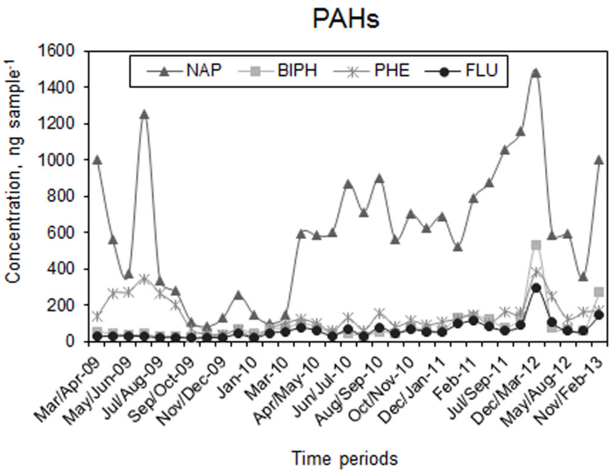

Fig. 2. PAHs concentration comparison.

was observed tendency of sharp concentrations decreasing during the winter.

The highest concentrations of PAHs - naphthalene (1482.99 ng sample^{-1}), biphenyl (533.14 ng sample^{-1}), phenantrene (384.10 ng sample^{-1}) and fluorene (293.04 ng sample^{-1}) were recorded during the winter of 2012. During the summer of 2009, naphthalene, biphenyl and fluorene have lower concentrations - 336.7, 26.58 and 24.16 ng sample^{-1}, respectively (Fig. 2). The lowest summer concentration of phenantrene was measured in 2010. The concentrations of the other 27 compounds included in this group are significantly lower and vary between 0.05 - 94 ng sample^{-1}.

The highest concentration in organochlorine pesticides group belongs to a-HCH (8.6 ng sample^{-1}), followed by p,p'-DDE (7.07 ng sample^{-1}), Fig. 3. The lowest concentration in this group of pollutants is 0.02 ng sample^{-1}.

Figs. 4 and 5 show the concentrations for every group. From December to June concentrations increase and then from July to November they gradually decrease.

PAHs concentrations are several times higher than those of the other POPs. The lowest concentrations of these pollutants were measured in the samples taken during October-November 2009, while the highest concentrations were measured in the samples taken during December-March 2012 (Fig. 5).

A tendency of concentrations increasing was observed during 2011 - 2012. The measured concentrations of POPs in the ambient air of the high mountain could be explained by the natural phenomena existing in the region of BEO - Moussala. As it is located in Rila National Park, the influence of the anthropogenic factor is minimized. At the foot of the mountain is situated the first skiing resort in Bulgaria - Borovets. Possible more serious air pollution can come from the snow-ploughs. Near by the resort is Samokov town. The main source for pollution is domestic wood and coal burning. There is also a wood factory. So, there are many hotels and restaurants, but their influence on the environmental pollution with POPs is negligible.

The monitoring data includes 48 POPs tracked over a 33-month period, i.e. the size of a dataset is 48x33. This dataset was processed by the self-organizing maps method using SOM TOOLBOX 2.0 in MATLAB computing environment. The data are structured and normalized and the self-organizing map is initialized and trained. The individual nodes are data vectors of the 48 POPs. The results are visualized using a U-matrix

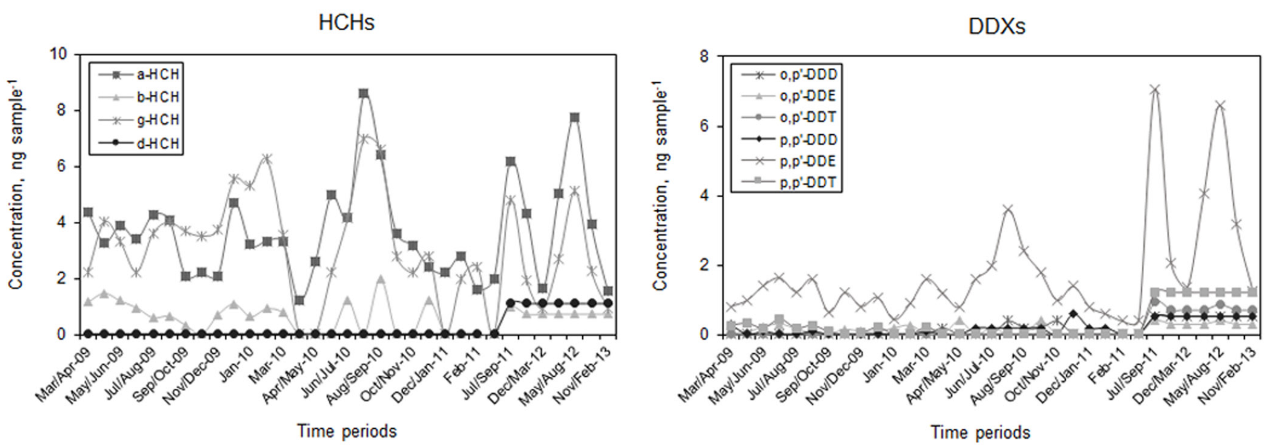

Fig. 3. Organochlorine pesticides concentration comparison.

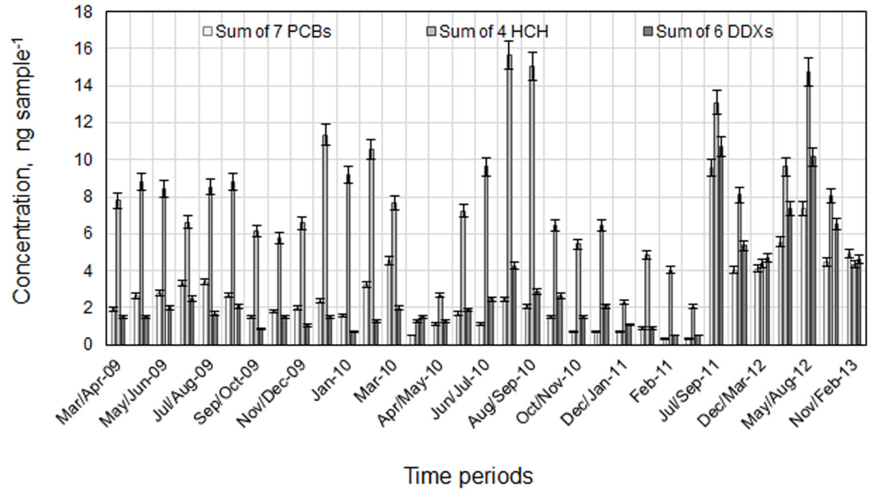

Fig. 4. Seasonal variations of PCBs, HCHs and DDXs concentrations in ambient air (BEO -Moussala, 2009 - 2013).

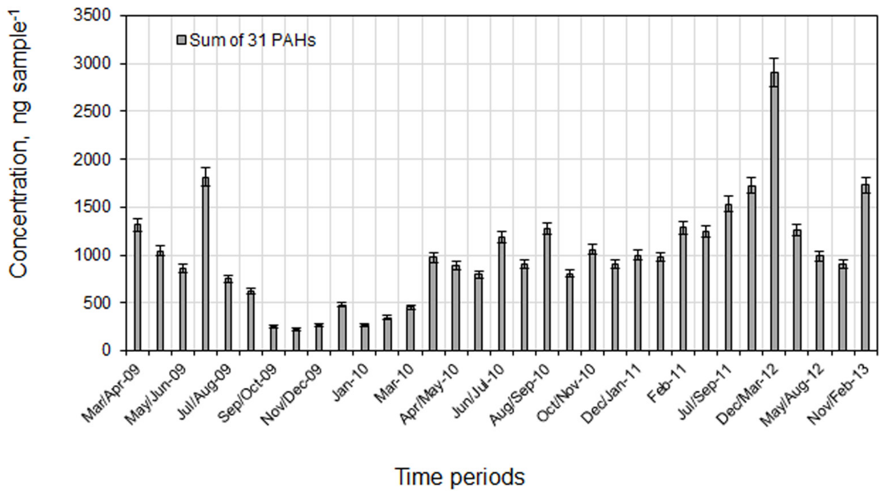

Fig. 5. Seasonal variations of PAHs concentrations in ambient air (BEO - Moussala, 2009 - 2013).

representing the distances between the nodes in the self-organizing map and the vector levels, which are showing the value of each variable in every node of the map. The U-matrix and the plots for all variables are presented in Fig. 6. Using the scale, easily can be seen the distribution of variables on the SOM and the distance between the nodes in U-matrix.

The months in the period of 2009-2011 are arranged in the upper part of the U-matrix, while the months of 2011-2013 are arranged in the lower one. The PCBs have similar behavior, but some differences only for PCB 118, PCB 138 and PCB 180 are observed. Positive behavior correlation of PCB 118, PCB 138, PCB 180 and o,p'-DDT, d-HCH, PER, p,p'-DDT, p,p'-DDD as well as HCB is clearly marked.

The individual variables (POPs) are presented according to their similarity in the self-organizing map for better illustration (Fig. 7).

Nine groups were clearly formed, and indeno(123cd) pyrene and phenantrene have a specific distribution (Outliers). The first group was consisted of PECB, ANT, the second one was consisted of BIPH, FLU and the third one - of NAP, ACE. A negative correlation between PeCB and ANT was observed in the first cluster.

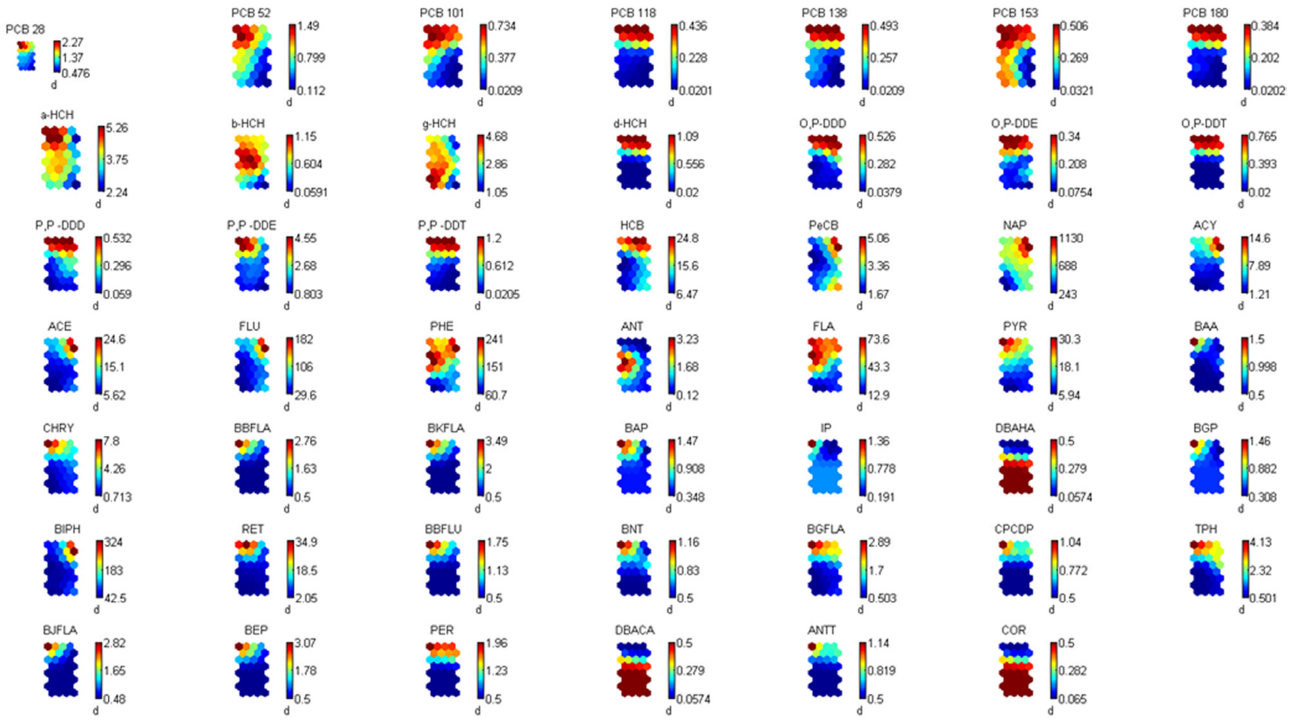

Fig. 6. Visualization of parameters distribution and distance between nodes in the POPs U-matrix.

The fourth group was consisted of five subgroups. The first one includes ACY and HCB and the second one - p,p’-DDD, o,p’-DDD, PCB 101, PCB 138. It should be noted that this fourth group also contains a negative correlated subgroup - DBAHA DBACA, COR. The fourth subgroup was consisted of p,p’-DDT, PCB 118, d-HCH, PCB 180, o,p’-DDE, o,p’-DDT, and the latter - of PER, TPH, BGFLA. The fifth group includes CPCDP, CHRY, ANTT, the sixth - BBFLA, BEP, BKFLA, RE, BBFLU and the seventh - p,p’-DDE, PCB 28, PYR. Grouping of BGP, BAA, BAP, BJFLA, BNT was observed in the eight group and PCB 153, PCB 52 as well as FLA formed the last ninth group.

Fig. 8 illustrates the periods grouping and already trained self-organizing map with the periods in the corresponding neurons (hits diagram). The hits diagram has dimensionality of 4x8 and contains all the 33 periods. This diagram shows the formation of two main periods. A grouping of the spring-summer period of 2011 and 2012 in the upper left side, and the autumn-winter period of 2012 and 2013 in the upper right side of the chart was observed. High concentrations of the POPs from first to third group (PECB, ANT, BIPH, FLU, NAP and ACE) were observed there. All periods from 2009 to early 2011 were grouped on the opposite side of the chart. There were included the POPs from forth to ninth group (ACY и HCB, p,p’-DDD, o,p’-DDD, PCB 101, PCB 138, negative correlated subgroup of DBAHA, DBACA, COR, as well as p,p’-DDT, PCB 118, d-HCH, PCB 180, o,p’-DDE, o,p’-DDT, PER, TPH, BGFLA, CPCDP, CHRY, ANTT, BBFLA, BEP, BKFLA, RE, BBFLU, p,p’-DDE, PCB 28, PYR; BGP, BAA, BAP, BJFLA, BNT, PCB 52, FLA). From the results obtained it can be concluded that the POPs grouped for the first period of time have high concentrations at the beginning of the campaign, while for the pollutants in the second period, there is a tendency of their concentrations increasing towards the end of the campaign.

On the basis of both criteria - POPs types and sampling periods, the clustering was implemented. As a result there is not clear POPs types grouping. The lack of similarities between the compounds implies that their clustering has occurred on a time basis, i.e. difference should be sought between the particular periods. The most clearly defined and clearly distinguishable clusters are intentionally selected, because apart from being in

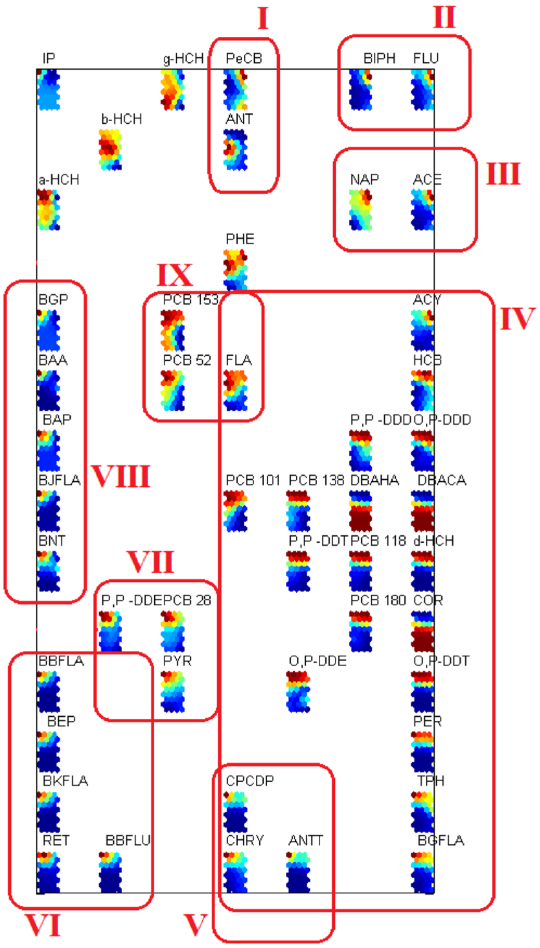

Fig. 7. Visualization of POPs clustering by similarity.

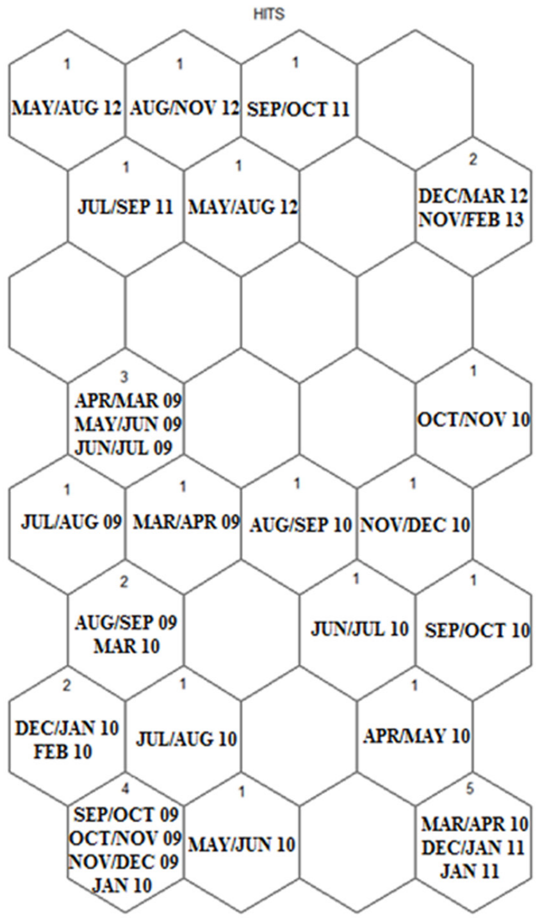

Fig. 8. Hit diagram of time periods.

the diametrically opposed sides of the chart, they have a similarity in the period that they outline. The probable reason for differences in ambient air load with POPs in identical periods of time in two consecutive years could be attributed to the significant advection difference during the two selected periods.

CONCLUSIONS

In the present study, a comparative analysis of POPs contamination trends of high-mountain ecosystems, which are one of the most sensitive "living organisms" on the Earth, has been made. It shows that the POPs concentrations in the ambient air of BEO - Moussala follow a certain pattern of behavior. From the analysis of the monitoring data from 2009 to 2013 it can be concluded that, under equally other conditions, the probable cause of the differences in the POPs atmospheric load in identical periods of two consecutive years can be attributed to the significant advection difference during the two selected periods.

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