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Article

Sensitivity of a Remote Alpine System to the Stockholm and LRTAP Regulations in POP Emissions

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Abstact: Persistent Organic Pollutants (POPs) have been restricted and prohibited at national level for several decades now and since the 21st century at international level under the Stockholm Convention and the Convention of Long-Range Transboundary Air Pollution (LRTAP). A high mountain lake sediment core was sampled in the Alps (Gossenköllesee) in summer 2010 and analyzed on POPs to examine whether the expected decreasing trends due to the implementation of the international Conventions could be observed. Higher POPs concentrations were observed in the sections corresponding to the period of large scale production and usage. *p,p'*-DDE and *p,p'*-DDD showed maximum concentrations in the core sections corresponding to the 1970s. These concentrations decreased to more or less constant levels in the top sediments, which is in agreement with the timing of past usage and banning of this pesticide. On the other hand, PCBs and HCB peaked in 1980s and the concentrations fluctuated afterwards. These observed profiles suggest that the studied site is still under influence of primary or secondary emissions and that the regulations of the international Conventions have still not been noticed in this site.

Keywords: POPs; high mountain sediment; effectiveness international conventions

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1. Introduction

Persistent organic pollutants (POPs), among them organochlorine compounds such as hexachlorobenzene (HCB), polychlorobiphenyls (PCBs) and 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDT), are xenobiotic organic chemicals that were introduced to the environment during the second half of the 20th century as pesticides, e.g., DDT, industrial products, e.g., PCBs, or miscellaneous sources, e.g., HCB [1–3]. Due to their persistence and toxicity, large scale production and usage of these compounds was restricted and banned in the 1970s and 1980s in many countries. Further on, in the beginning of the 21st century, controls on the production, use and emissions of POPs were introduced at international level through the Stockholm Convention within the framework of the UN Environmental Programme (UNEP) and the Convention of Long-Range Transboundary Air Pollution (LRTAP) of the programme of the UN Economic Commission for Europe (UNECE).

Unfortunately, POPs were already distributed globally [4–6] being ubiquitous pollutants in the environment. After emission, part of these compounds were atmospherically transported over long distances, giving rise to a widespread occurrence that also encompassed remote zones, such as the Polar or Alpine ecosystems [7–10]. In fact, the low ambient temperatures in these regions favored POP partitioning to vegetation, soils and surface waters by "cold-trapping" [11–13], which resulted in accumulation in biota [14]. The recent production and emission inventories show a decrease of POPs emissions into the atmosphere [1,2,15,16], which should result in decreasing atmospheric concentrations and environmental levels. Atmospheric data from the Arctic showed that some POPs, such as *p,p'*-DDT, have decreased, but others, such as HCB, have even shown slight concentration increases in the most recent years [17]. In the European continent, PCBs are still present in relatively high concentrations near the urban areas in central and North-Western Europe in comparison to remote sites, while HCB seems to be evenly distributed in the European atmosphere [18]. A study of the temporal trends of atmospheric POPs in United Kingdom and Norway between 1994 and 2008 [19] showed that PCB levels were declining with an average half-life rate of 8 years.

The European Alpine lakes may serve as sensitive environmental indicators to monitor the speed and direction of the environmental quality changes that occur in the continent [20]. These areas receive POPs from long-range atmospheric transport. After deposition or adsorption in the lake surface, part of these POPs are incorporated to the underlying sediments [21,22]. Accordingly, the sediment layers reflect the temporal changes in POP inputs because of the strong chemical stability of these compounds. These lakes are oligotrophic and situated above the regional tree-line [23,24]. Thus, their lower number of water column processes and inputs simplifies the relationship between atmospheric inputs and sediment records.

Previous studies have shown the increase of POPs in European alpine lakes around the second half of the 20th century and peak concentrations around 1970s and 1980s [23]. Nevertheless, only recently have decreases in PCB and DDT concentrations been observed [25], e.g., in two sediment cores from the Alps collected in 2009. Interestingly, in this later study, the lake that was fed by glacier melt water showed an increase in POP concentrations in the most recent years, which was interpreted as an influx of secondary POPs stored in the glacier in earlier years. In general, these data reflect the influence of primary and secondary sources, such as re-volatilization of POPs from soils as well as long-range atmospheric transport [19,26].

In order to gain more insight in POPs concentration trends in remote sites of the European continent, a sediment core was collected in the Alps (Gossenköllesee) 2417 m above sea level (m asl; 47°13′46″N, 11°00′51″E) in summer 2010 and analyzed for 7 PCBs, HCB, *p,p'*-DDTs (incl. *p,p'*-DDE and *p,p'*-DDD).

2. Experimental Section

2.1. Materials and Methods

Residue analysis n-hexane, dichloromethane, isooctane and acetone were from Merck (Darmstadt, Germany). Concentrated sulfuric acid (95%), anhydrous sodium sulfate pro analysis and powder copper (size < 63 mm) were also from Merck (Darmstadt, Germany). Glass wool was from Panreac (Castellar del Vallés, Spain). Sodium sulfate and glass wool were cleaned by Soxhlet extraction with hexane:dicloromethane (4:1, v/v) during 24 h before use. Copper was activated by sonication with 25% hydrochlorid acid (3x3 ml) and then rinsed several times with Milli-Q water to neutral pH and, subsequently, with acetone for water removal. This powder was stored in n-hexane in darkness prior to use.

In the present study, seven PCB congeners (#28, 52, 101, 118, 153, 138, 180) were investigated. In addition, the following organochlorine compounds have been analyzed: *p,p'*-DDT, 1,1–dichloro–2,2-bis(4-chlorophenyl)ethane (*p,p'*-DDD), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (*p,p'*-DDE), and hexachlorobenzene (HCB).

Standards of these compounds were from Dr.Ehrenstorfer (Augsburg,Germany). Standard mixtures were prepared in isooctane for instrumental calibration. Surrogate solutions of PCB congeners #30 and #209 were prepared for recovery calculation.

2.2. Sampling at Gossenköllesee

Gossenköllesee is a remote Alpine lake located at 2417 m asl in the Stubaier Alps, Austria. The lake area is 1.7 ha, with a maximum depth of 9.9 m. The catchment of about 30 ha mainly consists of moraines and crystalline boulders, and only 10% is covered with soils and heather type vegetation. The lake has been studied since the 1950s but has been the subject of detailed scientific research in the 1990s within the framework of several scientific projects. The information from the palaeolimnological studies [24] was used here to estimate the sedimentation rates and age of the sediment samples. Gossenköllesee was sampled at its deepest point in June 2010, using an UWITEC corer (a modified Kajak corer, 8.6 cm diameter, 60 cm long tube). The sediment core was immediately divided in sections of 0.25 cm in the first three centimeters and then in sections of 0.5 cm in the rest of the core. The fitted regression curve between the sediment depth and the sediment core dating was extrapolated to the actual sampling date in 2010 controlled by a cross-comparison of trends in organic matter. Given the uncertainties that result from this procedure, age estimates are only used to indicate rough temporal trends. Table 1 shows the age estimates including the error ranges for each layer. The sub-samples were stored in pre-cleaned aluminum foil at 0 °C during transport to the laboratory and at −20 °C until chemical analysis.

2.3. POPs Analyses

Samples were freeze-dried, homogenized and weighed before analyses. The dry weight of each sample was approximately 0.3 g. The sediments were extracted by sonication with a mixture of hexane and dichloromethane (4:1 (v/v), 3 × 15 ml). All sediments were spiked before extraction with the surrogate standards PCB#30 and PCB#209. Subsequently, the extract was concentrated to 1 mL by rotary evaporation and was purified three times with sulfuric acid. Active copper powder was added and left overnight for removal of sulfur containing compounds. This cooper powder was removed by filtration through sodium sulfate and rinsed with n-hexane. The elution was concentrated under a gently stream of nitrogen gas to almost dryness and redissolved in 100 µL internal standard solution (PCB#142) in isooctane.

Quantitative instrumental analysis of the extract was performed by GC-ECD (Agilent 7890A GC-uECD) using an HP-5 MS column (60 m length, 0.25 mm i.d., 0.25 µm film thickness) coated with 5% diphenyl-polydimethylsiloxane. The oven temperature program started at 90 °C (holding time 2 min) and then it was increased to 130 °C at 15 °C/min, and finally to 290 °C at 4 °C/min (holding time 20 min). Injector and detector temperatures were 250 °C and 320 °C, respectively. Injection volume was 2 µL Helium was used as carrier gas with a constant pressure of 30.46 psi.

2.4. Total Organic Carbon (TOC) Analysis

Sediment samples were extracted with HCL 3N to remove inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH and dried at 60 °C. The determination of TOC was performed by flash combustion at 1025 °C followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. The limit of detection was 0.1%.

2.5. Quality Control

External standards of all identified compounds were injected into the GC-ECD instrument at several concentrations ranging between 0.5 ppb and 25 ppb in order to obtain a calibration curve in the adequate concentration range for the samples. Recoveries for the analytical procedure based on surrogate data were 72 ± 8% for PCB30 and 87 ± 9% for PCB209. Procedural blanks were performed within each set of ten samples. Limit of detection (LOD) was established by mean of the blank value plus three times the standard deviation, while the limit of quantification (LOQ) was calculated by the mean blank value multiplied by three. The LOD values ranged between 5 and 30 pg, while the LOQ ranged between 7 and 61 pg.

3. Results and Discussion

The first 20 sub-samples were analyzed for POPs, since it was estimated that this part of the core would cover the period corresponding to the 19th, 20th and 21st century [24]. The seven PCB, HCB and *p,p'*-DDTs were detected in all samples. However, only the first 16 samples (4.5 cm depth) showed sediment concentrations above LOQ. In the case of *p,p'*-DDT and PCB#28, this was only the case in four samples. Therefore, *p,p'*-DDT and PCB#28 were not considered for further discussion.

The other PCB congeners and HCB had concentrations above the LOQ between sample#1 and #13. In the discussion of the results only data that showed values above the LOQ is used.

Figure 1. Concentrations (ng/g dw) of (**a**) hexachlorobenzene (HCB) (triangles); ∑polychlorobiphenyls (PCBs) (sum of #52, #101, #118, #153, #138, #180; black squares) and ∑DDTs (*p,p'*-DDE+*p,p'*-DDD; grey dots) in the sediment samples (#1 = top sediment).

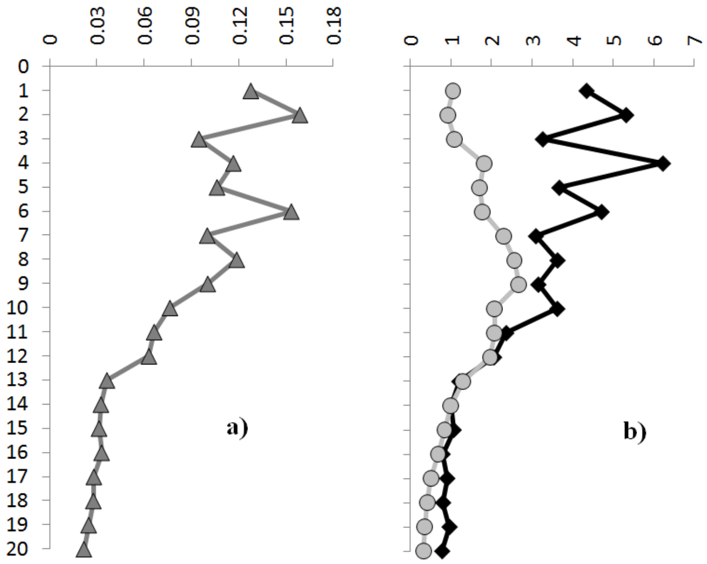


Table 1. Estimated dating, Total Organic Carbon (TOC) % values and Persistent Organic Pollutants (POP) concentrations (ng/g dw) for the sediment core collected in Gossenköllesee.

#	Est.dating	Age Error (± yrs)	TOC %	HCB	∑PCB	∑DDT
1	2006	15	8.78	0.13	4.3	1.0
2	2003	15	8.33	0.16	5.3	0.92
3	1999	9	8.52	0.09	3.3	1.1
4	1996	10	7.96	0.12	6.2	1.8
5	1992	8	8.90	0.11	3.7	1.7
6	1989	7	7.92	0.15	4.7	1.8
7	1985	9	7.93	0.10	3.1	2.3
8	1981	10	7.99	0.12	3.6	2.6
9	1977	13	8.02	0.10	3.1	2.7
10	1973	15	8.11	0.08	3.6	2.1
11	1968	16	8.25	0.07	2.3	2.1
12	1964	17	7.97	0.06	2.1	2.0
13	1959	19	7.98	0.04	1.2	1.3
14	1950	24	7.31	0.03	1.0	0.99
15	1940	24	7.26	0.03	1.1	0.84
16	1929	19	7.34	0.03	0.79	0.68
17	1918	13	7.51	0.03	0.91	0.50
18	1907	14	7.31	0.03	0.80	0.41
19	1895	21	7.36	0.02	0.96	0.36
20	1882	21	7.62	0.02	0.78	0.32

Figure 1a,b shows the concentrations of the POPs in the different samples. The lowest concentrations, below LOQ, were observed in the samples deeper than four centimeters depth, corresponding to the estimated dating before 1930s (Table 1). Therefore, any increase in the POPs concentration in the first 4.5 centimeters corresponds to the period after 1930s, although there are some uncertainties due to the lack of appropriate dating of the sampled core. Nevertheless, the concentration profiles of the POPs are consistent with the onset of the production and usage of these POPs in the European continent, since this started after the 1930s [1–3].

3.1. DDTs

The concentrations of ∑DDTs increase after sample #16 (>1930s) and increase steeply after sample #13 (>1950s) to reach a peak concentration of 2.7 ng/g dw in sample #9 (1970s). After that the concentrations decrease to levels around 1 ng/g dw in the most recent samples. The ∑DDTs consisted of *p,p'*-DDE (73 ± 5% of ∑DDT) and *p,p'*-DDD. There was a significant correlation between *p,p'*-DDE and *p,p'*-DDD ($r=0.92$; $p<0.01$; Table 2), suggesting the formation of these products within the lake or lake catchment from *p,p'*-DDT degradation. Nevertheless, there was a very constant ($r^2=0.95$; $p<0.01$) increase of the *p,p'*-DDD to the ∑DDTs contributions (Figure 2), corresponding to 1% per sample (or 0.25% per year) between sample #1 and #16 (post-1930s). This may indicate further formation of *p,p'*-DDD in the sediment. Nevertheless, this compound may also be produced from an increasing influx of *p,p'*-DDE from the catchment, where it could have been formed under aerobic conditions from *p,p'*-DDT in the soils. However, this later possibility is less probable due to the overall constant ($r^2=0.90$; $p<0.01$) decrease of *p,p'*-DDE concentrations in the first nine samples (post-1970s), which showed a calculated half-life of about 20 years in this lake since the peak concentration in the 1970s from the exponential fit of the concentrations and the core dating.

$$p,p'\text{-DDE}_i = p,p'\text{-DDE}_0\ e^{-\lambda ti} \tag{1}$$

where λ (0.034; Figure 3) is used to calculate the half-life ($t_{1/2}$) from

$$t_{1/2} = \ln 2/\lambda \tag{2}$$

Figure 2. Contribution (%) of *p,p'*-DDD to the ∑DDTs (*p,p'*-DDE + *p,p'*-DDD) in the sediment samples (#1 = top sediment). The linear regression was applied in the first 16 samples that had levels above limit of quantification (LOQ).

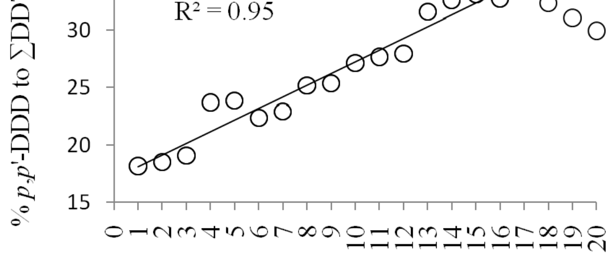
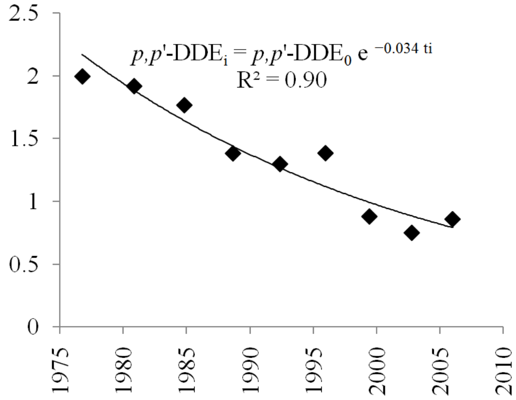
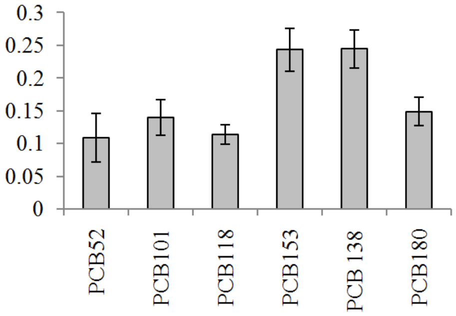


Figure 3. Decrease of *p,p'*-DDE concentrations (ng/g dw) as a relation to "time". The decrease rate, $\lambda = -0.034$.



The sediment profile for ∑DDT observed in Gossenköllesee is very similar to the one observed in Lake Engstlen in the Swiss Alps [25] over the same time period. The results indicate that the DDT concentrations have decreased after the 1970s in this part of the European continent as consequence of the restriction measures on the use of *p,p'*-DDT as pesticide, but that the rate of decrease is slowing down. This is further illustrated by the similar ∑DDT concentration in the most recent sediment samples. It is therefore possible that ∑DDT has reached certain equilibrium after a fast decrease due to prohibition of usage of this pesticide, but that recent levels are possibly influenced by secondary diffuse emission sources. This would be in agreement with observations in other areas, such as European background sites [19], where a fast decline of concentrations (half-lives between 3 and 8 years) was followed by a much slower decline (half-lives of 15 to 30 years).

Figure 4. Relative average composition of PCB congeners to ∑PCBs in the sample#1 to #13.



3.2. HCB and PCBs

HCB started to increase in the sediments after sample#13 (post 1950s) until sample#8 (1980s), and then the sediment concentration fluctuated. A similar profile was observed for PCBs, however, ∑PCBs reached this "fluctuation period" already in sample#10 (1970s). The relative compositions of the six quantified PCB congeners in the sediment samples were constant (Figure 4) indicating no significant changes in PCB mixture after burial into the sediment. The major compounds were PCB#153, #138, and #180, corresponding to the PCBs that are less-volatile and more hydrophobic, these have a tendency to partition to particles, and accumulate in sediments [20,22].

All PCB congeners showed remarkable correlations with HCB (Table 2), which is in contrast to *p,p'*-DDE and *p,p*'-DDD. This observation suggests that PCBs and HCB experienced similar environmental transport and fate after emission to the atmosphere and burial in the lake sediments. These compounds have long residence times in the environment due to their chemical stability against degradation. Therefore, the temporal concentration profiles in the sediment core may reflect the atmospheric emissions on the European continent. In contrast to *p,p'*-DDE and *p,p'*-DDD, which decrease after peak concentrations in the 1970s, there is no temporal trend for HCB and PCBs other than the fluctuations of sediment concentrations after approximately the 1970s. At least, no decrease can be observed for HCB and PCBs in the sediment core in the upper, more recent, sediment layers. This is in contrast to the temporal profile observed in the sediment core collected in the Swiss Alps [25], where a decrease of PCB concentrations was observed. This decrease was similar to the one observed for ∑DDTs. In the case of Gossenköllesee, PCBs and DDTs do not correlate and the absence of a decreasing trend of PCB and HCB concentrations could indicate that atmospheric inputs of these compounds into this lake have not decreased over the past decades.

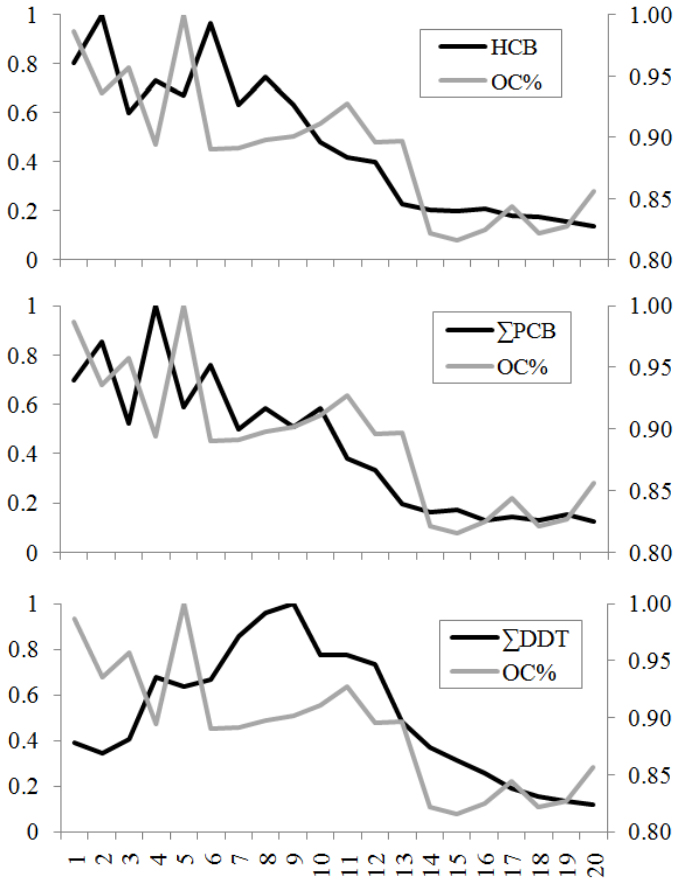
Table 2. Correlations (r; Pearson) between the analyzed POPs. Correlations with significance $p < 0.05$ are indicated with grey background, those with $p < 0.01$ are indicated in **bold**.

	***p,p'*-DDE**	***p,p'*-DDD**	**HCB**	**PCB #52**	**PCB #101**	**PCB #118**	**BCB #138**	**PCB #153**	**PCB #180**	**∑PCB**
p,p'-DDE		**0.92**								
p,p'-DDD	**0.92**									
HCB	−0.09	−0.41								
PCB#52	−0.31	−0.46	0.62							
PCB#101	−0.26	−0.43	**0.71**	**0.98**						
PCB#118	−0.13	−0.36	**0.83**	**0.88**	**0.94**					
BCB#138	−0.07	−0.37	**0.90**	**0.67**	**0.77**	**0.88**				
PCB#153	0.04	−0.29	**0.93**	**0.67**	**0.75**	**0.87**	**0.95**			
PCB#180	0.15	−0.14	**0.77**	**0.77**	**0.81**	**0.85**	**0.87**	**0.91**		
∑PCB	−0.12	−0.38	**0.86**	**0.89**	**0.94**	**0.97**	**0.92**	**0.92**	**0.93**	
∑DDT	**0.99**	**0.96**	−0.19	−0.35	−0.31	−0.20	−0.16	−0.05	0.07	−0.20

Changes in the sedimentation rates could also explain some of these observations. Over the past decades the lake has experienced an increase of ambient air temperatures, with the direct consequence that the ice-cover period has shortened. This, on its term, increased the biological activity in the lake, with an increase of phytoplankton growth [24] and higher capacity for absorption and transport of hydrophobic materials to the underlying sediments. These biological pump effects may enhance the burial of POPs in the sediments, which should be more significant for the higher molecular weight (HMW) POPs [21,27], such as PCB#153, 138 and 180.

An increase of organic material in the top sediment core sections was also observed in Gossenköllesee. The organic carbon contribution to the total sediment weight (OC%) increased in the second part of the sediment core, more or less in the same period as organic pollutants increased in the sediment, *i.e.*, after the 1940s (Figure 5). Nevertheless, there was no correlation between OC and the individual POP concentrations, including the HMW PCBs. As mentioned above, all PCB and HCB concentrations were highly correlated, but not those of *p,p'*-DDD and *p,p'*-DDE (Table 2) which also changed independently of the OC fluctuations. In addition, the fluctuations of OC between consecutive samples was much smaller (factor 0.1 ± 0.04) than those observed for HCB (factor 0.3 ± 0.2) or ∑PCB (0.4 ± 0.3). These results suggest that the *in-situ* events that had an influence on the changes in the sedimentary OC in the lake were not determining the temporal POP concentration changes.

Figure 5. Relative contributions OC%, HCB, ∑PCBs, and ∑DDT (OC% and POP concentrations divided by maximum OC% or concentrations in the sediment samples).



The fact that HCB and PCB concentrations in the lake sediments did not decrease over the past decades, but DDT concentration did, suggests a separate environmental fate of these two groups. Emission inventories indicate a decreasing trend of the emissions of all these POPs [15,16]. Nevertheless, PCBs and HCB were used in industrial applications and/or unintentionally emitted to the environment as by-products in industrial processes, which increases the uncertainty of HCB and PCB inventories and may underestimate their real emissions [28]. On the other hand, *p,p'*-DDT was used as pesticide, which makes the control on its production and application probably more effective once it was decided to restrict its use. Therefore, secondary diffuse emissions of HCB and PCBs may be important enough to maintain the atmospheric input to the studied remote Alpine lake. These emissions are probably temperature controlled, as several studies showed higher atmospheric PCB concentrations at higher ambient air temperatures, both in European background sites [29] and remote high mountain sites [10]. Nevertheless, it is beyond the scope of the present study to relate temperature changes in the region and in the present European continent to variations in HCB and PCB concentrations due to the uncertainty in the age estimates of the sediment layers. In contrast, the PCB concentrations in other remote alpine sites have shown decreasing concentrations. Further monitoring of the POPs concentrations in these remote areas is needed for a global assessment of the changes in the distributions of these compounds over the European continent as a whole and, specifically, in these pristine regions.

4. Conclusions

The temporal profiles of DDT in the high mountain sediment core collected in Lake Gossenköllesee showed an effective decrease after the 1970s, coinciding with the first control measures on production and usage of this pesticide. In the upper layers, corresponding to the recent decade, the concentrations were lower but more constant. On the other hand, HCB and PCBs showed no indication of concentration decreases, indicating that the regulation and banning of PCBs and HCB are not yet noticed in Gossenköllesee. Revolatilization of these compounds from secondary sources, e.g., soils, may explain this continued input to these lake sediments.

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Author Contributions

The work presented here was carried out in collaboration between all authors. Paul Pechan defined the research theme. Barend L. van Drooge, Karin Konig and Roland Psenner performed the sampling and sub-sectioning of the sediment core at Gossekӧllensee. Barend L. van Drooge and Joan Grimalt designed the analytical method and experiment. Guillem Garriga carried out the experiments. Barend L. van Drooge and Joan Grimalt analyzed the data, interpreted the results and wrote the paper. Karin Koinig and Roland Psenner provided data and approved the final paper. All authors have contributed to, seen and approved the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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