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Air concentrations and deposition of chlorinated dioxins and furans (PCDD/F) at three high alpine monitoring stations: Trends and dependence on air masses

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HIGHLIGHTS

- Alpine concentrations of PCDD/F in ambient air distinguishing four source regions.
- Air concentrations 1–2 orders of magnitude lower than in urbanized European areas.
- Partly decreasing temporal trends of ambient air concentrations but levelling of.
- Deposition rates in the same order of magnitude like at urban agglomerations.
- Domestic heating, coal burning and waste incineration as dominant sources.

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ABSTRACT

Ambient air concentrations and bulk deposition of polychlorinated dibenzo-*p*-dioxins and dibenzo–furans (PCDD/F) were monitored at three high Alpine stations in Germany (Schneefernerhaus/Zugspitze: 2650 m a.s.l.), Switzerland (Weißfluhjoch: 2663 m a.s.l.), and Austria (Sonnblick Observatory: 3106 m a.s.l.) from 2005 to 2018. High-volume active air samplers were selectively in operation on a daily basis according to predicted source-regions of air masses. Air concentrations showed only small differences between the three sites and were one or two orders of magnitude lower than in urbanized areas in central Europe. Calculation of source contribution revealed waste incineration, heating, and coal combustion as major sources of PCDD/F in ambient air. Air masses from the northeast were characterized by higher concentrations of PCDD/F than those from northwest and south. However, air masses from the northeast source region are significantly less frequent at the three Alpine stations than air masses from the other source regions. Only at Schneefernerhaus, the majority of congeners exhibit a clear decreasing temporal trend in ambient air concentrations. Deposition rates of PCDD/F measured at the three stations were almost as high as at monitoring stations in urban agglomerations. Despite lower precipitation rates in the central Alps, deposition of PCDD/F was higher at the Sonnblick Observatory than in the Northern Alps (Schneefernerhaus). Bulk deposition for Weißfluhjoch and Schneefernerhaus exhibit a decreasing temporal trend.

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1. Introduction

Meteorological conditions which are characteristic for mountain ranges, such as low temperatures, high levels of precipitation and pronounced valley winds, cause high reception of persistent organic pollutants (POPs) (Daly and Wania, 2005; Wang et al., 2007; Offenthaler et al., 2009). This is particularly the case for the Alps, which are surrounded by regions with pronounced industrial activities and a high population density (Iozza, 2010). According to van der Gon et al. (2007), total emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) in 2000 amounted to 11.7 kg toxicity equivalents (TEQ) yr^{-1} for Europe (UNECE official data and estimates). The emissions were 0.050, 0.017, 0.744, 0.406, 0.560, 0.245 and 0.027 kg TEQ yr^{-1} for Austria, Switzerland, Czech Republic, Germany, France, Italy, and Slovenia, respectively.

Within the international monitoring project MONARPOP ("Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants"), beginning in 2005, unprecedented measurements of chemicals which belong to the "Dirty Dozen" were performed in mountainous ecosystems in several regions of Austria, Italy, Slovenia, Switzerland, and Germany. In consequence, numerous scientific publications drew the attention to the Alpine region as a sink for POPs (Finizio et al., 2006; Belis et al., 2009; Jakobi et al., 2015).

Altitudinal profiles of POPs in soils and plant tissue of alpine ecosystems showed that for some compounds (e.g. organochloropesticides) there is an increase from valley floor to high elevations due to decreasing air temperatures (Kirchner et al., 2009). On the basis of horizontal transect measurements through the Alps, Offenthaler et al. (2008) found out that concentration levels of PCDD/F, polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) in humus and needles are higher in the northern and southern fringes of the Alps than in central Alps.

Continuous measurements of air concentrations and bulk deposition at high elevation sites at Hoher Sonnblick, Weißfluhjoch and Zugspitze (Schneefernerhaus) were an additional part of the MONARPOP project which are continued by the projects PureAlps in Austria and Bavaria/Germany. Hence, the time series presently ranges from 2005 to 2018 (only at Weißfluhjoch measurements ended in 2013). Evaluation of this comprehensive time-series on POPs started with a focus on organochloropesticides (OCPs). The respective results of deposition rates and air concentrations of OCPs have been published recently (Jakobi et al., 2015; Kirchner et al., 2016).

The present paper extends the evaluation of the MONARPOP/PureAlps data and the determination of PCDD/F in air and bulk deposition at the three high elevation sites. Deposition of PCDD/F can occur in dry gaseous, dry particulate and wet forms (Lohmann and Jones, 1998). Several studies at sites ranging from mountains (Suryani et al., 2015), polar regions (Oehme et al., 1996; Kallenborn et al., 2012, 2013), sparsely populated rural areas (Hovmand et al., 2007) to more polluted urban areas (Wallenhorst et al., 1997; Harrad, 2010) have been performed and give a range of atmospheric concentrations and deposition rates of PCDD/F for various parts of our globe. The present study supplements these studies with data from the Alpine region.

2. Materials and methods

2.1. Sampling sites and meteorological conditions

Sampling has been performed at three mountain summit stations: In Bavaria/Germany at Schneefernerhaus (UFS: 2650 m a.s.l.; 47.42°N; 10.98°E) in close vicinity of the highest mountain of Germany (Zugspitze), in Austria at Sonnblick Observatory (SBO: 3106 m a.s.l.; 47.05°N; 12.96°E), and in Switzerland at Weissfluhjoch (WEI: 2663 m a.s.l.; 46.83°N; 9.81°E). The horizontal distances between WEI, UFS, and SBO to the nearest settlement areas as possible sources of PCDD/F are 4, 10, and 20 km, respectively. The annual precipitation amounts monitored at UFS, SBO and WEI were 2551, 1829 and 1379 mm during 2005–2013; the amounts of precipitation show a certain dependency from the distance from the northern edge of the Alps (UFS: 20 km; WEI: 60 km; SBO: 70 km) and from the altitude. Jakobi et al. (2015) have provided more detailed information about the sites and the meteorological conditions during 2005–2013.

2.2. Sample collection

Air sampling of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) at the three stations was performed by using multichannel high-volume samplers (HVS; Dioxin Monitoring Systems: Kottingbrunn, Austria; Kroneis: Vienna Austria and Digitel: Hegnau, Switzerland) with a flow rate of 120 L min^{-1} based on the German guideline VDI 3498–1. The HVS were equipped with a switching unit of heated magnetic valves to select one of the 4 filter cartridges, an Ethernet interface and an extended control unit to forward and process control and status-information (Offenthaler et al., 2009). The filter cartridges were equipped with heated inlet tubes to avoid freezing of the glass fiber filters of the filter cartridges. $^{13}C_{12}$-labeled 1,2,3,4-TCDD was added as sampling standard prior to exposure of the cartridges. The HVS had to operate for 3 months to collect detectable amounts within the cartridges.

Until 2015, air sampling was designed to distinguish three predefined source regions: northwest (NW), northeast/east (NE) and southwest/south/southeast (S) (Fig. 1). A forth region of nominally undefined origin (UD) was assigned for air masses which remained less than three days over any of the three source regions (Kirchner et al., 2016). Such air masses mostly came directly from the Atlantic Sea. The selection of the four sampling filters was governed by daily trajectory forecasts calculated using the FLEXPART model developed by NILU (Stohl et al., 2005); the samplers were programmed on a daily basis by the Austrian Central Institute for Meteorology and Geodynamics (ZAMG), Regional Office Salzburg. After 2015, air sampling has been performed without differentiating the four source regions.

To sample atmospheric bulk deposition under the extreme climatic conditions at the Alpine sites, new funnel-adsorber samplers have been developed. Bulk deposition samplers according to German guideline DIN 19,739–1 were equipped with additional isolation, heated glass funnels to melt snow, and heated cartridge chambers to avoid frost shattering. Precipitation is collected in a funnel with a sampling area of 0.053 m^2, melts and subsequently runs through a glass cartridge, which is filled with styrene-divinylbenzene copolymer resin as a hydrophobic adsorber (XAD-2 resin, Supelpak-2SV, Supelco). Detailed description can be found in Offenthaler et al. (2009) and Jakobi et al. (2015). PCDD/F deposition rates are determined by both the amount of precipitation and its PCDD/F content.

2.3. Substances, chemical analysis and quality assurance/quality control

We monitored 7 toxic 2,3,7,8-chlorosubstituted congeners of the PCDD and 10 toxic 2,3,7,8-chlorosubstituted congeners of the PCDF, the sum of tetra- (TCDD and TCDF), penta- (PeCDD and PeCDF), hexa- (HxCDD and HxCDF) and heptachlorinated (HpCDD and HpCDF) and octachlorinated (OCDD and OCDF) homologues. The total sum of PCDD/F and the toxicity equivalent for humans (TEQ) based on the toxic equivalency factors (TEF) according to NATO/CCMS 1988 (I-TEF) and the World Health Organisation (WHO) 2005 (van den Berg et al., 2006) were calculated on a lower bound basis from thereof.

All sample materials (XAD-2 resins as adsorber material from deposition samplers, glass fiber filters and PUF plugs from active air samplers) were spiked with 17 $^{13}C_{12}$-labeled 2,3,7,8-substituted PCDD/F congeners prior to extraction (Cambridge Isotope Laboratories Inc., Tewksbury, Massachusetts, USA). $^{13}C_{12}$-labeled 1,2,3,4-TCDD was used as sampling standard to have all 17 $^{13}C_{12}$-labeled 2,3,7,8-substituted PCDD/F congeners available for recovery correction. For the active air

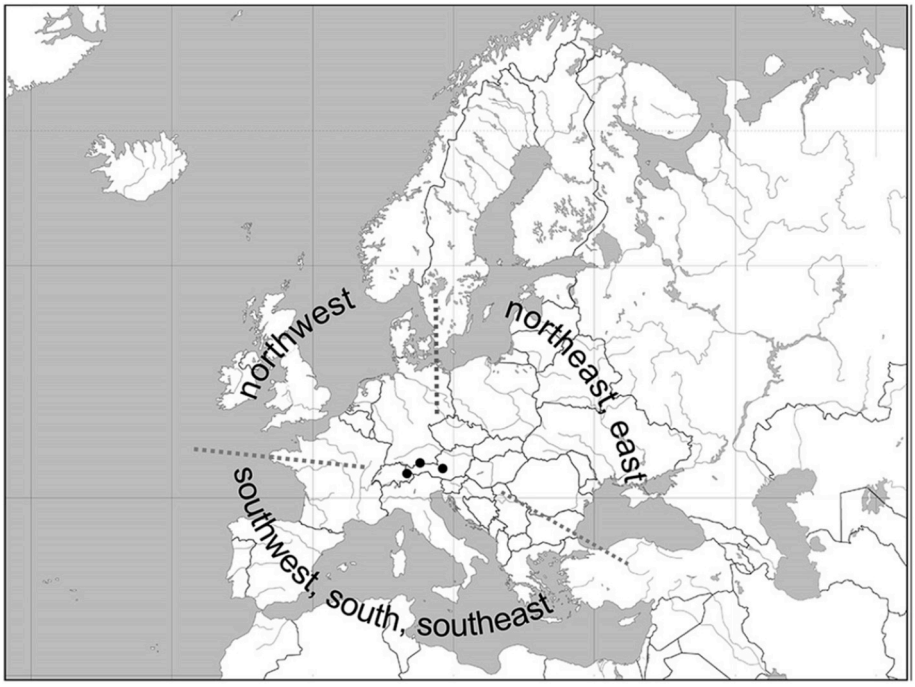

Fig. 1. Directional selectivity of active air sampling (Offenthaler et al., 2009).

samples extraction was carried out in a Soxhlet extractor for 12 h using toluene. For deposition samples, the outside of each cartridge was cleaned using toluene wetted pads. The so cleaned cartridges containing the sample material were extracted as a whole in a Soxhlet extractor equipped with a Dean-Stark water separator for three days.

The clean-up of the extracts was done by a semiautomatic three step liquid column procedure [H_2SO_4/Celite, mixed layer column (acidic silica, neutral silica, basic silica) and alumina B column], also including the separation of PCDD/F from PCB. The extracts were reduced to 50 µl by a gentle stream of nitrogen, $^{13}C_{12}$-labeled 1,2,3,4-TCDF was added as recovery standard prior to GC/HRMS measurement. The GC/HRMS measurement was carried out on a MAT 95XP high resolution mass spectrometer (Thermo Finnigan, Bremen, Germany) connected with two Trace GC Ultra gas chromatographs (Thermo Scientific). One GC was equipped with a DB-DIOXIN capillary column (Agilent J&W; length: 60 m, Ø: 0.25 mm, film thickness: 0.15 µm), the other one with a DB-5 capillary column (Agilent J&W; length: 60 m, Ø: 0.25 mm, film thickness: 0.25 µm), respectively. Each sample was analyzed with both GC columns to achieve a good separation of all 2,3,7,8-substituted congeners and the possibility to calculate the sum of homologue groups. The measurements were carried out at a mass resolution of 8000 to 10,000 in the single ion monitoring (SIM) mode with the two most intensive masses of the molecule ion cluster of each homologue group of the native and $^{13}C_{12}$-labeled PCDD/F. Quantification was done using isotope dilution method with the corresponding $^{13}C_{12}$-labeled extraction standard for each 2,3,7,8-substituted congener according to quality criteria given in ISO 16,000–14. For the sum of the homologue groups the area of every peak within the retention-time window which fulfils the quality criteria was summed up and quantified using isotope dilution method with one corresponding $^{13}C_{12}$-labeled extraction standard for each homologue group.

Field blank samples have been analyzed for ambient air as well as for deposition measurements. For ambient air measurements filter cartridges have been exposed in a meteorological cabin made of untreated wood to ambient air without suction for the same period as the cartridges at the active sampler. For deposition measurements two types of field blanks have been used during the project. In the early stage the glass cartridges filled with XAD-2 resin were exposed open to ambient air but protected from precipitation in a meteorological cabin, to estimate the passive sampling capacity. In that type of field blanks no detectable concentrations could be found for PCDD/F. Therefore, the type of field blanks has been changed to glass cartridges filled with XAD-2 resin, which were sent to the sampling site, stored closed in the heated sample chamber of the deposition sampler together with the sampled cartridge. At the end of the sampling period, the field blank cartridges were sent together with the deposition samples back to the laboratory. Blank values were always below 10% of the lowest measured concentrations of each batch and could therefore be accepted without subtraction according to ISO 16000–14.

The accuracy of the analytical method has been determined with regularly participation in proficiency tests (PT). The standard deviation of the method was determined by parallel sampling of ambient air at the same sampling site and separate determination. For results calculated as TEQ the standard deviation amounts to <10%. For individual congeners the mean standard deviation is in the range of 25%, near LOQ the standard deviation can raise up to 60% (Moche and Thanner, 1996).

Due to the used sampling procedure as described above the sampled air volumes are strongly depending on the weather conditions and thus differ from a few hundred cubic meters to several thousand cubic meters for the individual samples. For this reason the limits of quantification (LOQs) of the method also vary in a wide range from 0.001 to 0.08 fg m^{-3} for active air sampling. For deposition samples LOQs are in the range from 0.001 to 0.07 $pgm^{-2}d^{-1}$ for the individual congeners.

Breakthrough experiments have been carried out in the way that the two PU-foams were analyzed separately for some cartridges. PCDD/F could not be found in significant concentrations on the second PU-foam.

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

3. Results and discussion

3.1. Data availability and frequency of air masses

In our study, 19 (WEI) to 31 (UFS, SBO) sampling periods have been

evaluated. In the case of active air concentration monitoring, mean data availability (in percent of length of the entire time span) was 82%, 86%, and 90% for UFS, SBO, and WEI, respectively. Periods in which data availability due to station or device problems was lower than 40% were excluded (Kirchner et al., 2015). Deposition data were available in 97% (UFS), 94% (SBO), and 81% (WEI) of the entire time span.

Weather conditions at the three sites were mainly characterized by air masses originating in the Mediterranean region (S) (32–35%) and the NW region (27–32%). Relatively few air masses originated from the NE source region (11–15%), whereas the frequencies of air masses with the unspecific origin UD were 22–25%. The accuracy of forecasts, which had been evaluated for the first three years of measurements by *post hoc* inspection of the trajectories of air actually collected by each filter unit, was high for NE and NW, but lower in the case of prefrontal south-westerly winds and foehn events (Kaiser, 2009). Additional information about the trend of air masses arriving at the three sites can be found in Kirchner et al. (2015).

3.2. Mean air concentrations and seasonality

The concentrations of 17 2,3,7,8-substituted congeners, the sums of TCDD/F, PeCDD/F, HxCDD/F and HpCDD/F and the total sum of PCDD/F are shown in Table 1. Additionally, the toxicity equivalents (TEQ) according to NATO/CCMS (1988, I-TEF) and the World Health Organisation (WHO-2005) are reported (van den Berg et al., 2006). The concentrations were continuously normalized to 0 °C and 1013 hPa by the HVS according to the Avogadro equation (Ackermann and Knox, 2011). The overall concentrations of singular periods were calculated by weighting concentrations by the relative abundance of air masses from each source region. Based on calendar date, each period was attributed to the colder and warmer half of the year and calculated winter-to-summer ratios.

Regarding the entire period between 2005 and 2013/2018, dioxin concentrations in air were found to be 6.0–195 fg m^{-3} (sum PCDD/F) and 0.001–6.0 fg I-TEQ m^{-3}. For all three sites, PCDD ranged between 2 and 164 fg m^{-3}, and PCDF between 0.3 and 171 fg m^{-3}. The concentration ranges and medians of all congeners, the corresponding sums and TEQ values were similar for the three sites and did not differ significantly between them. However, some congeners were frequently below the limit of detection. After omitting the outliers, only OCDD at SBO and UFS was significantly higher than at WEI ($p < 0.05$).

At our Alpine sites, the PCDD/F concentrations were up to 1–2 orders of magnitude lower than those monitored in urban areas or emission centers. In the Rhine-Ruhr conurbation, annual means of PCDD/F concentrations were in the range of 15–50 fg I-TEQ m^{-3} in the period 2000–2010 (Bruckmann et al., 2013). During a monitoring program (1997–1999) performed in different urban regions of Austria (Moche and Thanner, 2003), annual means varied from 36 fg I-TEQ m^{-3} (Vienna) to 237 fg I-TEQ m^{-3} (Donawitz). In urban areas of Baden-Württemberg (Germany), average dioxin concentrations ranged from 53 to 99 fg I-TEQ m^{-3}, whereas the average PCDD/F concentrations in rural areas were found to be 14–27 fg I-TEQ m^{-3} in mid-nineties (Wallenhorst et al.,

Table 1
Concentrations of PCDD/F measured with HVS at Hoher Sonnblick (SBO) in 2005–2018, Weissfluhjoch (WEI) in 2005–2013 and Schneefernerhaus/Zugspitze (UFS) in 2005–2018: Ranges (minimum-maximum), medians and winter to summer ratios calculated on the basis of medians (including outliers).

Compound	SBO			WEI			UFS		
	Range fg m^{-3}	Median fg m^{-3}	Winter to summer ratio (medians) *p < 0.05	Range fg m^{-3}	Median fg m^{-3}	Winter to summer ratio (medians) *p < 0.05	Range fg m^{-3}	Median fg m^{-3}	Winter to summer ratio (medians) *p < 0.05
2,3,7,8-TCDD	n.d.-n.d.	n.d.	–	n.d.-0.4	n.d.	–	n.d.-0.1	n.d.	–
1,2,3,7,8-PeCDD	n.d.-0.3	n.d.	2.5	n.d.-0.2	n.d.	–	n.d.-0.2	n.d.	–
1,2,3,4,7,8-HxCDD	n.d.-3.2	n.d.	2.5	n.d.-0.8	n.d.	–	n.d.-0.5	n.d.	1.6
1,2,3,6,7,8-HxCDD	n.d.-3.2	n.d.	0.9	n.d.-1.0	0.1	0.6	n.d.-1.4	n.d.	1.2
1,2,3,7,8,9-HxCDD	n.d.-1.8	n.d.	1.0	n.d.-0.9	n.d.	–	n.d.-0.7	n.d.	0.8
1,2,3,4,6,7,8-HpCDD	n.d.-16.0	2.9	0.8	n.d.-9.7	1.9	1.6	n.d.-13.4	1.9	1.3
OCDD	4.1–56.7	9.3	1.0	n.d.-148	7.5	1.1	n.d.-40.0	8.7	1.5
Sum TCDD	n.d.-11.8	2.0	1.3	n.d.-8.4	1.4	1.2	n.d.-21.2	1.5	2.1*
Sum PeCDD	n.d.-10.9	0.5	0.7	n.d.-10.2	0.6	0.4	n.d.-15.1	0.7	3.5*
Sum HxCDD	n.d.-27.5	3.1	0.8	n.d.-15.9	3.8	1.4	n.d.-26.5	3.5	2.3*
Sum HpCDD	0.6–26.2	5.9	0.9	n.d.-18.5	5.9	1.4	n.d.-25.1	6.3	1.5
2,3,7,8-TCDF	n.d.-29.7	0.8	0.2*	n.d.-5.7	1.3	1.3	n.d.-19.9	1.4	0.6
1,2,3,7,8-PeCDF	n.d.-3.3	0.1	0.3*	n.d.-1.1	n.d.	–	n.d.-2.6	0.2	0.5
2,3,4,7,8-PeCDF	n.d.-5.1	0.3	0.4	n.d.-1.7	0.4	1.7*	n.d.-3.4	0.7	0.8
1,2,3,4,7,8-HxCDF	n.d.-3.4	0.3	0.9	n.d.-2.0	0.5	1.4	n.d.-4.8	0.3	1.4
1,2,3,6,7,8-HxCDF	n.d.-4.4	0.1	1.1	n.d.-3.3	0.2	0.7	n.d.-3.4	0.2	1.0
2,3,4,6,7,8-HxCDF	n.d.-4.3	0.3	1.2	n.d.-3.4	0.3	3.6*	n.d.-3.5	0.1	1.1
1,2,3,7,8,9-HxCDF	n.d.-3.5	n.d.	–	n.d.-0.6	n.d.	–	n.d.-0.2	n.d.	0.8
1,2,3,4,6,7,8-HpCDF	0.3–7.4	1.4	1.1	n.d.-7.8	1.7	1.0	0.2–8.4	1.9	1.2
1,2,3,4,7,8,9-HpCDF	n.d.-1.2	n.d.	0.9	n.d.-1.3	0.1	1.0	n.d.-1.4	n.d.	0.6
OCDF	n.d.-6.4	1.0	1.1	n.d.-4.1	0.8	3.5*	n.d.-5.8	0.4	1.0
Sum TCDF	n.d.-134	11.6	0.5	0.5–33.0	12.0	1.3	0.8–78.0	14.8	0.8
Sum PeCDF	n.d.-26.7	3.3	0.5	n.d.-17.5	3.8	1.1	n.d.-19.9	4.6	1.0
Sum HxCDF	n.d.-24.7	2.3	0.9	n.d.-18.2	2.7	0.8	n.d.-19.6	3.7	1.2
Sum HpCDF	0.3–19.6	2.8	1.3	n.d.-11.9	3.6	2.2*	0.5–14.5	3.7	1.3
Sum PCDD	**4.7–77.8**	**22.9**	**0.9**	**4.4–164**	**22.6**	**1.7***	**2.0–109**	**28.7**	**1.8***
Sum PCDF	**0.3–171**	**23.6**	**0.6**	**3.1–71.9**	**22.9**	**1.4**	**2.0–103**	**42.2**	**0.9**
Sum PCDD/F	**6.0–195**	**47.2**	**0.7**	**7.5–173**	**45.3**	**1.1**	**7.2–181**	**62.1**	**1.3**
TEQ (I-TEF)	**0.02–6.0**	**0.4**	**0.5**	**0.001–2.0**	**0.7**	**1.7***	**0.04–3.9**	**0.8**	**0.8**
TEQ (WHO, 2005)	**0.02–4.9**	**0.4**	**0.5**	**0.002–1.7**	**0.6**	**1.7***	**0.05–3.1**	**0.5**	**0.9**

1997). Around a steel plant area in northeast China, the air concentrations and WHO-TEQ values of PCDD/F were in the range of 94–4944 fg m^{-3} and 3–247 fg m^{-3}, respectively (Li et al., 2010). Within the National Dioxin Air Monitoring Network (NDAMN), PCDD/F concentrations in air were in the range of 6–15 fg TEQ m^{-3} in rural areas, and of 0.1–3 fg TEQ m^{-3} in remote areas of the USA (EPA, 2013). Rural background locations in Catalonia/Spain exhibit geometric mean concentrations of 16 fg TEQ m^{-3} (Parera et al., 2018). At a remote site (Zöbelboden) of the Austrian National Park "Kalkalpen" at 900 m a.s.l., the three-year mean from 1997 to 1999 was 2.7 fg I-TEQ m^{-3} for summertime and 4.4 fg I-TEQ m^{-3} for wintertime (Moche and Thanner, 2003). At an urban background and one rural site in Bavaria medians of PCDD/F concentrations were 6.7 and 9.0 fg WHO-TEQ m^{-3} in summertime and 33 and 35 fg WHO-TEQ m^{-3} in wintertime in 2002–2004 (Bayerisches Landesamt für Umwelt, 2006).

Results from Ny-Alesund, Spitsbergen (Norway), show that OCDD and OCDF concentrations in the air during summer 1995 were 4.4 and 3.8 fg m^{-3}, respectively and the sum of PCDD/F concentrations ranged between 67 and 105 fg m^{-3} in spring and summer samples (Schlabach et al., 1996).

Thus, the concentrations observed at three Alpine sites of our study (duration of each sampling period in 2005–2013: 3 months) were one order of magnitude lower than those monitored in Mediterranean urban air (Castro-Jimenez et al., 2017; Barbas et al., 2018) and up to one order of magnitude higher than those observed in arctic air at Spitsbergen and at Alert, Canada (duration of each period in winter 2000/01: 1 week), where PCDD and PCDF particle-phase concentrations ranged between 2.1 and 13 fg m^{-3} and 2.4 and 46 fg m^{-3}, respectively (Hung et al., 2010). During the four weeks of January 2001, where the highest concentrations at Alert had been monitored, average OCDD and OCDF concentrations were 1.3 and 1.5 fg m^{-3}, respectively. In contrast, OCDD and OCDF multi-annual means (medians) at SBO were 9.36 and 1.1 fg m^{-3}, respectively. It should be mentioned that in the Arctic samples the concentrations of OCDD and OCDF are in the same level, whereas at the Alpine sites the concentrations of OCDD are clearly higher than OCDF concentrations, which fits well to the known congener profile of ambient air data from lowlands. Possibly, the different OCDD/OCDF ratios indicate a pronounced influence of heating activities at the Alpine sites.

In the winter half years, atmospheric concentrations of some PCDD/F compounds were on average higher than in summer half years (Table 1); this tendency (significant only for some compounds) was observed at the two sites WEI and UFS (which are situated 450 m lower than SBO) but not at SBO. Only at WEI, the winter concentrations, expressed as I-TEQ and WHO-TEQ, were significantly higher than those in summer ($p < 0.05$). The higher the mountain site is, the more it reflects conditions of free atmosphere. Thus, the highest site, SBO is particularly decoupled from the adjacent valleys, especially during winter with low atmospheric convection. Hence, the winter periods are prone to temperature inversions which can trap emissions close to the ground level for several days (Lohmann and Jones, 1998; Kirchner et al., 2012). When capping inversions vanish, pollutants can be transported up to higher levels. Additionally, the horizontal distance between SBO to the nearest urban area is greater than in the case of UFS and WEI (Kirchner et al., 2015) and therefore local combustion processes play a minor role at SBO.

At Austrian low-land sampling sites (Moche and Thanner, 2003), winter/summer ratios of PCDD/F concentrations in the air were in the range of 1.4–7.0; at the mountain site Zöbelboden (900 m a.s.l.), the ratio is 1.6. A connection between cold temperatures and a rise in PCDD/F concentrations in the winter months was found similarly in Baden-Württemberg/Germany (Wallenhorst et al., 1997) and Catalonia/Spain (Parera et al., 2018). In a rural area of Taiwan, the PCDD/F concentration of four seasons from highest to lowest is winter, fall, spring, and summer; ambient air concentration in winter was higher by a factor of 3.4 and 3.9 for total PCDD/F concentration and I-TEQ value (Shih et al., 2006), whereas domestic heating is not found in this region. Around industrial sites in Shanghai, the winter-to-summer ratio of total 2,3,7,8-substituted PCDD/F concentrations was 2.6 due to seasonal variations in sources, environmental processes and meteorology (Die et al., 2015). Compared to these results the winter/summer ratios at the alpine summits of our study are clearly lower.

3.3. Median air concentrations in dependency on air masses

With respect to the time series, there are slight, mostly non-significant concentration differences regarding the four source regions (see Table S1). However, air mass origin was the primary source of the high variability regarding the singular air concentration data, similarly to the results of Sellström et al. (2009).

For some PCDD/F compounds, concentrations were significantly higher when air masses originated in the NE source region compared with those when air masses originated from elsewhere (NW, S, UD). Transport of PCDD/F to the Alpine region may originate directly from anthropogenic emission areas particularly in eastern central Europe (NE) and indirectly from re-emissions from reservoirs in the soil triggered by temperature-enhanced re-volatilization. At the Swiss station (WEI), higher PCDD/F levels in air masses originating from NE for quite all homologue sums could be determined relatively often (Fig. 2). This may be caused by the influence of sources from the adjacent Klosters-Davos area, western Austria, Bavaria, Czech Republic, and Poland. For OCDD and some congeners or sums of PCDF, the situation is similar at the Bavarian site (UFS), where relatively polluted air is transported via Loisach valley from the Munich area, north-western Austria and eastern central Europe. At the highest site in the Central Alps (SBO), which is situated above less densely populated valleys, PCDD/F concentrations in air coming from NE, NW, and UD are rather balanced. In contrast to WEI and UFS, the sum of PCDD/F measured at SBO does not show any significant dependency from one of four source regions in contrast to WEI and UFS. Median TEQ (I-TEF) is significantly higher at WEI with atmospheric transport from NE. No differences between the four source regions have been found in the case of SBO and UFS. However, air masses from the NE source region are significantly less frequent at the three sites than air masses from the other source regions.

Air originating from the Mediterranean region was frequently characterized by the lowest concentrations of PCDD/F. This is in contrast to other POPs, where some organochlorine pesticides (OCPs) are emitted predominantly in the Mediterranean region and other southern regions: Endosulfan and heptachlor concentrations show maximum concentrations at UFS, SBO, and WEI with air masses originating from S (Kirchner et al., 2016). Similarly to PCDD/F and other POPs with (former) industrial and technical use such as pentachlorobenzene, hexachlorobenzene, and pentachloroanisole have higher concentrations with air masses from NE.

Considering the rapid deposition particularly of Penta-to OctaCDD near source areas (Wania and Mackay, 1996) and the complex

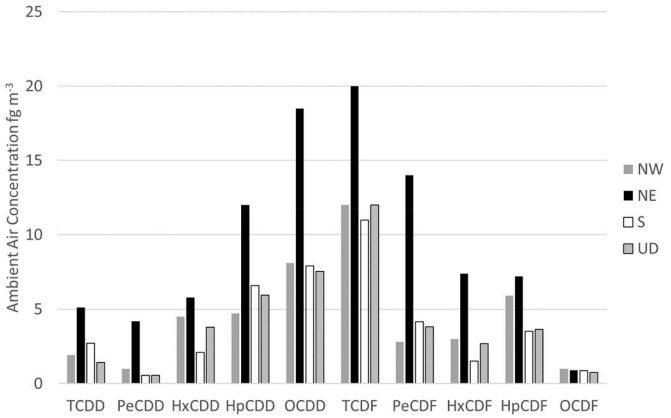

Fig. 2. Comparison of the PCDD/F homologue pattern of median ambient air concentrations at WEI.

long-range transport mechanisms, it is not surprising that differences between the relatively low concentrations of some PCDD/F congeners, such as 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD, for four source regions are relatively small. POPs can be transported directly or through multiple cycles of atmospheric deposition and subsequent volatilization from East-Asia via Russia or North America to Europe (Kirchner et al., 2016). For instance, back-trajectory analysis revealed that relatively high PCDD/F concentrations observed in Alert/Canada in winter 2000/2001 originated from air masses from Russia/Eurasia (Hung et al., 2002, 2010; Sellström et al., 2009).

3.4. Temporal trend of air concentrations

The PCDD/F air concentrations monitored at SBO, WEI and UFS decreased in the first 5 years of our measurements and increased slightly after 2010 (see Table S2). During 2005–2013, the trend was negative for some of the selected substances ($p < 0.10$). But only for a few analytes, a significant negative trend ($p < 0.05$; $p < 0.001$) was identified for this period. Fig. 3 shows the temporal trend for the sum of all measured PCDD/F in ambient air given in TEQ. Only for UFS there is a significant decline in the TEQ over the entire period detectable.

Concerning the single compounds, negative trends were more pronounced at UFS and WEI than at SBO. This may be caused by the different altitudes of three sites and by the fact that global emissions trends play a more important role at SBO as the summit with the highest share of air from the free troposphere. However, after 2013, slightly lower WHO-TEQ concentrations were observed at SBO and UFS in comparison to the first half of the entire dataset.

Since the late 1980s, a generally decreasing trend of PCDD/F air concentrations was observed in Europe (Coleman et al., 1997; EPA, 2013). The winter maxima of 847 air samples collected between April 1989 and March 1999 at different German sites - without special impact from nearby point sources - decreased by 50 percent (BLAG, 2001; Fiedler, 2003). Time series of PCDD/F in ambient air of a large conurbation in Rhine-Ruhr region (Germany) exhibited a pronounced decrease between 1988 and 2011 (Bruckmann et al., 2013); the concentrations in 1988 ranged from 130 to 332 fg TEQ m^{-3}, whereas the levels in 2011 ranged from 17 to 24 fg TEQ m^{-3}. Bruckmann et al. (2013) stated that the abatement measures at the sources have been successful, also because the differences of air concentrations between the stations had nearly vanished. The strongly decreasing trends monitored in Germany in the 1990s are consistent with those noted for UK urban centers and Catalonia/Spain (Katsoyiannis et al., 2010; Abad et al., 2007) and are caused by considerable emission reductions which

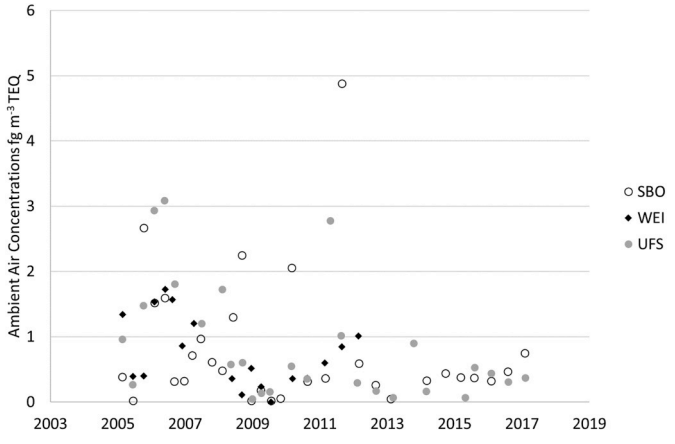

Fig. 3. Temporal trend of mean weighted concentrations in ambient air for total PCDD and PCDF in WHO-TEQ (2005) for Sonnblick Observatory (SBO) and Schneefernerhaus/Zugspitze (UFS) in 2005–2018, and Weissfluhjoch (WEI) in 2005–2013.

may also be a result of the implementation of the POP protocol (EMEP, 2015; van der Gon et al., 2007). According to the information of countries which are part of EMEP (European Monitoring and Evaluation Programme), anthropogenic emissions have decreased from 1990 to 2012 by 60% for PCDD/F. Maximum decrease in annual mean air concentrations of PCDD/F occurred in the beginning of this period, while at the end of this period concentrations levelled off (EMEP, 2015). For Catalonia/Spain a decrease of about 66%–68% between 1994 and 2015 is reported for industrial and traffic sources, whereas slight increases are reported for background sites (Parera et al., 2018). This observation fits very well to our results and indicates that concentrations of PCDD/Fs in ambient air have become more similar between industrial and rural sites in Europe. This supports the conclusion of Dopico and Gómez (2015) that non-industrial sources such as biomass burning and heating have become relevant sources, since abatement activities have mainly reduced emissions of industrial sources.

3.5. Source contributions

In order to estimate source contributions from the observed congener-patterns in ambient air, the EPA Positive Matrix Factorization 5.0 tool was used (EPA-PMF, USEPA, 2014). The four source regions NW, NE, S, and UD were treated separately, whereas the samples of the three measurement stations were merged, in order to have a sufficient high amount of data for statistical evaluation. The merging of data of the three stations is justified because the four source regions are defined for all of them in the same way. With EPA-PMF the time frame from 2005 till 2015 was evaluated, for which distinct datasets on the four source regions are given. At minimum, the input-datasets encompassed 17×61 data points (17 congeners and 61 samples). For the equation-based uncertainty the average limit of detection was used for each congener and an estimated error of ten percent. Missing samples were replaced by the congener median. Concerning the signal-to-noise-ratio of the statistical approach (S/N) of each congener, we excluded congeners with S/N smaller than 0.5 by marking them as “bad”. Congeners with S/N smaller than 1.5 were included to the calculation as “weak”. To execute the PMF in order to calculate the PMF-factors, we used 20 iterations by using a number of 6 contributing factors, expecting contributions from waste incineration, steel production, forest fire, coal burning and heating, traffic, and one undefined source. Congener patterns of the calculated PMF-factors were compared with congener patterns from the literature to estimate the contribution from different sources (Alcock et al., 1998; Aristizábal et al., 2011; Castro-Jiménez et al., 2008; Colombo et al., 2009; Colombo et al., 2013; Coutinho et al., 2015; Denys et al., 2012; Gullett and Touati, 2003; Gunes and Saral, 2014; Hagenmaier et al., 1994; Li et al., 2010; Lin et al., 2007; Mosca et al., 2012; Wang et al., 2013). If no clear pattern could be distinguished for PMF-factors, the unclear PMF-factors were merged into one which we depicted “undefined”.

Up to five contributing sources for PCDD/F in ambient air at the high alpine monitoring stations could be distinguished by applying the EPA-PMF. Fig. 4 depicts the estimated contributions for the investigated source regions.

As a dominant source of PCDD/F we distinguished domestic heating and coal burning, which was characterized by high concentrations of OCDD, 1,2,3,4,7,8,9-HpCDF and OCDF (Lin et al., 2007; Denys et al., 2012). This source contributed between 24 and 34 percent of PCDD/F ambient air concentrations.

Another dominant source was waste incineration, where we observed two slightly different patterns: Both patterns of waste incineration are characterized by high concentrations of 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD and 1,2,3,4,6,7,8-HpCDD. However, one waste incineration pattern named “waste incineration 1” did not additionally show high concentrations OCDD which is fitting to a signature for waste incineration reported by Colombo et al. (2009). The other waste incineration pattern “waste incineration 2” includes high concentrations of

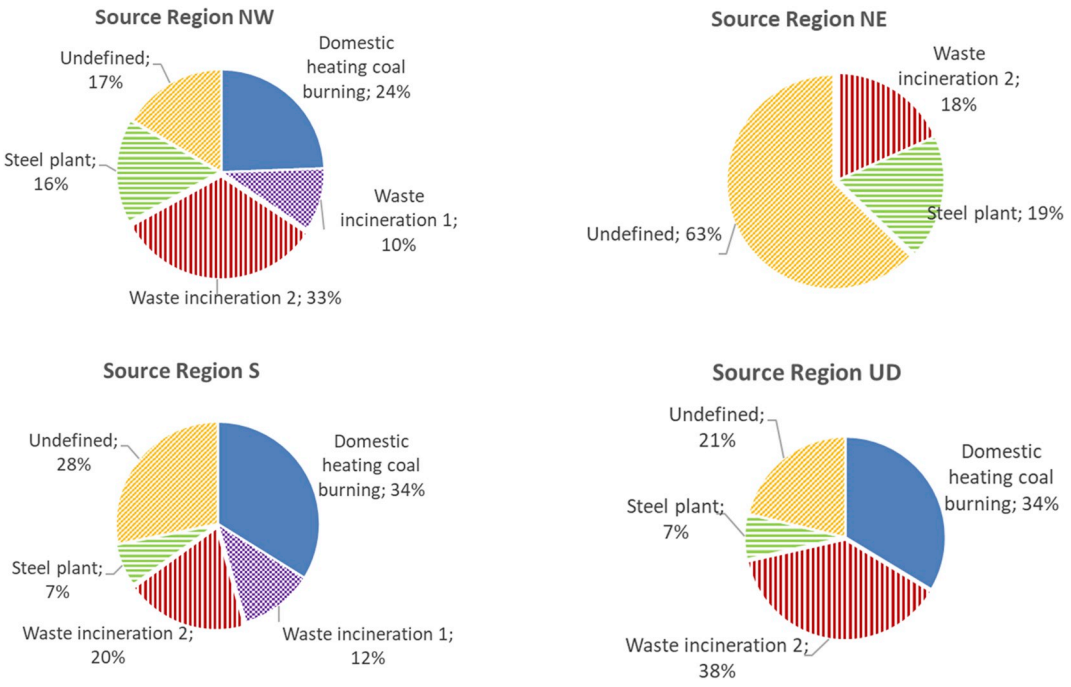

Fig. 4. Source contribution calculated by EPA-PMF for ambient air concentrations of PCDD/Fs.

OCDD which mirrors emissions from municipal waste incineration reported by Wang et al. (2013). Both waste incineration patterns together contributed between 18 and 43 percent of PCDD/F concentrations.

The third dominant source pattern which was elaborated by the EPA-PMF was characteristic for steel plants, where high concentrations of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF are indicative (Colombo et al. 2009, 2013; Coutinho et al., 2015). The emissions from steel plants contributed around 7 percent for the source regions S and UD, and 16 to 19 percent for the source regions NW and NE.

Using the EPA-PMF we were not able to attribute between 17 and 63 percent of PCDD/F ambient air concentrations to a specific source. These undefined sources did not show explicit characteristics in their congener profiles and may represent long-range atmospheric transport (LRAT) of a mixture of different sources.

Comparing the four source regions, it shows that the source regions NW, S, and UD show surprisingly similar patterns of source contributions. Only the source region NE is characterized by a huge proportion of 63 percent of PCDD/F ambient air concentrations which cannot be attributed to a specific source.

3.6. Deposition: range, seasonality and trend

Concerning the sum of PCDD/F, medians of bulk deposition rates were significantly different between the three sites ($p < 0.05$) with 321 pg $m^{-2}d^{-1}$ at SBO, 72 pg m^{-2} d^{-1} at UFS, and 30 pg m^{-2} d^{-1} at WEI. The median deposition rates of PCDD/F - calculated in TEQ values (WHO, 2005) - were 2.2, 0.8 and 0.14 pg TEQ m^{-2} d^{-1}, respectively.

Using a Spearman rank correlation, deposition fluxes at SBO and UFS show a weak but significant positive correlation for TEQ ($R = 0.503$, $p < 0.01$) and Sum PCDD/F ($R = 0.395$, $p < 0.05$). This indicates similarities of PCDD/F deposition fluxes at these two sites. However, as established by other studies in Europe for instance Ispra/Lago Maggiore in Northern/Italy (Castro Jimenez et al., 2012), our results show a high temporal variability of the PCDD/F atmospheric deposition fluxes (Fig. 5).

Deposition is dominated in the majority of the samples by the higher chlorinated congeners (see Table 2). The sum of HpCDD, OCDD, HpCDF, and OCDF accounts for 42–97% (Median 74%) of the sum of PCDD/F. Most dominant is OCDD which on its own accounts for 18–75% (Median

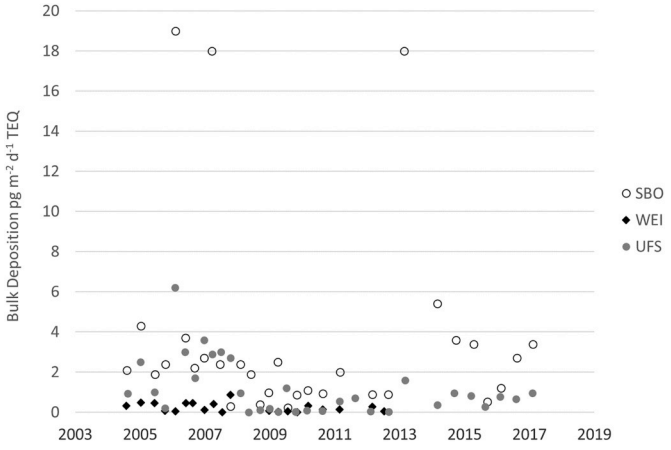

Fig. 5. Bulk deposition rates of PCDD/F in TEQ (WHO, 2005) at Sonnblick Observatory (SBO) in 2005–2018, Weissfluhjoch (WEI) in 2005–2013, and Schneefernerhaus/Zugspitze (UFS) in 2005–2018.

48%) of the sum of PCDD/F.

At SBO, extremely high deposition rates for Sum PCDD/F (4037 and 6439 pg m^{-2} d^{-1}) were monitored during two periods (11/2006–3/2007 and 1/2008–4/2008, respectively). These high values do not coincide neither with high air concentrations at SBO nor with high deposition rates at WEI and UFS. The pattern of the two samples with extremely high deposition rates are characterized by a high amount of higher chlorinated congeners (92% and 95%). The most dominant congeners of these two events are OCDD (with 2800 and 4700 pg m^{-2} d^{-1}) followed by 1,2,3,4,6,7,8-HpCDD (with 550 and 800 pg m^{-2} d^{-1}), OCDF (with 130 and 94 pg m^{-2} d^{-1}) and 1,2,3,4,6,7,8-HpCDF (with 71 and 68 pg m^{-2} d^{-1}). This fingerprint suggests LRAT with no indication of nearby emission sources (Castro-Jimenez et al., 2010; Castro-Jimenez et al., 2017).

The sum of 2,3,7,8-PCDD/F, which is not reported in Table 2, ranged between 10.2 and 5742 pg m^{-2} d^{-1} at SBO and is comparable to the deposition flux at Ispra/Lago Maggiore were the total PCDD/F-TEQ

Table 2
Bulk deposition rates of PCDD/F at Sonnblick Observatory (SBO) and Schneefernerhaus/Zugspitze (UFS) in 2005–2018, and Weissfluhjoch (WEI) in 2005–2013; Ranges (maximum-minimum), medians and winter to summer ratio calculated on the basis of medians (including outliers).

Compound	SBO			WEI			UFS		
	Range pg m^{-2} d^{-1}	Median pg m^{-2} d^{-1}	Winter to summer ratio (medians) *p < 0.05	Range pg m^{-2} d^{-1}	Median pg $m^{-2}d^{-1}$	Winter to summer ratio (medians) *p < 0.05	Range pg m^{-2} d^{-1}	Median pg m^{-2} d^{-1}	Winter to summer ratio (medians) *p < 0.05
2,3,7,8-TCDD	n.d.-0.4	0.1	–	n.d.-n.d.	n.d.	–	n.d.-0.4	n.d.	–
1,2,3,7,8-PeCDD	n.d.-4.0	0.7	2.3*	n.d.-0.3	n.d.	–	n.d.-1.2	0.2	1.0
1,2,3,4,7,8-HxCDD	n.d.-5.6	0.8	1.5	n.d.-0.5	n.d.	–	n.d.-2.8	0.3	1.5
1,2,3,6,7,8-HxCDD	0.3–16.0	1.7	1.6	n.d.-0.8	n.d.	–	n.d.-7.4	0.6	1.1
1,2,3,7,8,9-HxCDD	0.5–10.0	1.5	1.4	n.d.-0.3	n.d.	–	0.1–5.6	0.8	1.4
1,2,3,4,6,7,8-HpCDD	0.8–800	32.5	1.3	n.d.-14.0	3.3	1.7	1.3–54.0	13.0	1.3
OCDD	3.2–4700	140	0.9	n.d.-n.d.	11.5	1.3	1.5–120	30.5	1.4
Sum TCDD	n.d.-16.0	1.4	2.3*	n.d.-11.0	n.d.	–	n.d.-43.0	1.6	3.9*
Sum PeCDD	n.d.-38.0	3.5	2.2*	n.d.-1.1	n.d.	–	n.d.-29.0	2.0	2.0*
Sum HxCDD	1.7–100	13.5	1.8*	n.d.-3.8	1.0	3.4*	0.5–69.0	7.9	1.3
Sum HpCDD	3.2–1200	54.5	0.8	n.d.-25.0	5.5*	1.4	0.4–83.0	16.0	0.8
2,3,7,8-TCDF	n.d.-5.7	1.1	1.4	n.d.-1.7	0.4	0.5	0.3–8.6	0.6	1.0
1,2,3,7,8-PeCDF	n.d.-5.6	0.7	1.4	n.d.-0.6	n.d.	–	n.d.-1.3	0.3	1.1
2,3,4,7,8-PeCDF	0.2.-14.0	1.2	1.4	n.d.-0.6	n.d.	–	n.d.-2.8	0.8	1.4
1,2,3,4,7,8-HxCDF	0.4.-22.0	2.1	1.7	n.d.-1.0	0.2	1.5	0.2–6.1	0.7	1.4
1,2,3,6,7,8-HxCDF	0.3–16.0	1.2	1.2	n.d.-1.0	n.d.	–	n.d.-4.5	0,5	1.2
2,3,4,6,7,8-HxCDF	0.1–20.0	1.1	1.4	n.d.-0.7	n.d.	–	n.d.-5.7	0.5	1.5
1,2,3,7,8,9-HxCDF	n.d.-1.8	0.1	1.8*	n.d.-n.d.	n.d.	–	n.d.-0.4	0.1	–
1,2,3,4,6,7,8-HpCDF	1.5.-72.0	9.2	1.6	n.d.-3.0	1.2	0.6	0.8.-25.0	1.9	1.1
1,2,3,4,7,8,9-HpCDF	0.1–20.0	1.5	1.5	n.d.-0.2	n.d.	–	n.d.-3.1	0.2	2.4*
OCDF	1.2–130	13.0	0.8	n.d.-2.5	0.3	1.0	1.1–9.6	2.5	0.9
Sum TCDF	0.9–83.0	18.0	1.5	n.d.-6.8	2.4	1.1	0.6–38.0	8.7	1.3
Sum PeCDF	1.1–120	13.0	1.5	n.d.-4.7	1.5	2.0	0.6–25.0	6.7	1.4
Sum HxCDF	1.8–150	11.0	1.3	n.d.-2.9	1.3	0.7	0.7–31.0	4.4	1.4
Sum HpCDF	1.5–130	11.0	1.9*	n.d.-5.3	2.3	1.0	0.4.-35.0	5.3	1.3
Sum PCDD	**8.7–6040**	**240**	**0.9**	**n.d.-110**	**18.0**	**1.3**	**5.0–278**	**44.0**	**1.2**
Sum PCDF	**8.3–466**	**60.0**	**1.2**	**0.6–16.8**	**8.4**	**0.9**	**2.8–117**	**24.0**	**1.3**
Sum PCDD/F	**17.0–6439**	**321**	**0.9**	**1.0–120**	**30.0**	**1.2**	**15.0–369**	**72.0**	**1.7***
TEQ (I-TEF)	**0.3–22.5**	**2.5**	**1.5**	**n.d.-0.9**	**0.2**	**1.7**	**n.d.-6.2**	**0.9**	**1.4**
TEQ (WHO, 2005)	**0.2–19.0**	**2.2**	**1.6**	**n.d.-0.9**	**0.14**	**1.7**	**n.d.-6.2**	**0.8**	**1.3**

deposition flux monitored during one week was 20 pg TEQ m^{-2} d^{-1} in 2005 (Castro-Jiménez et al., 2008).

In contrast to air concentrations, the deposition rates determined in our study differ less than 1–2 orders of magnitude from deposition rates at lowland or urban sites and are partly in the same magnitude as measurements performed closer to sources. At an urban background site and two rural sites in Bavaria, one in the sub-alpine region, the medians of PCDD/F deposition rates were in the range of 1.7–5.2 pg WHO-TEQ $m^{-2}d^{-1}$ in 2002–2003 (Bayerisches Landesamt für Umwelt, 2006). Urban background deposition rates of PCDD/F of about 10 pg TEQ m^{-2} d^{-1} were found for North-Rhine Westphalia/Germany (Landesanstalt für Umweltschutz Baden-Württemberg, 2004). These deposition rates are almost comparable with the deposition of 5–10 pg WHO-TEQ $m^{-2}d^{-1}$ at the remote site Eifel/Germany (Bruckmann et al., 2013). The total PCDD/F-TEQ deposition flux monitored into Lake Maggiore/Italy during one week in 2005 was 20 pg TEQ m^{-2} d^{-1} (Castro-Jiménez et al., 2008). The bulk deposition of PCDD/F measured at three forest sites in Denmark was in the range of 2.2–3.3 pg TEQ m^{-2} d^{-1}; the low variation indicates that PCDD/F have been distributed in the air masses during long-range atmospheric transport (Hovmand et al., 2007). For Japan, deposition rates of 30.1–45.6 and 15.6 pg TEQ m^{-2} d^{-1} were measured in urban and mountain areas, respectively (Ogura et al., 2001). At Lulin/Taiwan, an atmospheric background station (2862 m a.s.l.), the deposition of PCDD/F amounted to 0.7 pg TEQ m^{-2} d^{-1} (Suryani et al., 2015). The total daily dry and wet deposition flux of PCDD/F-TEQ measured in two cities of Northern China in 2014 was in the range of 15–70 pg m^{-2} (Zhu et al., 2017).

The sum of PCDD/F tends to decrease significantly at UFS and WEI, while WHO-TEQ are declining significantly at UFS only (see Table S3). The deposition rates of the single PCDD/F congeners declined more at UFS than at WEI and SBO.

The decline of the deposition rates of many PCDD/F compounds is pronounced during the first seven years until 2012. After 2012 we observe a quite constant level or even a slight increase. Particularly at SBO the increase after 2010 is pronounced and there is no trend to lower deposition rates detectable if the whole period from 2005 to 2018 is considered. For UFS and WEI slightly decreasing trends could be found for the entire period from 2005 to 2018 and 2005–2015, respectively. Fig. 5 shows the temporal trend of deposition of the sum of PCDD/F for the three monitoring stations.

Within the framework of the European Monitoring and Evaluation Programme (EMEP), PCDD/F deposition decreased more than twice

since 1990 (EMEP, 2015). Their analysis indicated that for the Netherlands the reduction of deposition flux from 1990 to 2012 occurred mainly in the beginning of this period and was driven by the reduction of national emissions for PCDD/F. Bruckmann et al. (2013) stated for North-Western Germany, that in parallel to the air concentrations the deposition rates also decreased considerably within the last two decades. However, the decrease of PCDD/F deposition at the remote site Eifel was less pronounced than at sites in urban centers, as important local sources are lacking and the levels are dominated by LRAT. At the Eifel site, the WHO-TEQ deposition revealed a decline by 50%, whereas at the city of Dortmund the deposition of PCDD/F decreased by 75% since 1990.

4. Conclusions

The developed air sampling strategy comprising four filter cartridges, which were selected based on trajectory forecast by remote control, worked satisfactory and with a high accuracy with regard to source regions. The sampling campaign showed that air masses with higher PCDD/F concentrations arrived preferably from the northeast region, but due to the lower arrival frequency of air masses from that region their impact on the Alps is of less importance. Thus, none of the predefined source regions is a predominant PCDD/F source for the Alps.

A clear time trend with decreasing air concentrations could be found from 2005 until 2010, but since 2010 the concentrations are increasing again, especially for the most eastern summit (Sonnblick Observatory) where they reach concentrations which are even higher than in 2005. Thus, over the entire sampling period no overarching time trend could be detected. We conclude that the main reduction in PCDD/F ambient air concentrations over Europe happened due to emission reduction measures prior to the start of this monitoring project. The found ambient air concentrations and deposition rates reflect the current situation with nearly unchanged emissions during the last decade.

Source contribution of measured ambient air concentrations revealed that for the source regions northwest, south, and undefined, waste incineration, heating and coal burning contributed about two thirds of measured concentrations. Only the source region NE showed a distinct pattern where more than half of the measured concentrations could not be assigned to a distinct source and a larger proportion of steel plants played a role.

The most surprising finding was that deposition rates at the mountainous sites are almost in the same range as in rural lowlands and closer to sources. This was astonishing because the detected ambient air concentrations were one to two orders of magnitude lower than ambient air concentrations found in rural lowlands. A possible explanation for this finding are the higher precipitation rates at the mountainous sites on the one hand and on the other hand the fact that due to the low temperatures the majority of precipitation falls as snow, which has a different scavenging effect than rain. In regard to these findings the question arises if ambient air concentration or deposition measurements give the more accurate picture of the environmental load concerning PCDD/F and POPs in general. Within the Global Monitoring Plan of the Stockholm Convention which has been ratified by all Alpine countries except Italy (Qu et al., 2019) it is foreseen that ambient air concentrations are used to evaluate the POP input into the environment. However, as shown in the present study, ambient air concentrations are not directly proportional to site specific deposition rates. Therefore, it should be discussed if deposition measurements are a necessary component of long-term monitoring in order to assess the environmental burden of POPs, at least at sites with extreme weather conditions such as the Alps or the Arctic.

To investigate the impact of the measured deposition rates on bioaccumulation of PCDD and PCDF in the food-web of the alpine biosphere, two projects entitled PureAlps have been motivated by the present study. These projects are carried out from 2016 to 2020 by the Bavarian Environment Agency in the surroundings of Mt Zugspitze and by the Environment Agency Austria in the National Park Hohe Tauern in vicinity of the Sonnblick.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

M. Kirchner: Writing - original draft, Formal analysis, Investigation. **K.P. Freier:** Writing - review & editing, Formal analysis, Investigation, Funding acquisition, Project administration. **M. Denner:** Funding acquisition, Project administration. **G. Ratz:** Investigation. **G. Jakobi:** Investigation. **W. Körner:** Investigation, Validation. **E. Ludewig:** Project administration. **M. Schaub:** Conceptualization, Project administration. **K.-W. Schramm:** Conceptualization, Validation, Project administration. **P. Weiss:** Conceptualization, Funding acquisition, Project administration, Validation. **W. Moche:** Conceptualization, Methodology, Resources, Investigation, Writing - review & editing, Validation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.117199.

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