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Ambient Air Levels of Organochlorine Pesticides at Three High Alpine Monitoring Stations: Trends and Dependencies on Geographical Origin

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ABSTRACT

Many persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs), which are emitted into air, occur ubiquitously in different environmental compartments worldwide. OCPs are measurable in conspicuous concentrations in the air not only near emission regions but also in background areas, as in the Alps. In the present study, we analyzed OCPs in air samples between 2005 and 2013 at three high Alpine stations (Weißfluhjoch, Switzerland: 2663 m a.s.l.; Sonnblick, Austria: 3106 m a.s.l.; and Schneefernerhaus, Germany: 2650 m a.s.l.). The air concentrations of OCPs at these stations were lower than those in source regions but higher than those in the Arctic region. Concentration differences between sites were found to be relatively small. To distinguish the influences from different European source regions, four filters of low-volume active air samplers were operated alternately according to a trajectory prediction method. Air masses from the northeast (i.e., Bavaria and Eastern Central Europe) and the south (i.e., Mediterranean countries) were characterized by higher concentrations of OCPs (e.g., pentachlorobenzene and hexachlorobenzene) compared with those arriving from the Atlantic Ocean. Additionally, we evaluated the temporal trend of the single compounds; only a few compounds such as endosulfan exhibited a clear decreasing trend.

Keywords: Organochlorine pesticides (OCPs); Active air sampling; Alps; Trajectories; Atmospheric transport; Trend.

INTRODUCTION

Since the late 1990s, scientists have investigated on the role of high mountains in the global transport of persistent organic pollutants (POPs) and the fate of such compounds in the mountainous ecosystems of the Rocky Mountains (Blais *et al.*, 1998; Daly and Wania, 2005), Sierra Nevadas (LeNoir *et al.*, 1999), European Alps (Weiss *et al.*, 1998; Vighi, 2006), Pyrenees (Grimalt *et al.*, 2001), and Himalayas (Wang *et al.*, 2006). The interregional Monitoring Network in the Alpine Region for POPs (MONARPOP), which started in 2003, investigated the fate of chemicals partly belonging to the “dirty dozen” in different environmental compartments of Alpine ecosystems in several regions of Austria (Tyrol, Salzburg, Lower Austria), Italy (Lombardy and Veneto), Slovenia, Switzerland, and Germany (Bavaria). Belis *et al.* (2009) stated that the POP masses stored in forests (spruce needles, soil) within the Alps are higher than the corresponding emissions in the Alpine region, indicating that the Alps are a sink for POPs. An analysis of pesticides measured in different altitudinal profiles between the valley floor and the tree line revealed that the amount of many

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substances enriched in the upper organic soil horizon increased with the altitude mainly as a result of increasing precipitation (deposition) and decreasing temperature (degradation) (Kirchner *et al.*, 2009). Altitudinal distributions of POPs have been monitored in various mountains by several researchers (Estellano, 2008; Meire *et al.*, 2012). According to studies conducted at sites ranging from remote areas such as mountain regions (Fernandez *et al.*, 2002; Choi *et al.*, 2009), polar regions (Kallenborn *et al.*, 2012; Kallenborn *et al.*, 2013), and national parks (Dvorská *et al.*, 2012; Kim *et al.*, 2012) to more polluted rural and urban areas (Mandalakis *et al.*, 2002), the approximate concentration range of POPs is known for a larger part of the world.

The aim of this study is to quantify the concentrations of organochlorine pesticides in the air of three high Alpine summits and their dependency from air masses belonging to four different source regions. As the measurements have been continued after the MONARPOP project and now encompass a time period of quite 10 years, the data set is appropriate for detailed evaluations, such as trend analysis and comparison between summer and winter periods.

METHODS

Sampling Sites and Meteorological Conditions

Sets of high- and low-volume air samplers were installed at three summit stations: the Environmental Research Station Schneefernerhaus (UFS; altitude: 2650 m a.s.l.; latitude: 47.42°N; longitude: 10.98°E) in Bavaria, 300 m below Zugspitze summit, the highest mountain in Germany; the High Sonnblick/Zittelhaus station (SON; altitude: 3106 m a.s.l.; latitude: 47.05°N; longitude: 12.96°E) in Austria; and the Weißfluhjoch station (WEI; altitude: 2663 m a.s.l.; latitude: 46.83°N; longitude: 9.81°) in Switzerland. Zugspitze belongs to the Wetterstein Mountains in the Northern Limestone Alps and is a border mountain between Austria and Germany; the distance between Zugspitze and the northernmost mountain range of the Bavarian Alps is approximately 20 km. The Rauris Sonnblick is a peak of the Austrian Central Alps and is situated 70 km from the Austrian Alpine foothills and 80 km from the southernmost mountain range of the Venetian Alps (Italy). WEI is located in the Western Alps, approximately 60 km from the northern edge (Swiss Plateau) and 110 km from the southernmost mountain range of the Lombardian Prealps. The horizontal distances between WEI, UFS, and SON to the nearest urban areas as sources of POPs (Davos: 11,000 inhabitants, 1560 m a.s.l.; Garmisch-Partenkirchen: 27,000 inhabitants, 700 m a.s.l.; Rauris: 3,000 inhabitants, 1000 m a.s.l.) are approximately 4, 10, and 20 km, respectively.

UFS and SON are particularly suitable locations for monitoring atmospheric POP concentrations because they belong to the Global Atmospheric Watch (GAW) program, in which all meteorological parameters and numerous greenhouse gases are continuously measured (Kaiser *et al.*, 2007; Offenthaler *et al.*, 2009). At WEI, the Swiss Federal Institute for Forest, Snow and Landscape Research WSL measures meteorological data.

Mean monthly temperatures vary between –11.4 and 2.2°C (Climate normals: 1961–1990) with an annual mean of –4.8°C on Zugspitze (2962 m a.s.l.); at UFS, mean monthly temperatures are approximately 2°C higher. At SON, monthly temperatures range from –12.8 to 1.8°C (annual mean: –5.7°C). Monthly mean temperatures vary between –9.2 and 4.9°C at WEI, with an annual mean of –2.5°C. At all three summit stations, the annual mean temperature increased by approximately 0.5°C during 1981–2010 from 1961–1990 (Kirchner *et al.*, 2012). Annual mean precipitation amounts (2001–2010) are 2,003, 2,671, and 1,397 mm at UFS, SON, and WEI, respectively. Kirchner *et al.* (2012) and Jakobi *et al.* (2015) have provided a detailed description of the meteorological conditions at these stations.

Sample Collection

As part of MONARPOP (2005–2007), the air sampling of organochlorine pesticides (OCPs) was initiated at the three stations by using temperature-controlled low-volume samplers (LVSs; DIGITEL, Hegnau, Switzerland). Because the concentrations at the three stations were relatively low, gas phase and particle-bound POPs were not distinguished. The LVSs with a flow rate of 30 L min^{-1} were equipped with a carousel for switching between several filter cartridges. An Ethernet interface and an extended control unit were installed to forward and process control- and status-information (Offenthaler *et al.*, 2009). Because the atmospheric concentrations were low, active air samplers had to operate for 3 months to collect detectable amounts for each cartridge (according to VDI-DIN-2464-04). Although the aim was to perform the filter changes at all three sampling sites within 2 weeks, adverse weather conditions made this not always possible. Construction at the three stations, hardware failures, power outages, and computer program faults reduced the number of measurement hours by 15% on average.

Air sampling was designed to distinguish three source regions, northwest (NW), northeast-east (NE), and southwest-south-southeast (S) (Fig. 1), and a fourth region of nominally unspecified origin (UD) for air masses that remained fewer than 3 days over any of the three source regions (Offenthaler *et al.*, 2009). For UFS and WEIS, the first three regions correspond to Rhine-Main region, Ruhr region, Northern France, Belgium and Netherlands (NW), Munich area, Czech Republic, Eastern Germany, Poland and Northern Austria (NE) and the Mediterranean region (S); for SON, Munich area belongs to source region NW. The selection of the four sampling filters was controlled by daily trajectory forecasts calculated using the FLEXPART model developed by NILU (Stohl *et al.*, 2005) and applied by the Austrian Central Institute for Meteorology and Geodynamics (Kaiser, 2009). The total number of filters (cartridges) exposed at the three mountain sites was 312 (26 periods, 4 source regions) and 78 field blanks. The mean volume of air sampled (related to each of the 4 source regions) was in the range of 394–890 m^3, 301–809 m^3, 300–992 m^3 for SON, UFS, and WEI, respectively.

Substances, Chemical Analysis and Statistics

In this study, OCP concentrations were measured to evaluate the amount of the following substances, resulting

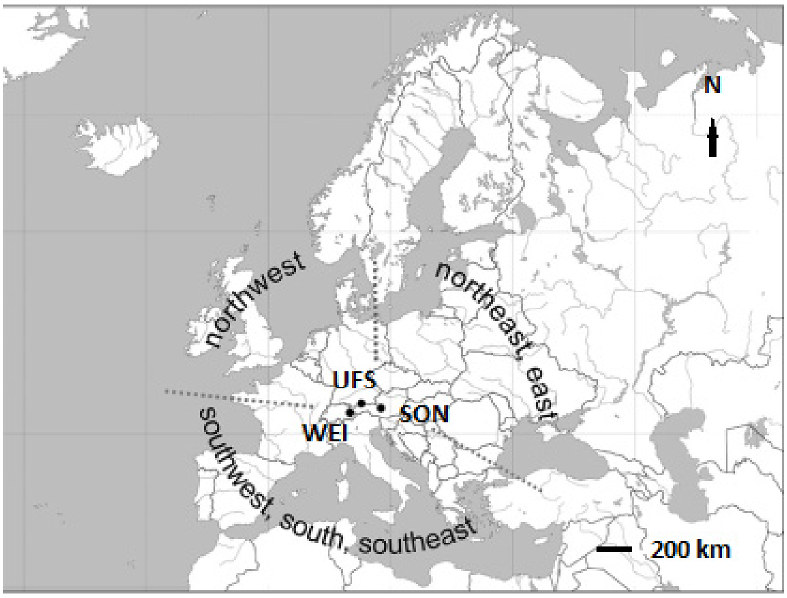

Fig. 1. Geographical selectivity (source regions) of active air sampling: UFS = Schneefernerhaus/Zugspitze (D), WEI = Weißfluhjoch (CH), SON = Sonnblick (A).

from the use of insecticides: hexachlorocyclohexanes (HCHs); dichlorodiphenyltrichloroethanes (DDTs) and their major metabolites and breakdown products (dichlorodiphenyldichloroethane: DDD; dichlorodiphenyl-dichloroethylene: DDE); chlordane; heptachlor; aldrin and its major metabolite, dieldrin; mirex; and the rodenticide and insecticide, endrin. Additionally, the atmospheric concentrations of endosulfan (I and II), an acaricide and insecticide; the metabolic product pentachloroanisole (PCA; from pentachlorophenol), which was used as a fungicide and wood preservative (Su *et al.*, 2008); the former fungicide and current incineration by-product of power plants and waste incinerators, hexachlorobenzene (HCB) were analyzed, as well as the by-products pentachlorobenzene and octachlorostyrene (OCS). Although most of these pesticides are no longer used worldwide, OCPs can be re-emitted from soils and vegetation into the atmosphere. Because of its threats to human health and the environment, a global ban on the manufacture and use of endosulfan was negotiated under the Stockholm Convention on persistent organic pollutants in April 2011. However, endosulfan continues to be widely used, particularly in India, the world's largest user and producer of this insecticide (Pathak *et al.*, 2008); however, India has agreed to phase out the use of endosulfan by 2017. In 2009, the production and agricultural use of γ-HCH (lindane) was banned under the Stockholm Convention; it is still used only in some developing countries. Some OCPs are of great concern because they possess carcinogenic and mutagenic properties. POPs can be found in gaseous phase and adsorbed to aerosols.

Detailed information about the chemical analysis, the quality assurance and the quality control are given in the supplementary material. Type and working conditions of the GC-HRMS (gas chromatography coupled with high-resolution mass spectrometry) analyzing system can be found in Table S1. Due to the relatively cold temperatures at the three sites, stability of the trials is high.

Standard statistical methods were applied for data presentation (mean, range, and median). Pearson's correlation and a t test were used for trend analyses of compounds; $p = 0.05$ and $p = 0.001$ denoted statistical significance (Anderson and Finn, 1996).

RESULTS AND DISCUSSION

Air Flow Regime Frequency

In this study, 23 respectively 26 measuring periods were attributed to the warmer and cooler half of the year ("summer" and "winter") based on calendar date. Measurement periods, data availability (in % of the measurement period), and the frequency of the four air flow regimes (related to the four source regions) are given for the three sites in the supplementary material (Table S2). Device or station problems during December 2005–March 2006 and August 2008–February 2009 at WEI and during October 2007–November 2008 at UFS reduced the number of available measurement hours. Measurement periods in which data availability was low were excluded, yielding mean data availabilities of 82%, 86%, and 90% for UFS, SON, and WEI, respectively; the threshold of data availability was arbitrarily set as 40%.

UFS, SON, and WEI were mainly influenced by the S source region (yearly mean: 35%, 33%, and 32%, respectively) and the NW source region (yearly mean: 27%, 30%, and 32%, respectively), whereas relatively few air masses originated from the NE source region, particularly at WEI (yearly mean: 12%, 15%, and 11%, respectively) (Kaiser, 2009). The frequencies of air masses originating from the UD source region at UFS, SON, and WEI were 25%, 22%, and 25%, respectively. The probability that the predicted source region corresponds with the actual source region is high, but seems to decrease from the NE and NW to the S. The forecast achieves a high predictability in high pressure weather systems with NE transport direction. Predictability may be lower in low pressure situations, with prefrontal southwesterly winds and foehn events (Kaiser, 2009; Richner and Hächler, 2013). Low pressure systems are frequently characterized by fast-changing weather conditions (changing wind direction and precipitation).

During the 8 years of continual concentration measurements, the frequency of air masses originating from the various source regions was mostly unchanged, except that of air masses from the NW source region affecting SON, for which a negative trend ($p < 0.05$) was observed. In addition, at WEI, the air masses from the UD source region increased ($p < 0.05$). Regarding the long-term development of the general weather pattern during 1950–2008, SW air masses significantly increased ($p < 0.05$) and NE air masses decreased in the Northern Alps (Zugspitze, UFS) (Kirchner *et al.*, 2012).

Mean Concentrations and Seasonality, Comparison to Worldwide Concentration Levels

Table 1 shows the averaged data of several OCPs monitored at the three Alpine stations; the concentrations are continuously normalized to 0°C and 1013 hPa by the LVSs according to the Avogadro equation (Ackerman and Knox, 2006). The overall concentrations of singular periods were calculated by the product of air mass concentrations and the relative duration of occurrence of air masses from each source region. Using these results, we then calculated the median concentrations of each substance and sampling period. Because the length (3–4 months) of sampling periods could not be used to derive annual means, results from the total period (December 2005–April 2013) were averaged, yielding a multiannual median and indicating the range during the entire period (2005–2013). Additionally, the summer-to-winter ratios were calculated according to the medians of concentrations.

DDT: The multiannual medians of *p,p'*-DDT were 0.441, 1.65, and 0.942 pg m^{-3} at SON, WEI, and UFS, respectively. The concentrations at UFS ($p < 0.05$) and WEI ($p < 0.001$) were significantly higher than those at SON; no significant differences were found between UFS and WEI. Thus the Western Alpine site (WEI) may be stronger influenced by emissions from Po basin. The corresponding medians of *o,p'*-DDT and *p,p'*-DDE ranged from 0.494 to 0.753 pg m^{-3} and from 1.20 to 1.64 pg m^{-3}, respectively. The sum of DDXs was 2.33, 3.86, and 3.63 pg m^{-3} at SON, WEI, and UFS, respectively. The concentrations during the sampling periods exhibited a seasonal distribution with higher levels mostly in the warmer season. However, the differences between the warmer and cooler half of the year were significant ($p < 0.05$) only for *p,p'*-DDT and *o,p'*-DDT at WEI and UFS. There was also a positive significant correlation found between *o,p'*-DDT concentrations and air temperature for all three sites. The *p,p'*-DDT/*p,p'*-DDE ratios were 0.349, 1.35 and 0.612 at SON, WEI, and UFS, indicating that residues monitored at WEI appeared to be from a younger source. Earlier air measurements of *p,p'*-DDT in the Lombardian Alps revealed means of 2.1 (Alpe Pianalunga, 1600 m a.s.l.), 0.9 (Punta Indren, 3300 m a.s.l.) and 5.5 pg m^{-3} (Colle del Lys, 4250 m a.s.l.) (Finizio et al., 2006). Similar to that measured at UFS, the *p,p'*-DDE concentrations measured in the Central Pyrenees, Spain, varied from 0.9 to 12 pg m^{-3} (Van Drooge *et al.*, 2004). Compared with values measured in the Arctic areas, the values monitored at the three Alpine sites were higher by a factor of 3–5 (Hung *et al.*, 2010). Compared with values measured on the Tibetan Plateau, which is affected by monsoon-transporting air masses from India, the values obtained in this study were lower by a factor of 2–10 (Sheng *et al.*, 2013). In comparison to the presented alpine sites, the mean air concentrations of *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDE at Mount Everest were 3.7, 5.1, and 5.1 pg m^{-3}, respectively (Li *et al.*, 2006). The measurements of *p,p'*-DDT and *p,p'*-DDE obtained along the Pacific coast of East Asia varied widely from undetectable levels to 112 and 42.8 pg m^{-3} (Ding *et al.*, 2009). In southern China, the means of *p,p'*-DDT and *p,p'*-DDE concentrations reached 130 and 300 pg m^{-3} during the summer months (Wang *et al.*, 2007). Unlike in the present study, *p,p'*-DDT and *o,p'*-DDT were undetectable in the Arctic atmosphere of Greenland (Bossi *et al.*, 2008). There only DDT-related transformation products (*p,p'*-DDE: 0.41 pg m^{-3}; *o,p'*-DDE: 0.56 pg m^{-3}) could be found.

α-HCH and γ-HCH: The multiannual medians of α-HCH concentrations from all three alpine stations were similar, ranging from 6.29 pg m^{-3} (UFS) to 8.75 pg m^{-3} (WEI); differences were not significant, suggesting that α-HCH has no regional source and the levels are indicative of the background concentration in the central European alpine area. At WEI, γ-HCH concentrations (multiannual median: 6.26 pg m^{-3}) were lower than those monitored at UFS (multiannual median: 9.56 pg m^{-3}). The observed extremely high value at SON (212 pg m^{-3}) may have been caused by past local wood preservation measures. A chemical analysis of wood samples from the Alpine hut, Zittelhaus, could confirm this hypothesis (Jakobi *et al.*, 2015). Hence, the γ-HCH values measured at SON do not reflect the Alpine background situation. The difference between summer and winter concentrations was significant ($p < 0.05$) at UFS. Despite the long sampling intervals (3 months), temperature can explain a major fraction of the variability in the air concentrations of both γ-HCH and α-HCH. Both substances show a significant correlation with air temperature at all three sites; Wania *et al.* (1998) found similar results for sites in Canada. The relatively uniform α-HCH concentrations were consistent with the fact that technical HCH was withdrawn from use in 1991 (Li and Macdonald, 2005; Bossi *et al.*, 2008). These values were lower by a factor of 2 than those monitored 10 years before in other European mountains, such as the Central Pyrenees and High Tatras (Van Drooge *et al.*, 2004). Air samples from Antarctica were characterized by an α-HCH concentration range of 0.02–0.46 pg m^{-3} (Kallenborn *et al.*, 2013). In southwest Greenland, concentrations (vapor and particle phase) of α-HCH and γ-HCH were in the ranges 10.3–66.3 and 1.9–11.4 pg m^{-3}, respectively (Bossi *et al.*, 2008). On the Tibetan Plateau, the mean concentration of α-HCH during 2008–2011 was 12.1 pg m^{-3}, with higher concentrations in spring and autumn and a lower

Table 1. OCP concentrations measured using LVS at the three summit stations: Medians of the entire sampling period, range (minimum–maximum), and summer/winter ratio were calculated according to medians (* 0.05 level of significance).

Compound	SON			WEI			UFS		
	Range pg m^{-3}	Median pg m^{-3}	Summer to winter ratio (medians) *$p < 0.05$	Range pg m^{-3}	Median pg m^{-3}	Summer to winter ratio (medians) *$p < 0.05$	Range pg m^{-3}	Median pg m^{-3}	Summer to winter ratio (medians) *$p < 0.05$
p,p'-DDT	0.171–1.32	0.441	1.29	0.240–3.72	1.65	2.78*	0.240–8.36	0.942	3.06*
o,p'-DDT	0.139–1.29	0.494	1.80*	0.132–2.28	0.749	2.67*	0.073–4.98	0.753	2.27*
p,p'-DDD	0.028–0.295	0.046	1.00	0.012–0.661	0.067	1.54	0.030–0.766	0.046	1.67
o,p'-DDD	0.013–0.157	0.021	0.990	0.014–0.339	0.040	1.33	0.012–0.832	0.034	2.00
p,p'-DDE	0.715–5.56	1.20	1.05	0.222–3.58	1.22	1.23	0.546–10.1	1.64	1.79
o,p'-DDE	0.074–0.416	0.119	1.07	0.046–0.284	0.113	1.09	0.053–0.798	0.217	1.31
α-HCH	3.65–29.2	7.42	2.26*	2.38–21.3	8.75	2.18*	2.56–21.0	6.29	2.16*
β-HCH	0.047–0.383	0.130	2.86*	0.034–0.896	0.154	1.90	0.048–0.354	0.148	2.12*
γ-HCH	37.9–837	212	2.47*	1.15–28.3	6.26	2.08*	2.69–33.0	9.56	2.37*
δ-HCH	0.043–6.05	0.065	1.97	0.038–0.581	0.055	1.00	0.034–0.347	0.971	1.70
ε-HCH	0.044–0.201	0.060	1.41	0.027–2.10	0.060	1.01	0.036–0.227	0.060	1.41
pentachlorob.	17.8–79.6	35.2	0.961	14.3–92.9	36.3	1.12	21.1–126	36.5	1.04
hexachlorob.	54.7–204	96.0	1.20	33.4–190	85.5	1.43*	38.7–114	75.9	1.47*
pentachloroan.	4.53–31.0	8.35	1.86	2.42–22.5	6.93	1.64*	3.05–17.7	5.86	2.19*
octachlorost.	0.391–1.54	0.850	1.33	0.274–1.68	0.716	1.60*	0.080–1.01	0.685	1.61*
trans-chlord.	0.189–0.636	0.329	0.75	0.145–3.60	0.491	1.42	0.064–0.905	0.301	1.02
cis-chlordane	0.237–2.15	0.803	1.30	0.280–4.93	0.757	1.89*	0.275–1.77	0.665	1.66*
oxy-chlordane	0.220–1.48	0.502	1.80*	0.144–1.35	0.49	1.92*	0.116–1.04	0.421	2.09*
heptachlor	0.015–0.102	0.036	0.747	0.010–0.437	0.042	1.17	0.011–0.072	0.035	1.04
cis-hept.epox.	0.658–4.41	1.25	1.87	0.364–4.46	1.41	1.93*	0.234–3.15	1.22	2.09*
adrin	0.015–0.024	0.018	1.00	0.012–0.118	0.018	1.00	0.011–0.165	0.018	1.90
dieldrin	0.898–5.44	1.56	1.57	0.523–5.38	1.92	1.78*	0.241–4.18	1.51	2.00*
endrin	0.007–0.353	0.055	1.19	0.017–0.362	0.047	0.924	0.022–0.311	0.059	0.940
endosulfan I	3.10–89.0	13.6	1.26	2.24–90.8	13.7	1.18	2.67–79.9	10.5	1.10
endosulfan II	0.093–7.57	0.460	3.85*	0.061–7.00	0.620	2.05*	0.091–5.58	0.430	1.22
methoxychlor	0.058–0.194	0.094	1.00	0.058–0.086	0.096	1.00	0.057–0.346	0.096	0.715
mirex	0.040–0.345	0.092	1.56	0.032–1.05	0.097	1.64	0.045–0.207	0.092	1.23

concentration in summer (monsoon season) (Sheng *et al.*, 2013). During a short monitoring study in wetlands in India (summer 2006), Zhang *et al.* (2008) noted that atmospheric mean concentrations of α-, β-, γ-and δ-HCH were 25, 17, 61 and 3 pg m^{-3}, respectively.

Pentachlorobenzene: The concentrations were relatively homogenous across the Alps with multiannual medians of approximately 36 pg m^{-3} and no differences between summer and winter (ranges of 17.8–79.6, 14.3–92.9, and 21.1–126 pg m^{-3} at SON, WEI, and UFS, respectively). The uniform distribution of pentachlorobenzene is consistent with a compound having a long atmospheric lifetime (Bailey *et al.*, 2009). In the Lys Valley, Italian Alps, Jaward *et al.* (2005) recorded a mean concentration of 20 pg m^{-3}. Concentrations similar to those measured in the Alps have been monitored in other European mountains, such as the Central Pyrenees and High Tatras (34 and 38 pg m^{-3}, respectively) (Van Drooge *et al.*, 2004). A significantly lower mean concentration (approximately 5 pg m^{-3}) was measured in the Arctic (Hung *et al.*, 2010), whereas in wetlands in India, concentrations exceeding 100 pg m^{-3} are frequent (Zhang *et al.*, 2008).

Hexachlorobenzene: HCB was the most abundant OCP at the three sites, with medians of 92.5 pg m^{-3} (SON), 85.5 pg m^{-3}, (WEI) and 75.9 pg m^{-3} (UFS). Differences in HCB between sites were not statistically significant. Summer/winter ratios were the highest at UFS and WEI; there was a positive correlation between concentrations and air temperature. In the center of Zurich, Switzerland, Schmid *et al.* (2014) observed relatively low concentrations (45–67 pg m^{-3}). In the Lys Valley, Italian Alps, a mean concentration of 35 pg m^{-3} was monitored (Jaward *et al.*, 2005). In the Mount Everest region, Li *et al.* (2006) measured mean concentrations of 4.8–12.6 pg m^{-3} at an altitude of 4976 m a.s.l.

Pentachloroanisole: PCA levels were the highest at SON (4.53–31.0 pg m^{-3}) and lowest at UFS (3.05–17.7 pg m^{-3}); median concentrations were 8.35, 6.93 and 5.86 pg m^{-3} at SON, WEI, and UFS, respectively. The difference between summer and winter half-year periods (medians) was the highest at UFS. Results from six Arctic monitoring stations (during the time period 2000-2003) indicated a similar range of 0.3–47.0 pg m^{-3} with a median of 3.8 pg m^{-3} (Su *et al.*, 2008).

Octachlorostyrene: The concentrations of OCS varied from 0.080 to 1.68 pg m^{-3} at the three stations; the concentrations recorded at SON were significantly higher ($p < 0.05$) than those recorded at UFS. Summer/winter ratios ranged from 1.33 to 1.61. Similar concentrations have been found in the Arctic region (range: 0.03–2.4 pg m^{-3}) (Su *et al.*, 2008).

Chlordane: The ranges of *trans*-, *cis*- and *oxy*-chlordane were 0.064–3.60, 0.237–4.93, and 0.116–1.48 pg m^{-3}, respectively. Concentrations of trans-chlordane measured at WEI were significantly higher ($p = 0.049$) than those measured at UFS. In southwest Greenland, cis-chlordane and trans-chlordane ranged from 0.1 to 0.9 pg m^{-3} and from 0.3 to 0.7 pg m^{-3}, respectively (Bossi *et al.*, 2008).

Heptachlor: This compound was noted in low concentrations near the detection limit (0.018 pg m^{-3}) at all three stations, with significantly higher values at WEI compared with those at SON (conc. SON: $p = 0.002$; conc. WEI > conc. SON: $p = 0.008$). In the Mount Everest region at about 4400 m a.s.l., Li *et al.* (2006) observed significantly higher mean concentrations of 3.3–22.2 pg m^{-3}. The multiannual concentration ranges of the metabolite cis-heptachlor epoxide were 0.7–4.4 pg m^{-3} (SON), 0.4–4.5 pg m^{-3} (WEI), and 0.2–3.1 pg m^{-3} (UFS). Su *et al.* (2008) observed lower concentrations (range: 0.1–2.3 pg m^{-3}) in the Arctic region, whereas Estellano *et al.* (2008) recorded extremely high short-term air concentrations of heptachlor epoxide (up to 250 pg m^{-3}) in the Bolivian Andes.

Aldrin and dieldrin: Aldrin concentrations were frequently below the detection limit (0.018 pg m^{-3}) at the three Alpine stations. The median concentrations of dieldrin measured at SON, WEI, and UFS were 1.56, 1.92, and 1.51 pg m^{-3}, respectively. The differences in dieldrin concentrations between the summer and winter half-years were lowest at SON and greatest at UFS. In comparison, the concentrations at six circumpolar monitoring stations (mean: 0.5 pg m^{-3}) were significantly lower (Su *et al.*, 2008) than those measured in the Alps. In the Brazilian mountains, atmospheric concentrations ranged from values below the detection limit to 19 pg m^{-3}; Meire *et al.* (2012) determined these measurements after Brazil ceased the consumption of aldrin in 2005.

Endosulfan: The concentrations of endosulfan I varied widely at SON, WEI, and UFS between the sampling periods, with multiannual medians of 13.6, 13.7, and 10.5 pg m^{-3}, respectively. Considering the calculation of means, the marked decreasing trend of endosulfan must be considered. The medians of endosulfan II were 0.430–0.620 pg m^{-3}, with higher concentrations during the summer periods. The summer/winter ratio of endosulfan I (1.10–1.26) shows no substantial difference between the concentrations in summer and winter half years; consequently, there was no correlation between concentrations and air temperature. The weak seasonal signal at the three stations may have been caused by the great distance from the sources, low time resolution of the applied measurements, and elevated concentrations that may also occur in April and May (spring maximum event) (Weber *et al.*, 2010). Endosulfan concentrations reported worldwide vary widely (to up to several ngm^{-3}) (Pozo *et al.*, 2006). In Arctic atmospheres, the mean concentrations of endosulfan I are significantly lower than those recorded in this study at the three Alpine stations. At eight circumpolar stations, the average air concentration was 4.2 pg m^{-3} (Su *et al.*, 2008). Schlabach *et al.* (2007) reported 3.4–25.1 pg m^{-3} of endosulfan I in Birkenes, southern Norway, and 5.2–13.2 pg m^{-3} in Ny-Ålesund on Spitsbergen, Norway. Compared with our recorded concentrations, the higher mean concentration of endosulfan I (27.6 pg m^{-3}) near Mount Everest (4400 m a.s.l.) may be due to the close vicinity to source regions (Li *et al.*, 2006). In Tuscany, Italy, median air concentrations of endosulfan I were about 60, 30, and 70 pg m^{-3} for several urban, rural, and agricultural sites, respectively (Estellano *et al.*, 2012). In the Serra dos Orgãos National Park, Brazil, concentrations of endosulfans I and II ranged from 50 to 5,600 pg m^{-3} (Meire *et al.*, 2012); Brazil remains one of the three biggest users of endosulfan worldwide (Li and Macdonald, 2005). In Dalian, Northeast China, concentrations of endosulfan I varied between 0.1 and 52.6 pg m^{-3} during the night and between 0.6 and 43.8 pg m^{-3} during the day (Li *et al.*, 2012). The mean ratio of endosulfan I to endosulfan II (1.1–1.4) was lower than that observed at the three Alpine stations (27–39).

Mirex: The median concentrations were about 0.100 pg m^{-3} at the three stations (LOQ: 0.070 pg m^{-3}). Summer/winter ratios were 1.23–1.64. To the best of our knowledge, to date, little data pertains to the atmospheric concentrations of mirex. During a short measuring study at a coastal site in Qingdao, China, Lammel *et al.* (2007) measured mirex in air at an average level of 79 pg m^{-3}.

Generally, the concentrations of some OCPs monitored at the three Alpine sites were highly dependent on air temperature. They decreased with decreasing temperature and showed higher values in summer than in winter. Similar results were found for several National Parks in the Western United States (HAGEMAN *et al.*, 2006). The temperature effect observed in the Alps was stronger at the lower sites UFS (2650 m a.s.l.) and WEI (2663 m a.s.l.) than at SON (3106 m a.s.l.). Temperature independence occurs rather at temperatures below freezing (Primbs *et al.*, 2008), which is still more frequent at SON.

Geographic Origin

Table 2 lists the OCP concentrations obtained from the four air filters, which were designed to distinguish samples from one of the three source regions of air masses that had remained fewer than 3 days over any of the other source regions or to collect from the fourth class of samples, representing air masses of undetermined origin (UD) (Kaiser, 2009; Offenthaler *et al.*, 2009). Slight, mostly nonsignificant differences in OCP concentrations derived from the four source regions are apparent. Thus, the transport of air masses to the Alpine region may originate directly from anthropogenic emission areas in Europe and indirectly from re-emissions from reservoirs in the soil that are triggered by temperature-enhanced revolatilization. Table 3 shows the numerical ranking of the POP median concentrations and the significance in differences among the four source regions. At SON, the DDT and DDE concentrations were usually the highest when air masses originated in the S and NE source regions and were significantly higher compared

Table 2. OCP concentrations measured using LVS at the three summit stations: Medians of different air masses from the four source regions NW, NE, S and UD. UD refers to air masses of undetermined origin.

Compound	SON				WEIS				UFS			
(pg m^{-3})	NW	NE	S	UD	NW	NE	S	UD	NW	NE	S	UD
p,p'-DDT	0.302	0.240	0.623	0.277	1.31	2.80	1.45	1.34	0.837	0.990	1.10	0.613
o,p'-DDT	0.338	0.393	0.504	0.349	0.519	1.40	0.950	0.575	0.876	1.23	0.920	0.362
p,p'-DDD	0.046*	0.046*	0.046*	0.046*	0.046*	0.046*	0.046*	0.051	0.046*	0.046*	0.046*	0.046*
o,p'-DDD	0.022*	0.022*	0.022*	0.022*	0.022*	0.022*	0.022*	0.026	0.022*	0.022*	0.036	0.022*
p,p'-DDE	0.965	1.42	1.33	0.917	0.887	2.05	1.60	0.945	1.70	2.60	2.18	0.821
o,p'-DDE	0.090	0.153	0.151	0.085	0.093	0.170	0.190	0.095	0.240	0.370	0.510	0.101
α-HCH	8.50	9.33	8.00	8.81	6.16	13.9	9.96	6.17	7.65	8.33	9.10	3.74
β-HCH	0.110	0.092	0.170	0.064*	0.067	0.064*	0.127	0.112	0.176	0.064*	0.177	0.064*
γ-HCH	245	290	185	132	4.13	11.2	8.10	5.87	9.00	16.6	11.1	5.43
δ-HCH	0.055*	0.055*	0.055*	0.055*	0.055*	0.055*	0.055*	0.055*	0.055*	0.055*	0.055*	0.055*
ε-HCH	0.060*	0.060*	0.060*	0.060*	0.060*	0.060*	0.060*	0.060*	0.060*	0.060*	0.060*	0.060*
pentachlorobenzene	37.8	38.8	34.7	36.2	31.3	47.1	43.4	33.1	38.9	50.9	44.3	21.3
hexachlorobenzene	94.6	105	92.5	89.5	75.4	115	99.0	83.8	83.5	107	103	49.4
pentachloroanisole	9.73	9.76	7.45	8.29	5.47	9.82	7.62	6.03	6.91	8.90	9.00	4.16
octachlorostyrene	0.800	0.877	0.905	0.748	0.64	0.880	0.811	0.732	0.770	0.854	0.842	0.401
trans-chlordane	0.382	0.230	0.335	0.325	0.351	0.561	0.609	0.381	0.319	0.465	0.406	0.193
cis-chlordane	0.765	0.668	0.749	0.845	0.546	1.12	1.00	0.667	0.775	0.820	0.874	0.429
oxy-chlordane	0.515	0.339	0.476	0.430	0.352	0.605	0.600	0.412	0.521	0.421	0.512	0.279
heptachlor	0.030	0.018*	0.027	0.018*	0.018*	0.042	0.067	0.018*	0.018*	0.018*	0.053	0.018*
cis-heptachlor epoxide	1.41	0.970	1.28	1.42	0.927	1.59	1.90	1.08	1.43	1.13	1.47	0.754
aldrin	0.018*	0.018*	0.018*	0.018*	0.018*	0.018*	0.018*	0.018*	0.018*	0.018*	0.018*	0.018*
dieldrin	1.40	1.00	1.47	1.69	1.08	2.13	2.25	1.65	1.87	1.30	1.80	0.910
endrin	0.036	0.022*	0.090	0.060	0.022*	0.022*	0.059	0.032	0.031	0.022*	0.080	0.022*
endosulfan I	12.3	10.8	17.7	13.5	9.94	16.6	19.0	9.49	10.6	11.9	15.5	6.28
endosulfan II	0.272	0.215	0.802	0.468	0.351	0.651	0.928	0.581	0.280	0.510	0.923	0.27
mirex	0.096	0.070*	0.105	0.093	0.070*	0.090	0.099	0.096	0.078	0.098	0.084	0.086

* mean value of LOQ.

with those when air masses originated from the NW. Thus, major source regions probably are located in Italy, such as the Po basin, Southern Germany, the Czech Republic, and Poland. At UFS, concentrations originating from the NE, S, and NW were balanced, but were significantly higher than those originating from the UD. At WEI, a higher contamination was measured, presumably because of stronger influences from Southern Germany and Italy; however, an unambiguous assignement to emission areas is impossible. At SON, the *p,p'*-DDE-to-*p,p'*-DDT ratio caused by S air masses tended to be lower than those caused by NE air masses ($p < 0.05$). In areas with recent DDT exposure, the DDE/DDT ratio may be low, whereas in areas in which substantial time has passed since exposure, the DDE/DDT value may be higher. DDT can gradually degrade and transform into the stable metabolite DDE. During a POP-monitoring study performed in Haidel (1160 m a.s.l.) at the borders of Austria, the Czech Republic, and Germany (in the time period 2003 and 2006), *p,p'*-DDT (*p,p'*-DDE) concentrations were the highest when winds blew from the SE (NE); *p,p'*-DDE may originate from less recent sources in Czech Republic (Kirchner, 2007).

The HCH concentrations at WEI caused by NE air masses were mostly higher than those caused by air masses from southern and northwestern Europe or the Atlantic Ocean (UD). At UFS, concentrations caused by S, NE and NW air masses were significantly higher than those caused by air masses from the UD. At SON, only β-HCH concentrations differed between NE and NW air masses. The α-HCH-to-γ-HCH ratio (less than 0.9) indicates a more recent introduction of γ-HCH into the environment (Romanic and Krauthacker, 2004). The α-HCH/γ-HCH ratio calculated at WEI was 0.451–1.24 for the different source regions; the α-HCH/γ-HCH ratio for the NW was significantly lower than the other ratios, possibly indicating that air masses from the NW transport more recent γ-HCH input to the station. For example during a monitoring study at Haidel in the Bavarian Forest in 2003–2006, HCH concentrations were highest when the wind blew from the NW (Kirchner *et al.*, 2007). The results obtained for a site on the Monte Rosa Massif (Colle del Lys, 4250 m a.s.l.) during a 3-day period indicated the high relevance of NW air masses; France was the largest user of γ-HCH in Europe before 1990 (Breivik *et al.*, 1999; Finizio *et al.*, 2006). However, our results confirmed these findings only during July–November 2006.

Pentachlorobenzene, HCB, PCA, and OCS concentrations differed non-significantly among the four source regions at SON. At WEI, the concentrations of these four substances were highest when air masses originated in Southern Germany and Eastern and Central Europe. Air masses from the NE caused significantly higher concentrations than did air masses from the NW. Furthermore, regarding OCS, more polluted air masses travelled from the Italian Po valley to

Table 3. OCP concentration ranking (medians) related to the four source regions with significance of differences between the corresponding source regions NW, NE, S and UD (*t* test). Results are given for the three summit stations SON, WEI and UFS.

Compound	SON		WEI		UFS	
	ranking	Sign p < 0.05	ranking	Sign p < 0.05	ranking	Sign p < 0.05
p,p'-DDT	S, NW, UD, NE	S > NW p = 0.001	NE, S, UD, NW	NE > NW p = 0.005 NE > UD p = 0.021 NE > S p = 0.024	S, NE, NW, UD	
o,p'-DDT	S,NE, UD, NW	S > NW p = 0.002 NE > NW p = 0.039	NE, S, UD, NW	NE > NW p = 0.003 NE > S p = 0.035 NE > UD p = 0.037 S > NW p = 0.040	NE, S, NW, UD	NE > UD p = 0.000 S > UD p = 0.001 NW > UD p = 0.042
p,p'-DDD	S, UD, NE, NW	-	S, UD, NE, NW		NE, NW, S, UD	-
o,p'-DDD	NE, S, NW, UD	-	S, UD, NE, NW		NE, S, UD, NW	-
p,p'-DDE	NE, S, NW, UD	S > NW p = 0.014 S > UD p = 0.032	NE, S, UD, NW	NE > NW p = 0.000 S > NW p = 0.000	NE, S, NW, UD	NE > UD p = 0.006 NE > NW p = 0.044 S > UD p = 0.000 NW > UD p = 0.006
o,p'-DDE	NE, S, UD, NW	NE > NW p = 0.041 S > NW p = 0.005 S > UD p = 0.016	S, NE, UD, NW	S > NW p = 0.000 NE > NW p = 0.000 NE > UD p = 0.023	NE, S, NW, UD	NE > UD p = 0.000 S > UD p = 0.000 NW > UD p = 0.029
α-HCH	NE, UD, NW, S		NE, S, UD, NW	NE > NW p = 0.000 NE > UD p = 0.028 NE > S p = 0.025 S > NW p = 0.000	S, NE, NW, UD	S > UD p = 0.000 NE > UD p = 0.003 NW > UD p = 0.004
β-HCH	S, NW, NE, UD	NE > NW p = 0.027	S, UD, NE, NW		S, NW, NE, UD	S > UD p = 0.045 NW > UD p = 0.045
γ-HCH	Local influence		NE, S, UD, NW	NE > NW p = 0.014 NE > S p = 0.033	NE, S, NW, UD	NE > UD p = 0.001 S > UD p = 0.002 NW > UD p = 0.001
pentachlorobenzene	NE, NW, UD, S		NE, S, UD, NW	NE > NW p = 0.001 NE > UD p = 0.046 NE > S p = 0.015 S > NW p = 0.043	NE, S, NW, UD	NE > UD p = 0.001 NE > NW p = 0.037
hexachlorobenzene	NE, NW, S, UD		NE, S, UD, NW	NE > NW p = 0.004 NE > S p = 0.029	S, NE, NW, UD	S > UD p = 0.000 S > NW p = 0.039 NE > UD p = 0.000 NE > NW p = 0.038 NW > UD p = 0.001
pentachloroanisole	NE, NW, UD, S		NE, S, UD, NW	NE > NW p = 0.010 NE > S p = 0.020	S, NE, NW, UD	S > UD p = 0.000 NE > UD p = 0.001 NW > UD p = 0.007

Table 3. (*continued*).

Compound	SON		WEI		UFS	
	ranking	Sign $p < 0.05$	ranking	Sign $p < 0.05$	ranking	Sign $p < 0.05$
octachlorostyrene	S, NE, NW, UD		NE, S, UD, NW	NE > NW $p = 0.010$ S > NW $p = 0.037$	S, NE, NW, UD	S > UD $p = 0.000$ NE > UD $p = 0.000$ NW > UD $p = 0.000$
trans-chlordane	NW, S, UD, NE		S, NE, UD, NW		NE, S, NW, UD	NE > UD $p = 0.000$ S > UD $p = 0.000$ NW > UD $p = 0.004$
cis-chlordane	UD, NW, S, NE		NE, S, UD, NW		S, NE, NW, UD	S > UD $p = 0.000$ NE > UD $p = 0.003$ NW > UD $p = 0.007$
oxy-chlordane	NW, S, UD, NE,		NE, S, UD, NW		NW, S, NE, UD	S > UD $p = 0.001$
heptachlor	NW, S, UD, NE	NW > NE $p = 0.004$ S > NE $p = 0.014$ UD > NE $p = 0.011$	S, NE, UD, NW	S > NW $p = 0.001$ NE > NW $p = 0.044$	S, NE, NW, UD	S > UD $p = 0.005$ NW > UD $p = 0.006$
cis-heptachlor epoxide	UD, NW, S, NE		NE, S, UD, NW	NE > NW $p = 0.049$	S, NW, NE, UD	S > UD $p = 0.002$ S > NW $p = 0.014$
dieldrin	UD, S, NW, NE		S, NE, UD, NW	S > NW $p = 0.038$ NE > NW = 0.028	NW, S, NE, UD	S > UD $p = 0.002$ NW > UD $p = 0.004$
endosulfan I	S, UD, NW, NE	S > NW $p = 0.029$	S, NE, NW, UD	S > NW $p = 0.007$ NE > NW $p = 0.006$	S, NE, NW, UD	S > UD $p = 0.007$ S > NW $p = 0.027$ NE > UD $p = 0.023$
endosulfan II	S, UD, NW, NE	S > NW $p = 0.032$ S > NE $p = 0.025$	S, NE, UD, NW	S > NW $p = 0.015$ NE > NW $p = 0.013$ UD > NW $p = 0.044$	S, NE, NW, UD	S > UD $p = 0.013$ S > NW $p = 0.020$
mirex	S, NE, UD, NW		S, NE, NW, UD		S, NE, NW, UD	S > UD $p = 0.000$ NE > UD $p = 0.014$

WEI. At UFS, the concentrations caused by S, NW, and NE air masses significantly differed from those caused by air masses from the Atlantic Ocean that arrived at the station more rapidly.

Cis-, *oxy*- and *trans*-chlordane concentrations did not show significant differences for SON and WEI. At UFS, concentrations influenced by air masses from the S, NE, and NW were higher than concentrations in air masses from the UD sample. The highest concentrations of heptachlor were measured, when air masses from S reached the three stations. At SON, concentrations influenced by air masses from S were significantly higher than those influenced by air masses from NE were ($p < 0.05$). Air masses originating from S and NE caused significantly higher contamination levels than did those originating from NW.

Dieldrin, endosulfan I (Fig. 2), and endosulfan II had the highest concentrations when air masses originated from the Mediterranean and other southern regions. At SON, air masses from the S were significantly more contaminated with endosulfan II than were those from the NE ($p < 0.05$). In general, at WEI and UFS, differences between the contamination caused by air masses from the S and NW regions were significant. The spatial distribution of more elevated concentrations of endosulfan in the Central Alps compared with that in Bavaria may reflect the agricultural activities and former use of this substance in Southern Europe (Weber *et al*., 2010). Furthermore, re-emissions caused by high temperatures in the Italian Po basin and elsewhere in Italy and Southern Europe can be assumed Jakobi *et al*. (2011). Becker *et al*. (2011) estimated that in the Arctic environment, air masses from temperate, subtropical, and tropical regions may contribute to the amount of endosulfan I in the ratio of 57:40:3, respectively, and of endosulfan II in the ratio of 66:33:1, respectively. For a remote mountain site in southwestern China, Xu *et al*. (2011) found that HCH and DDT levels increased when air masses originated from India and Southeast Asia during the summer monsoon. Generally, the movement of air masses containing OCPs to Europe and the European Alps may occur during warmer seasons, when higher temperatures increase the mobility of semivolatile compounds. POPs tend to spread from source areas such as India or China to a larger geographical distribution through multiple cycles of atmospheric deposition and subsequent volatilization. POPs can be transported from China through North America to Europe (Primbs *et al*. (2008).

Temporal Trend

Because of worldwide restrictions on compound use, the majority of OCPs did not increase during 2005–2013, and some of the selected substances decreased ($p < 0.10$). For only a few analytes, a significant negative trend ($p < 0.05$; $p < 0.001$) was identified. According to the medians of calculated singular weighted concentrations of OCPs, Table 4 reports the linear tendencies or trends with p values. Since annual temperatures at WEI, SON and UFS did not show any trend between 2005 and 2013, an influence of air temperature can be excluded, except for seasonal variations.

The DDT and DDE concentrations at WEI and UFS decreased only slightly in 2005–2013; however, the time trend was consistently nonsignificant ($p > 0.05$). Holoubek *et al*. (2007) reported a similar trend at the Kosetice Observatory in the Czech Hydrometeorological Institute; no trend in the data of DDX in 1996–2005 was detected. In the present study, for HCHs, only the isomer α-HCH tended to decrease significantly, particularly at WEI. During the decade before 1996–2005, HCH data obtained at the Kosetice Observatory did not reveal any trend (Holoubek *et al*., 2007). In the present study, the concentrations of pentachlorobenzene and pentachloroanisole exhibited a similar tendency to decrease; however, the decline was significant only for pentachlorobenzene at UFS.

HCB concentrations did not show any significant trend at the Central Alpine stations (SON and WEI) or at the Bavarian station (UFS). At the Kosetice Observatory, air concentrations of HCB significantly increased during 1996–2005 (Holoubek *et al*., 2007). In the present study, the only substance with a slightly positive trend was OCS, which is mainly a by-product of waste-material burning and other thermal processes. Little is known regarding the global emissions of OCS or its geographical distribution (Chu *et al*., 2003). However, only UFS revealed a significant increase in OCS concentration.

Among all measured substances, only endosulfan I (Fig. 3) and endosulfan II tended to decrease at all three stations. The three curves in the figure are characterized by high

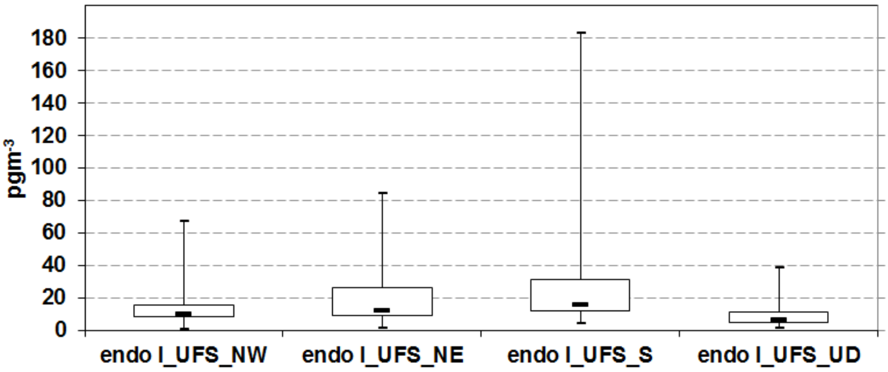

Fig. 2. Boxplots of endosulfan I concentrations at UFS for the three source regions (NW: Northwest; NE: Northeast; S: South) and the UD sample (representing air masses of undetermined origin).

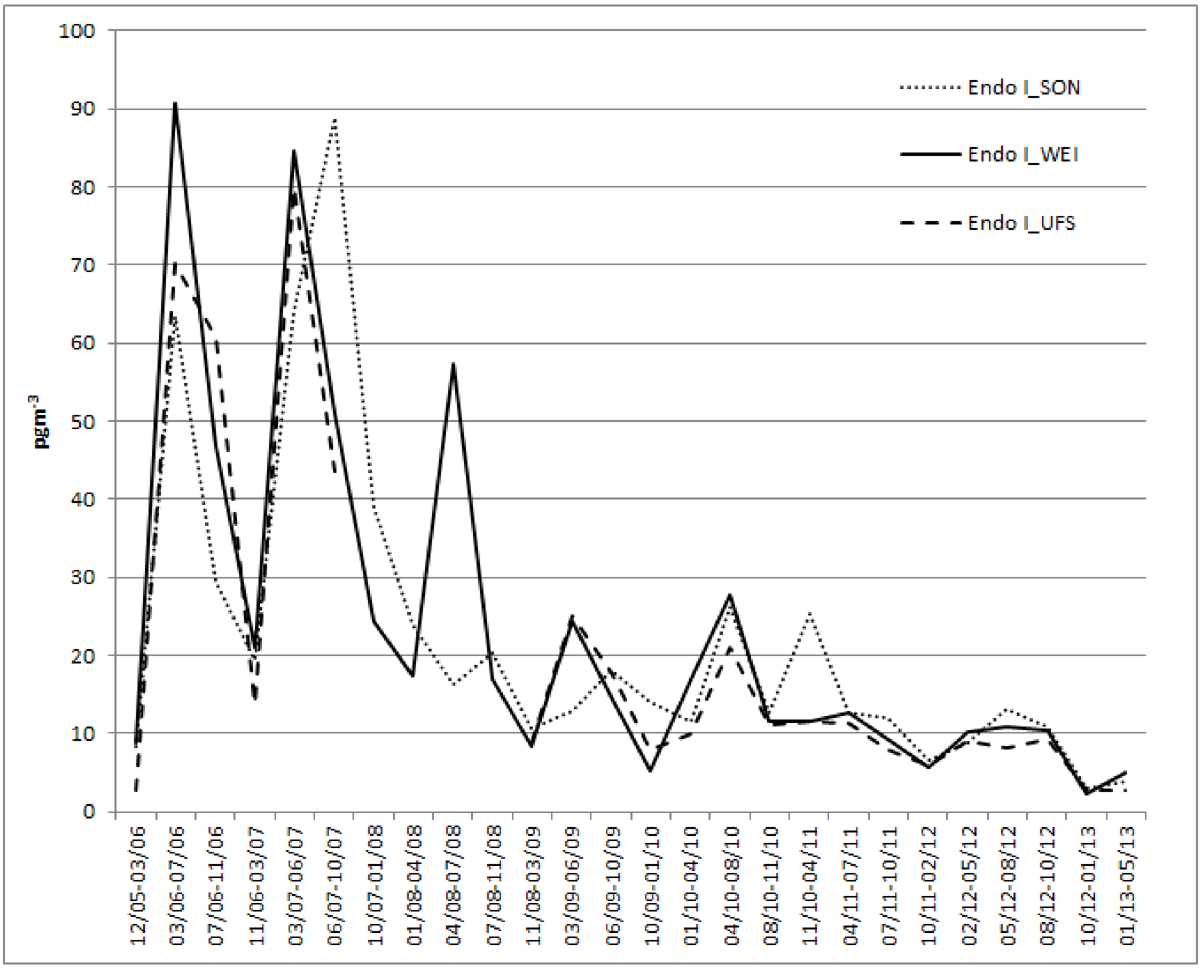

Fig. 3. Time series of endosulfan I air concentrations at SON, WEI, and UFS between December 2005 and May 2013. During the period no temperature trend could be observed.

values during the summer months of 2006 and 2007. Using data from stations located in Alert and Tagish, Schlabach *et al.* (2007) assumed that endosulfan air concentration levels in the Arctic did not substantially decrease between the early 1990s and 2005. Heptachlor concentrations in the air exhibited a negative tendency. However, only at SON the decline was significant ($p = 0.05$).

CONCLUSIONS

In this study, we monitored the air at three high Alpine observatories in the Bavarian, Austrian, and Swiss Alps during 2005–2013. At these monitoring stations, OCP concentrations were significantly lower than those in regions adjacent to greater emission sources in other continents (e.g., China, South America) but higher than those in the Arctic. However, a direct comparison of our data with literature based results is difficult, because the samples analyzed in these studies were taken even a few years earlier. For many compounds a time trend and seasonal differences may have occurred. Only for some compounds such as pentachlorobenzene and hexachlorobenzene, data are directly comparable to our measurements because such trends can be excluded.

Our OCP measurements revealed slight regional differences between the Central and the Northern Alps. DDX and HCH concentrations were slightly higher at WEI and UFS in the Western Alps compared with concentrations at SON in the Eastern Alps, which are less influenced by possible emissions from the Italian Po basin. Pentachlorobenzene, HCB, PCA, OCS, and endosulfan I were observed in higher concentrations in the Central Alps (SON and WEI). Comparing the data of the three sites, UFS and WEI concentrations were more similar than SON and WEI or SON and UFS concentrations. Therefore in the future, the concept of measurements could be modified either at WEI or UFS. The major shortcoming of our study is that we could include only monitoring stations from the Northern and Central Alps. Adequate measurements to be performed by Italian national and regional agencies would be desirable. Future studies regarding the POP contamination in the Alps should comprise sites in the Lombardian Alps near to the Padan Plain.

With the aid of trajectory forecasting-based monitoring procedures, we determined that air masses moving from the NE (i.e., south Bavaria, the Czech Republic, or Poland) and from the S (the Mediterranean and other subtropical and tropical countries) to UFS and WEI were more contaminated with OCPs than were those originating from the NW (Rhine-

Main region, Belgium, or the Netherlands) or the Atlantic Ocean. However, the significant dependency of only a few compounds on the ambient air levels from the origin of the air masses demonstrated the ubiquitous distribution of POPs, attributable to their long-range atmospheric transport and a strong mixing of air masses. Additionally, continuing re-volatilization and deposition processes are crucial causes of such atmospheric transport. In the future, it would be reasonable to change the trajectory-based monitoring procedures at least at one of the three Alpine sites. Instead of the distinction of the four source regions, air sampling could be designed to distinguish two layers in the atmosphere (lower and higher troposphere). So, direct influences from the emission centers in the two pre-alpine regions (North and South) could then be separated from influences due to long-range transport.

Because of the high cost of analytical procedures, most results in the literature have been obtained during relatively short monitoring studies (Pozo *et al*., 2006; Zhang *et al*., 2008; Lammel *et al*., 2009; Estellano *et al*., 2012). Hence, the long-term monitoring concept of the present study enabled us to evaluate temporal trends of POP air concentrations. We observed the behavior of POPs in the air after the production of numerous compounds had been banned in Europe and many other parts of the world. Because of the high persistence of POPs in the environment, a statistically significant decline was detected during 2006–2013 only for some compounds, like endosulfan. Despite having the sharpest decrease among all monitored OCPs, endosulfan continues to be used as an insecticide worldwide (Weber *et al*., 2010). In order to check the effectiveness of international regulations, monitoring activities need continuation in the next years and are to be extended to novel POPs such as hexachlorobutadiene and polybrominated flame retardants as well as polyfluorinated compounds.

Future evaluations of our data include further POPs, such as PCBs, PCDD/Fs and PAHs in the air and in the precipitation (deposition). We aim to test for correlation among the various POP and OCP concentrations at a single site and among the three Alpine sites.

In order to investigate temperature effects on POP concentrations in the air, a higher temporal sampling resolution of measurements (1–2 months) at one of the three sites would be necessary. In this case, only selected OCP compounds are to be included because atmospheric concentrations of some OCP compounds are near the limit of quantification (DDDs, δ-HCH, ε-HCH, aldrin, endrin, mirex).

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SUPPLEMENTARY MATERIALS

Supplementary text and data associated with this article can be found in the online version at http:/www.aaqr.org.

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