3 Monitoring of persistent pollutants at the UFS

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Fig. 1: Measurement equipment at the UFS for sampling ambient air and deposition for the detection of persistent organic pollutants. Picture: KF, LfU

3.1 Summary

At the UFS, levels of persistent organic pollutants (POPs) in ambient air and deposition are determined since 2005. The results of these monitoring activities contribute to international control and regulation of such chemicals.

POP are emitted from anthropogenic burning, industrial processes or products, and are characterized by four properties: They are resistant to environmental degradation through chemical, biological, and photolytic processes, they are prone to bio-accumulate, and they are toxic to wildlife and humans. Moreover, most of these pollutants are semi-volatile and can be transported globally through the atmosphere in gaseous phase or attached to aerosols.

Monitoring devices are active air samplers characterized by low volume (30 L/min) and high volume (100 L/min) throughput and heated bulk deposition samplers. The samplers are equipped with filters and trapping cartridges, employing adsorbents which are conditioned to capture the target substances.

At intervals of three months, the sampling-cartridges are exchanged and analysed in laboratories. Gas chromatography coupled to mass spectrometry in combination with a stable isotope dilution analysis (SIDA) enables the accurate determination of the content of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and halogenated flame retardants (HFRs).

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Results indicate the importance of cold-condensation effects. Even though air concentrations at the alpine summits are up to two orders of magnitude lower than in urbanized regions, deposition rates are similar or only slightly lower. Hence, to determine the impact of persistent chemicals into mountain-ecosystems the measurement of bulk deposition is essential. Source regions of the measured POPs can be identified as regional and global.

The monitoring enables a control of international chemical's legislation. It shows that concentrations in air for about 30 % of OCP and several brominated flame retardants have been decreasing since 2005. However, for the majority of the pollutants significant reductions cannot be observed. For emerging compounds, the results proof the potential for persistency and long-range transport and show that regulation of individual chemicals often causes a substitution by chemicals which may have similar problematic properties.

3.2 The relevance of chemicals monitoring in the Alps

In an industrialized world, the unspoiled nature of the Alps and its sensitive ecosystems are no longer guaranteed. Air currents carry persistent organic pollutants (POPs) that originate from sources all over the globe into the Alpine region. Moreover, the Alps are located in the heart of Europe, one of the most industrialized and agriculturally active regions in the world. Due to the cooler temperatures in the Alps, pollutants can be deposited via condensation effects. In addition, the Alps act as a meteorological barrier: the accumulation of air masses causes the highest rainfall in Europe, which also scavenges pollutants from the air.

Especially for the Alps with unique ecosystems and a high biodiversity, the early detection of inputs of problematic substances is important. In addition, high-quality food and feed products originate from the Alps and a significant part of the regional and supra-regional water supply in Bavaria, Austria, Switzerland, northern Italy, Slovenia and the South of France relies on a high environmental quality in the Alps.

Substances that combine persistent, bioaccumulative and toxic properties (PBT) are particularly critical for humans and the environment:

Tab. 1: PBT-Characteristics

P	Persistency: The substance is persistent in the environment, so it is hardly degradable. Neither chemical-physical nor biological processes in water, soil or air are able to decompose the substance to any significant extent. The degradation is particularly difficult in cold climates.
B	Bioaccumulation: The substance is bioaccumulating. It prefers to concentrate in the tissue of living organisms. The reason for this is usually the solubility in fat of the substances and the lack of the possibility of excretion. Bioaccumulative substances accumulate strongly via the food chains, which also means that the pollutants occur in higher concentrations in particularly sensitive media, such as breast milk.
T	Toxicity: The substance is toxic to organisms. The toxicity of the substances depends mainly on their concentration and the duration of their action; in the case of carcinogenic or mutagenic substances, it is considered that a threshold cannot be established.

Into the environment, POP are emitted for example as active ingredients of pesticides or unintentionally, for example as by-products in combustion processes. Of all chemicals produced worldwide, more than 2,000 substances have the potential for PBT properties, which equates to several million tonnes per year of produced quantities (Scheringer et al., 2014).

Most of these chemicals remain where they are used as they have a low evaporation pressure and a low tendency to enter the atmosphere. However, the escape of very small amounts from products into the ambient air already leads to globally measurable contaminations. Contaminants from combustion processes, such as PCDD/Fs or PAHs, are directly emitted into the atmosphere.

The distribution of pollutants takes place via air currents and is coupled to the water cycle. Higher concentrations can be measured near the sources. However, because of their longevity and atmospheric long-range transport, pollutants reach remote areas. There, they can accumu-

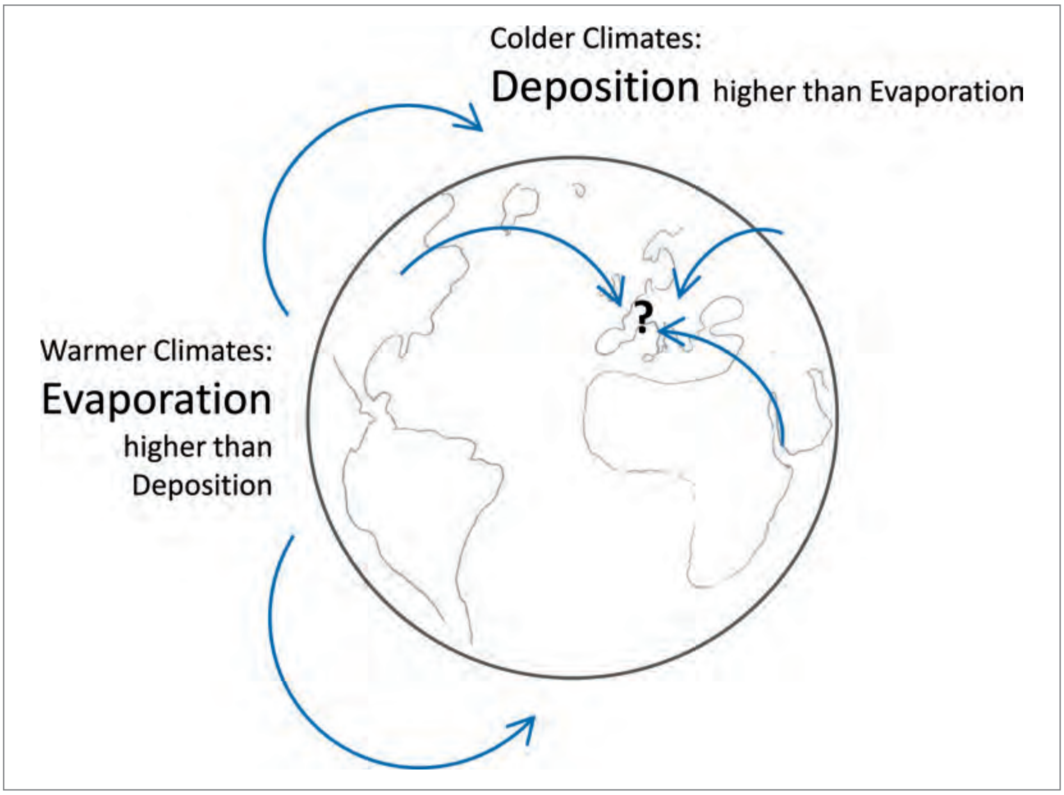

Fig. 2: Unevenly distributed temperatures over the globe lead to the phenomenon of "global distillation" (Wania and Mackay, 1996) at the poles and "cold trapping" in mountain areas such as the Alps. Source: KF, LfU

late through increased condensation, especially in cool regions such as the poles, where deposition is greater than evaporation ("global distillation", see Fig. 2). Therefore, PBTs are detected even in areas where they have never been produced or used, such as in the Arctic or Antarctic.

Mountain ranges in the mid latitudes such as the Alps can be regarded as further hot-spots of deposition because they are located in the same latitudes as the sources but local temperatures are considerably lower and precipitation rates are in many cases higher. A comparison of the atmospheric loads of POPs in the Alps with those of the surrounding regions, shows that the alpine soils (see Fig. 3) are a considerable sink for POPs, which are mainly emitted from regions outside of the Alps (Belis et al., 2009). This indicates that the phenomenon of a cold trap is an underlying mechanism for the deposition in the Alps.

Fig. 3: The contents of POPs in the alpine soils indicate that from a global perspective the Alps are a sink of pollutants. Even if the concentration levels in the soils are at the lower range compared to other comparable soils in central Europe, the Alps cannot be regarded as uncontaminated. Picture: Robert Traidl, LfU

For most chemicals, the principle applies that a harmful effect begins at a certain concentration. However, if a pollutant does not degrade and additionally accumulates through the food chain, it is often only a matter of time before problematic concentrations in organisms are reached.

To cope with this risk on a precautionary basis, pollutants must already be recorded when entering ecosystems from the air. For this reason, to protect Alpine ecosystems, a monitoring of atmospheric concentrations and depositions rates of POPs was established in 2005 for the Alpine region under the project MONARPOP (Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants, Federal Ministry of Agriculture, Forestry, Environment and Water Management, 2009). Up to date, this POPs monitoring is continued at the UFS and in parallel at the Sonnblick Observatory (SOB) in Austria within the projects called PureAlps (till 2015 also the monitoring station at Weissfluhjoch/Switzerland was part of the projects). Considering a mountain range in the mid latitudes, the gathered time series are worldwide unique in their duration and extent.

If new POPs are detected in the environment, only international measures are able to diminish concentration levels and deposition loads substantially. Additionally, regulated POPs need to be regularly monitored in order to evaluate if the applied measures are effective in reducing loads. With its results, the monitoring at the UFS delivers important data on emerging and well known POPs. This contributes to the further development and effectivity control of chemicals legislation such as REACH[4] of the European Union and the international Stockholm Convention on POP.

3.3 Active sampling of persistent pollutants in ambient air

Ambient air samples are taken at the UFS in order to be analysed for a huge number of individual POPs (see Table 2). These include PCDD/Fs, PCBs, OCPs, PAHs and HFRs.

Tab. 2: Chemicals which are focus of the monitoring

Class of substances	Examples	Sources
Organochlorine pesticides (OCP)	DDT and derivatives Lindane Hexachlorobenzene Endosulfane	Insecticide Insecticide and wood preservatives Fungicide and combustion processes Insecticide
Polycyclic aromatic Hydrocarbons (PAH)*	Benzo [a] pyrene Phenanthrene	Combustion processes
Polychlorinated dibenzo-p-dioxins and dibenzo-furans (PCDD/F)	2,3,7,8-TCDD (Seveso dioxin)	Combustion processes and by-product of chemical syntheses
Polychlorinated biphenyls (PCB)	PCB 126 (dioxin-like PCB) Indicator PCB: PCB 28, 52, 101, 138, 153, 180	Plasticizer, flame retardant, insulating oil, combustion processes
Halogenated flame retardants (HFR)*	Polybrominated diphenyl ethers (PBDE), e.g. DecaBDE, Hexabromocyclododecane (HBCD), Decabromodiphenylethane (DBDPE)	Flame protection in plastics and textiles Flame protection in building-insulation Substitute for decabromodiphenyl ether
Perfluorinated surfactants*# and Fluorotelomer alcohols*	Perfluorooctanoic acid (PFOA)	Water-repellent coatings
Mercury*#		Chloralkali electrolysis, combustion of stone and Brown coal

* substances marked with an star have not been continuously measured since the beginning of the monitoring or are only part of focus projects such as POPAlp, EMPOP and PureAlps

\# substances marked with an hash are only measured in deposition

Most POPs are semivolatile organic compounds (SVOCs) with a vapour pressure between 10 Pa and 10^{-5} Pa at thermodynamic standard temperature (25 °C), representing a range of boiling temperatures from 240–260 °C to 380–400 °C, at standard atmospheric pressure. In spite of their low vapour pressures SVOCs occur in the atmosphere at least partially in the gaseous phase. Any distribution ratio from 100 % in the gaseous phase to complete attachment to aerosols is possible depending on the vapour pressure of the compound, ambient air temperature and aerosol concentration. Therefore, any sampling method for the assessment of ambient air concentrations of POPs must collect total suspended aerosols as well as the POPs in the gaseous phase.

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[4] Registration, Evaluation, Authorisation and Restriction of Chemicals

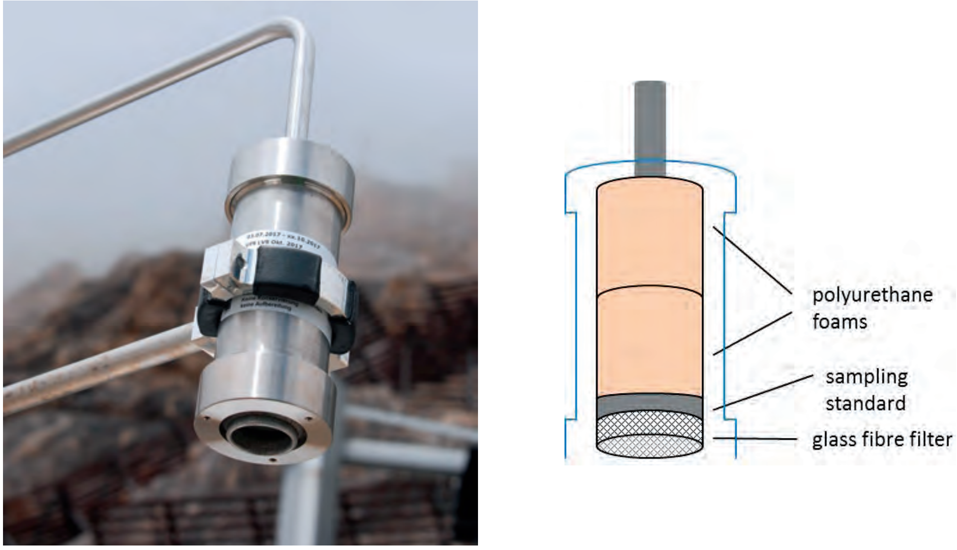

Fig. 4: Filter cartridge for sampling halogenated flame retardants (left) and sketch depicting the assembly. Picture: KF, LfU

For this purpose ambient air is continuously sucked by a pump unit through a sampling cartridge equipped with a glass fibre filter at the open side at the bottom to collect the particulate air components (Fig. 4). The used filter has a separation ratio of 99.8 % for particles with aerodynamic diameters > 0.3 µm (VDI 2464 part 2). After passing the glass fibre filter, gaseous air components of organic compounds boiling at high temperatures are adsorbed on the surface of a hydrophobic material. This adsorbent should have a large surface area and a high porosity with low resistance to the air flow and is packed in a sleeve made either of glass or stainless steel.

In the samplers at UFS, two different materials are used: In the cartridges for the OCP samples a granulate of styrene-divinylbenzene-copolymer (XAD-2 resin), packed into a glass sleeve, is used as described in detail in the German guideline VDI 2464 part 4.

For assessing ambient air concentrations of HFRs, PCDD/Fs and PCBs the sampling cartridge is equipped with a steel sleeve with two cylindric polyurethane foams with open pores, according to the guideline VDI 2464 part 3 (see Fig. 1, foams: height: 50 mm, diameter: 60 mm) for HFRs and VDI 3498 part 1 for the PCDD/F and PCB. The PU foams are made of toluylenediisocyanate (TDI) and polyoxypropylentriol with a density of 25 kg/m^3 or TDI polyether soft foam with a density of 33 kg/m^3.

Sampling of ambient air concentrations is done separately concerning the classes of substance (a) PCDD/Fs and PCBs, (b) OCPs and PAHs, and (c) HFRs. The measured volumes are all referred to standard conditions of 0 °C and 1013.25 hPa.

For PCDD/Fs and PCBs, due to very low target concentrations of femtograms per cubic meter ambient air, a high volume sampler (HVS) is used, which is operated at a flow rate of 100 L min^{-1} (6 m^3 h^{-1}). Due to the pressure drop which is caused by the air drawn into the cartridge, under the high-alpine meteorological conditions at UFS, water vapour is condensating and immediately freezing. To prevent this effect, the filter cartridges are equipped with heated inlet tubes to avoid freezing (Fig. 5).

For OCPs/PAHs and HFRs low volume samplers (LVS) are used with a flow rate of 30 L min^{-1} (1.8 m^3 h^{-1}). The sampling is done separately for OCPs and HFRs in order to obtain two separated samples, because extraction, clean-up and measurement are performed separately for these two classes of POPs. The sampling of OCPs follows the guideline VDI 2464 part 4 and the sampling of HFRs is performed according to VDI 2464 part 3.

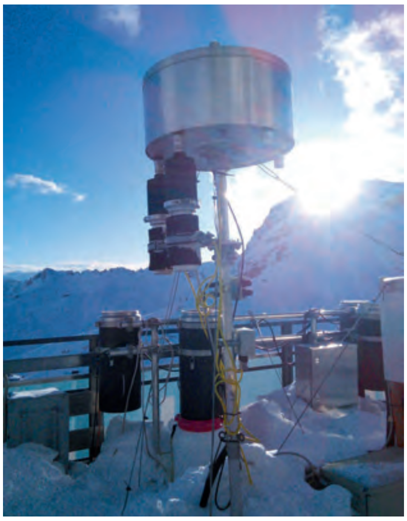

Fig. 5: In the front/top: Filter cartridges for sampling PCDD/Fs which are equipped with heated inlet tubes to avoid freezing (the mouth of the sampling system facing downward). Behind: Funnel adsorber deposition samplers. Picture: GR, LfU

Prior to use, all sampling materials must carefully be cleaned to avoid any contamination with the compounds to be determined: Glass fibre filters are heated for at least 5 h to 450 °C, then wrapped in aluminum foil and stored in a closed wide-neck flask until used for sampling. XAD-2 resin and PU foams are generally precleaned by extraction with those solvents which are used to extract the POPs of interest after sampling. Although it is strongly recommended to purchase high purity XAD-2 resin, precleaning of the whole glass sleeve filled with XAD-2 resin by Soxhlet extraction with acetone/n-hexane 1/3 (v/v) is necessary for the analysis of OCPs (VDI 2464 part 4).

Nevertheless, for each series of air samples or each single sample a corresponding field blank sample cartridge must be prepared in exactly the same way as the sample cartridge(s), transported to the sampling site, briefly opened to simulate the exchange of a cartridge, and stored closed in the darkness (e.g. wrapped in aluminum foil) either at the sampling site or in a refrigerator in the laboratory during the whole sampling period. Afterwards this field blank sample is processed and analysed in parallel to the corresponding air sample(s) in the same way to detect and quantify possible field blank values of the pollutants of interest.

If a field blank value is quantifiable, the limit of quantification (LOQ) is twice the field blank value referred to the sampling volume of each corresponding sample (VDI 2464 part 3). To be accepted as quantifiable, the value (absolute mass) of a compound in an air sample must be at least twice the corresponding field blank value.

By using automated control-units (DPA 96 MV, DIGITEL Elektronik GmbH, Austria) which are accessible via internet, the daily status of the HVS and LVS is controlled remotely. In the same way the throughput of air and additional metadata can be downloaded at the end of each sampling period.

In order to investigate the characteristics of different air masses, the HVS and LVS are equipped with a multi-channel system which can be used to sample four cartridges in one sampling period. For example, between 2006 and 2015 three predefined source regions have been investigated: northwest (NW), northeast/east (NE) and southwest/south/southeast (S). If the origin of the air masses was unspecified or was prevailing less than three days in one of the regions, it was classified as undefined and a fourth cartridge was used (UD) (Kirchner et al., 2016). The four available channels were selected on a daily basis after including the results of meteorological calculations using the FLEXPART model. The channel selection can be done automatically using computing-on-demand for the FLEXPART calculation and a subsequent upload of control commands to the automated control-units of the HVS and LVS.

3.4 Sampling of persistent pollutants in deposition

Deposition is the transfer of particles and molecules from the atmosphere to solid and liquid surfaces and thus a main pathway for the entrance of airborne persistent pollutants into terrestric and aquatic ecosystems. Atmospheric deposition occurs predominantly in precipitation periods (wet deposition) but as well during dry weather conditions (dry deposition). In theory, atmospheric deposition is the sum of deposition consisting of gases which adsorb to surfaces, gases which are dissolved in precipitation, non-sedimenting particles which are scavenged by precipitation and sedimenting particles. In practice, a bulk deposition sampler does not completely cover the atmospheric deposition, but collects fractions of it, such as the gases which are dissolved in precipitation, the particles which are scavenged by precipitation and the major fraction of sedimenting particles.

One of three established sampling methods for bulk deposition of persistent organic pollutants is the funnel adsorber method which is standardized for PCDDs/PCDFs (VDI 2090-2) and low volatile PAHs (VDI 4320-4). These guidelines recommend an exposure period of 30 days.

To sample deposition of POPs under extreme climatically conditions, specially constructed funnel adsorber deposition samplers (Fa. Kroneis GmbH, Austria) are used (Fig. 6). These are standard funnel adsorber deposition samplers, following the guidelines DIN 19739-1, VDI 2090-2 and VDI 4320-4, with a circular area of 0.053 m^2 which are additionally equipped with isolation, heated glass funnels to melt snow, and a heated cartridge chamber to avoid freezing and frost shattering. The precipitation flows from the funnel through a glass cartridge equipped with a glass wool filter and a hydrophobic adsorbent (see Fig. 7), and ends up in a collecting tank in

Fig. 6: Heated funnel adsorber deposition samplers which are used at the UFS. Picture: KF, LfU

order to allow the quantification of precipitation. The adsorbent is the same material as used for active air sampling: A granulate of high purity, precleaned XAD-2 resin.

As for ambient air sampling the parallel exposure and processing of field blank samples is mandatory to fulfil high quality demands of the analytical results. To quantify the transfer of persistent pollutants from the atmosphere into adjacent compartments the analytical data are expressed as deposition rates which is given in mass flow density (e.g. pg m^{-2} d^{-1}).

As sampling-period for active-air sampling and deposition sampling three months are chosen. This makes sure that enrichment of POPs in the adsorbents is sufficient to achieve measurements well above limits of quantification. After three months of exposure, filter cartridges are exchanged by hand and are transported into the laboratory for chemical analysis.

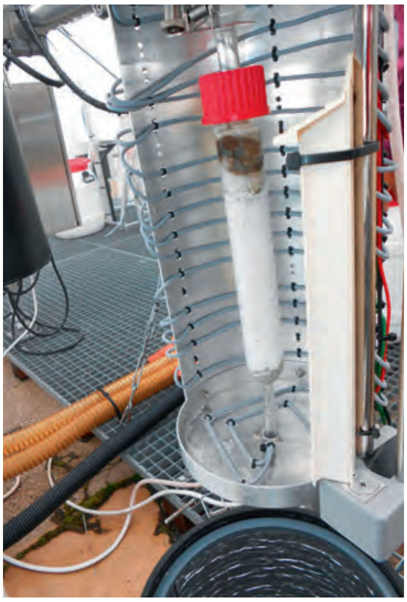

Fig. 7: The interior of the funnel adsorber sampler: in the upper part of the cartridge there is included glass wool in order to collect particulate matter, the white material in the lower part is the adsorbent (XAD-2 resin). Picture: GR, LfU

3.5 Chemical analysis

The chemical analysis of the various investigated compounds is principally based on gas chromatography coupled with mass spectrometry in combination with stable isotope dilution analysis (SIDA). In the following, the clean-up and analysis of OCPs is used as an example for the methodology. The analytical procedures for PCDD/Fs and HFRs are described in the respective VDI guidelines[5].

Sampling and analytical method for quantitative determination of 31 OCPs in ambient air is performed according to VDI 2464 part 4[6]. Using a sampling system, the ambient air is passing through a filter and a glass cartridge filled with an Amberlite® XAD-2® adsorbent (poly-aromatic resin) adsorbing the hydrophobic compounds such as OCPs. Adding of sampling standards that are not expected to occur in ambient air and their recoveries allow to monitor the sampling process errors. Analytical procedure based on sample extraction and two clean-up steps using a stable isotope dilution assay (SIDA) enables the trace analysis of target compounds by gas-chromatography high resolution mass spectrometry (GC-HRMS).

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[5] PCDD/Fs: VDI 3498 part 1; HFRs: VDI 2464 part 3

[6] VDI 2464 part 4 (draft): 2017-12, Ambient air measurement – Indoor air measurement – Measurement of persistent organic pollutants (POPs) with GC/HRMS, Beuth Verlag GmbH, Berlin

Before exposure, the filter cartridges are carefully prepared to fulfil high quality standards for trace analyses. Prior to cartridge preparation, the entire glass equipment including glass wool and adsorbent is carefully cleaned by the specified purification process to ensure the prevention of contamination. 50 g of Amberlite® XAD® adsorbent are placed in the glass sampling cartridge equipped with a glass frit. After filling, a plug of glass wool was pressed on the top of the adsorbent. Three sampling standards ($^{13}C_{12}$-PCB60, $^{13}C_{12}$-PCB127, $^{13}C_{12}$-PCB159) are added in an amount of 1000 pg for each at least three positions on the bed of the adsorbent. The filled glass cartridge is sealed with a glass stopper and a glass case (Fig. 8). The cartridge for field blanks is prepared in the same way.

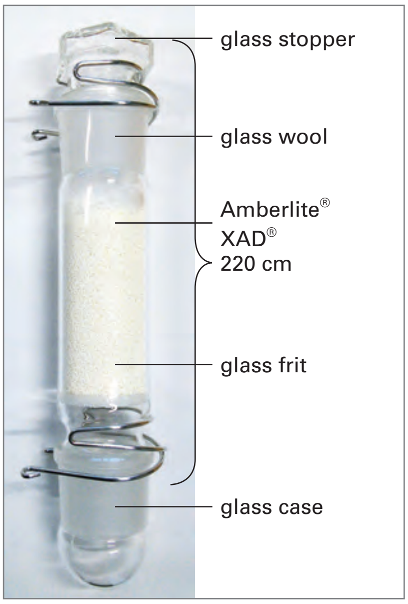

Fig. 8: Glass sampling cartridge filled with Amberlite® XAD® adsorbent. Picture: GR, LfU

After exposure of the cartridge in the field at the UFS, the outer wall of the exposed immission glass cartridge is cleaned with the extractant prior to extraction. After the spiking of the glass wool with stable isotopically labeled standards (^{13}C- and ^{2}H-), the cartridge containing filter, glass wool, and adsorbent is placed in a Soxhlet apparatus, and extracted with a mixture of 3 volumes of n-hexane and 1 volume of acetone for 24 hours at minimum rate of two cycles per hour. Sample extract is concentrated to 1 mL using a rotary evaporator and underwent two clean-up procedures (Fig. 9).

The first clean-up is performed using a multiple layer column containing 10 g neutral silica (treatment at 450 °C), 5 g Alumina B (deactivated with 3 % water), 2 g anhydrous sodium sulphate and a mixture of 1 volume of n-hexane and 1 volume of dichloromethane as eluent. The column absorbents are conditioned with 60 mL eluent solvent prior to elution. The eluate is then solvent-exchanged to acetonitrile, concentrated to approx. 0.5 mL and further purified using a selective solid phase extraction (SPE) with octadecyl modified endcapped silica phase (C_{18}ec) (clean-up 2). The conditioning and elution is then conducted each with 5 mL acetonitrile. After concentration of the eluate to 0.5 mL, the sample is solvent-exchanged to 20 µL n-nonane in an inserted vial. The final concentration to 20 µL acetonitrile is performed under a nitrogen stream at 45 °C. Afterwards, the recovery standard is added to the sample for calculation of recovery of surrogate standards.

After the successfull clean-up, the samples are transferred to a GC-HRMS system. Analysis of OCPs in ambient air samples is performed using a gas chromatograph equipped with a 30 m capillary column Rtx-CLPesticides2 (0.25 mm ID, 0.2 µm df, Restek GmbH, Bad Homburg). The sample volume of 0.5 µL is injected by means of GERSTEL cooled injection system (GERSTEL GmbH & Co. KG, Muelheim an der Ruhr) in splitless mode at 120 °C ramping with 12 °C/sec to 280 °C hold for 5 min. The following oven temperature was used: 60 °C/1.5 min, rate 12 °C/min up to 140 °C, rate 6 °C/min up to 300 °C/10 min. The GC to MS transfer line and ion source temperature was set at 300 °C and 260 °C, respectively. A total of 31 OCPs are quantified in electron impact ionization mode (EI+) at 47 eV operating in selective ion monitoring mode (SIM). Two or three exact masses (*m/z*) according to VDI 2464 part 4 are monitored for each target compound using a lock and calibration mass obtained from perfluorophenanthrene (FC-5311). The instrumental method is calibrated using response factors for each analyte integrating sampling, surrogate and recovery standards.

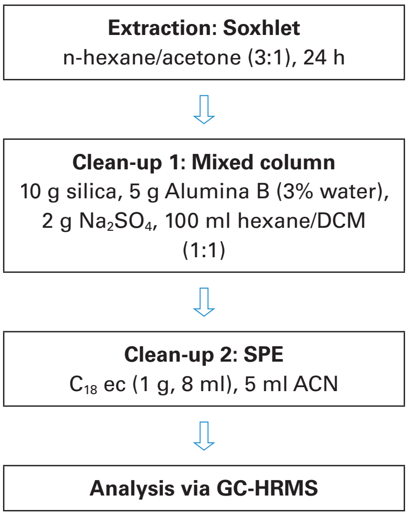

Fig. 9: Flow chart for OCP analysis.

3.6 Time series of persistent pollutants at the UFS

In general, several dozen individual compounds with PBT properties are measured above the analytical limit of quantification at the UFS. These include currently released flame retardants and combustion products. Also measured are OCPs, although these have not been allowed to be used in Europe for a long time.

Referring to the insecticide DDT and its transformation products as an example, we see that these substances can still be detected in every single sample, although their use in Europe has been prohibited since the 1990s. At the beginning of the monitoring in 2005, as part of the MONARPOP project (Federal Ministry of Agriculture, Forestry, Environment and Water Management, 2009), only 21 countries worldwide, mainly in tropical Africa and India, used DDT to combat malaria (UNEP, 2007). The ratio of DDT and its transformation products, as determined at the UFS, indicates that the substances are reaching the Alps from sources in Europe and in the tropics (Kirchner et al., 2016). This means that aged DDT still escapes from the former main European areas of application, for example from the soils of the Po Valley in northern Italy. Recently, “young” DDT is registered from tropical countries like India.

The measured substances are only detectable at low concentrations in the air on the Alpine summits. Values in urban or industrial air are three to a hundred times higher (Kirchner et al., 2018; Kirchner et al., 2016). Compared to Arctic regions, the concentrations at the Alpine peaks, with exceptions to substances such as pentachlorobenzene and BDE 209, are on a similar scale.

The pollutants reach the northern and central Alps to one third by air-masses from the Mediterranean region and another third from northwestern source regions with maritime background (Fig. 10). About 15 percent of the air masses reach the Alps from the northeast, the remaining air masses cannot be assigned to any exact source-region (Kirchner et al., 2016).

The northeast air masses are usually the most heavily contaminated with polychlorinated biphenyls (PCBs) and polychlorinated dioxins (PCDD/F) (Kirchner et al., 2018). However, this origin occurs less frequently, because the Alps are less influenced by air blowing from northeast.

Fig. 10: Origin of air-masses and source dependent differences in concentrations of persistent organic pollutants (2006–2015). Source: Mario Wilhelm, LfU

Therefore, about all of the source-regions, with the exception of UD (direct transport from the Atlantic), contribute approximately equally to the entry of these hardly degradable pollutants. Air masses from the Mediterranean and the NE are more heavily polluted with organochlorine pesticides, especially when compared to Atlantic air masses. These different concentrations with respect to the source-regions of flow confirm that some of the transported pollutants are residues from regional European sources.

Significant decreases in air concentrations for the period 2006 to 2015 can be reported for about one-third of organochlorine pesticides (see Table 3). This demonstrates the efficacy of the ban on the production and use of pollutants such as heptachlor and trans-chlordane (banned since 2004), lindane and pentachlorobenzene (since 2009) by the Stockholm Convention.

Tab. 3: Pollutants for which a reduction in concentrations can be demonstrated (statistically significant). „Current concentration level" corresponds to the annual mean value of the 2015 measurements of Sonnblick, Weissfluhjoch and Zugspitze.

Substance/Class of substances	**Decrease 2006–2015**	**Current concentration level in Alpine ambient air [picogram per cubic meter of air]**
α-HCH	–55 %	5,51
Lindane (γ-HCH)	–68 %	4,92
Pentachlorobenzene	–24 %	39,31
Pentachloroanisole	–47 %	6,13
4,4′-DDT	–56 %	0,67
Chlordane (trans + cis)	–51 %	0,77
Heptachlor (+ cis-heptachlorepoxide)	–45 to –50 %	0,97
Endosulfan-I + II	–93 %	3,41
2,4,4′-tribromodiphenyl ether (BDE 28)	–64 %*	0,14

* For BDE 28, only measured values are available at the Zugspitze from 2012 on – therefore the percentage decrease refers to the years between the end of 2012 and mid-2016 (not yet statistically hedged).

Even the major component of DDT (4,4′-DDT) shows a decline in the period from 2006 to 2015, which is over 50 percent. Most notably, a decline of over 93 percent between 2006 and 2015 for the insecticide endosulfane was observed which has been included in the Stockholm Convention since 2011, but has been banned in the European Union since 2005 (Fig. 11). This decrease demonstrates that, even before the entry into force of the global ban, restrictions at the level of the European Union are able to reduce air concentrations to a relevant extent.

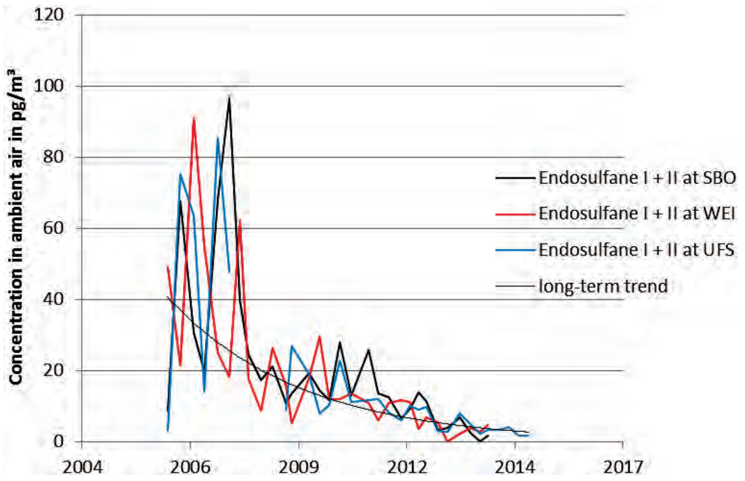

Fig. 11: Time series of ambient air-concentrations of endosulfane I and endosulfane II at Sonnblick Observatory (SBO), Weissfluhjoch (WEI) and UFS.

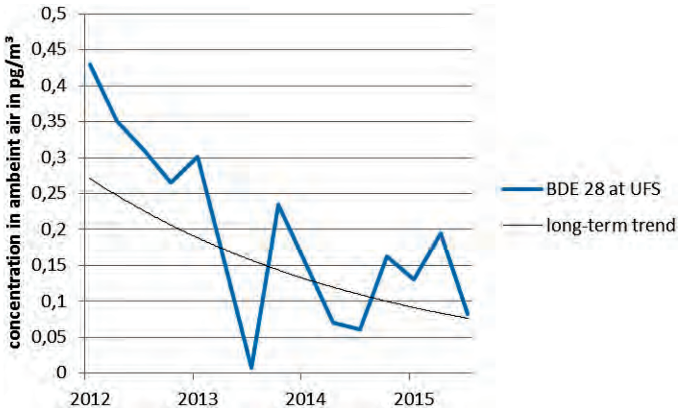

Fig. 12: Time series of ambient air-concentrations of BDE 28, a halogenated flame retardant of the first generation

A tendency for decreases in ambient air concentrations – probably due to EU legislation – is also visible for HFR of the first generation. For instance, 2,4,4'-tribromodiphenyl ether (BDE 28), most volatile component of the technical pentabromodiphenylether used as flame retardant, is very probably decreasing (see Fig. 12). Penta- and octabromodiphenyl ethers have been banned in new products in the EU since 2004. The use of decabromodiphenyl ether has been severely restricted in electrical and electronic equipment since 2006. However, the measurement series from 2013 is still too short to be able to derive statistically reliable statements.

The same can be stated for the deposition of BDE 209, the main component of decabromodiphenyl ether (DecaBDE), which was included by the European Union in the list of substances of very high concern under the REACH Regulation. Since May 2017, DecaBDE is also part of the Stockholm Convention. Between the first measurements of BDE 209 in the deposition at the Zugspitze 2008 and the last evaluated data from 2016 there is a decrease of about 90 percent (Freier K. P., Kirchner M., Denner M., Ratz G., Weiss P., Körner W., Moche W. (2019): Monitoring of Persistent Pollutants in the Alps, Bavarian Environment Agency & Environment Agency Austria; https://www.bestellen.bayern.de/shoplink/lfu_all_00161.htm).

More problematic are substances that are internationally regulated but do not decrease visibly in the past ten years referring to ambient air-concentrations and deposition, such as PCDD/Fs and PCBs.

With the beginning of the 1990s, the installation of appropriate exhaust gas filters in waste incineration and industrial plants reduced PCDD/F concentrations in metropolitan areas by about 80 percent (UBA, 2014). PCBs are also produced to a limited extent in combustion processes, but they were additionally used in large quantities as softeners and insulating oils until the end of the 1970s, so they still escape from buildings (joint sealants, paints) and improper disposal of transformers and capacitors. Since 2004, PCDD/Fs and PCBs are part of the Stockholm Convention.

From the beginning of the measurements in 2006, decreasing PCDD/F and PCB concentrations could be ascertained for the Alps, which until around 2010 proved the success of the mitigation measures. However, the concentration decrease stagnated after 2010 and in some cases substances even increased again from 2013 onwards. The same pattern is also shown for the input of PCDD/F by precipitation: Levels of deposited PCDD/Fs are similar to those deposited in 2006 (Fig. 13). There are also marked peaks visible that are four times higher than the usual deposition rates. The reasons of for these maxima could not be clarified so far.

Overall, PCDD/F and PCBs continue to enter the Alpine ecosystems, with a trend towards increasing levels of airborne concentrations in recent years. For this reason, it must be clarified on an international level, where similar effects can be observed, what causes the renewed increase in air concentrations, and whether further action is required. The extent to which living organisms in the Alps are burdened by these entries is investigated in the PureAlps projects 2016–2019 (Freier et al. 2019).

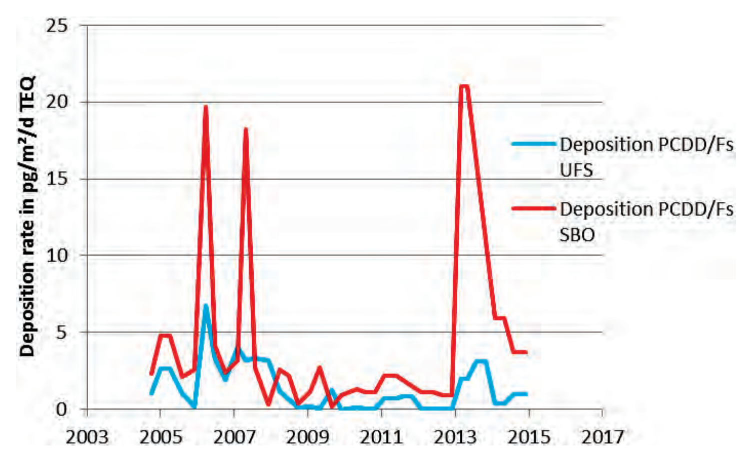

Fig. 13: Time-series of deposition of dioxins and furans (given as sum in toxicity-equivalents, TEQ)

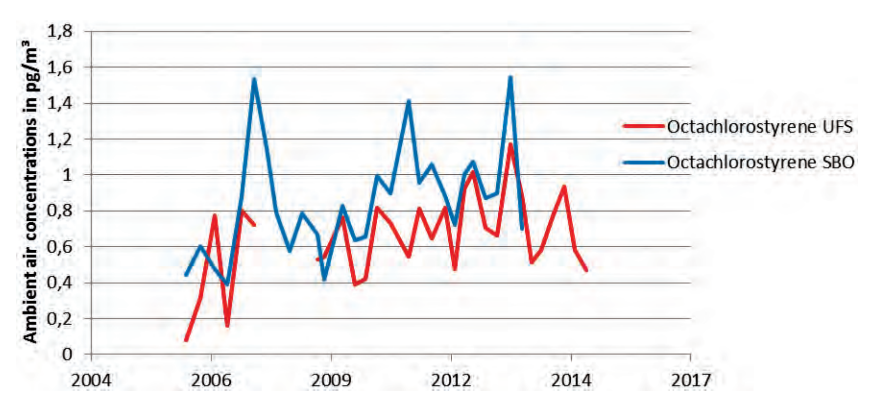

Fig. 14: Time series of Octachlorostyrene from UFS and Sonnblick Observatory (SBO)

From the group of OCP and related compounds, octachlorostyrene (OCS) can be identified as a possible problem case, a substance that has hitherto been neither nationally nor internationally regulated. Since the beginning of the program, ambient air concentrations of OCS have been steadily increasing at the alpine monitoring stations (see Fig. 14): The increase of 33 % over the past ten years is statistically significant.

OCS is classified as a PBT substance (UBA, 2016) and it is also suspected that it acts as a hormone for certain organisms (WHO, 2013). OCS results from the extraction of aluminum and magnesium in chlorine chemistry and the combustion of plastics containing chlorine. Concerning the deposition in the alpine area, it is currently completely unclear, from which sources the OCS originates. The simultaneous measurement of high concentrations of penta- and hexachlorobenzene, however, suggests that the source of all three substances is the production of highly chlorinated solvents, such as perchloroethylene and carbon tetrachloride (Weber et al., 2011; Zhang et al., 2015). Therefore, it would be desirable for OCS to record internationally the main sources and quantities emitted in order to develop measures to prevent further increases in ambient air concentrations.

3.7 Detecting emerging pollutants

In the framework of chemical regulations, particular attention must be paid on risks due to irreversible pollutant inputs. Therefore, PBT substances that are considered novel pollutants, so-called emerging pollutants, are also being investigated within the chemicals monitoring at the UFS.

Emerging pollutants are only recently observed in the environment and are not or only partially regulated. The present monitoring should help to make the risk of these novel chemicals more manageable.

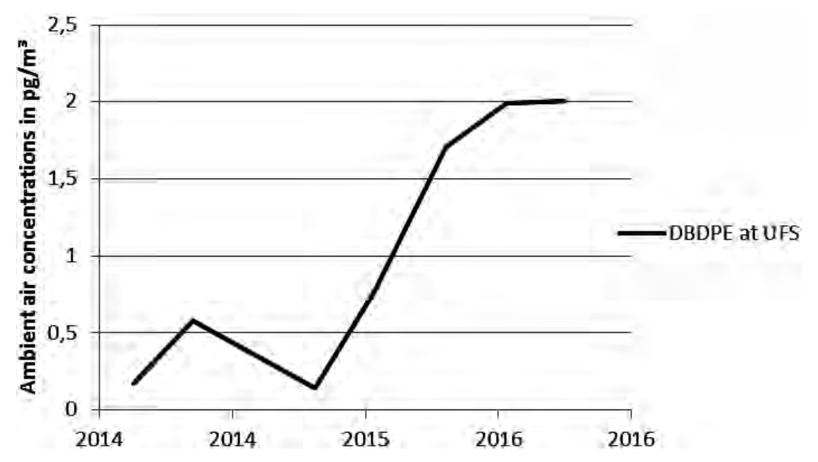

Fig. 15: Time-series of the halogenated flame retardant Decabromodiphenylethane (DBDPE)

Increasing demands on the fire protection of materials and at the same time increasing production volumes of plastics lead to a worldwide increasing use of novel flame retardants. Many of them are evaluated as PBT substances (Shaw et al., 2010), but so far are neither nationally nor internationally regulated. Therefore, new flame retardants are also monitored at the UFS. A total of eight of these novel substances have already been detected until 2017 in the air, seven also in precipitation.

Particularly noteworthy for the novel substances is decabromo-diphenyl-ethane (DBDPE). Several thousands of tons of this flame retardant were introduced into the EU back in 2001, and since the bans and restrictions on older flame retardants, such as DecaBDE, it has been increasingly used as a substitute. The reason for the use as a substitute lies in its similar properties compared to the previously used DecaBDE, which also suggests the similar chemical structure. This similarity extends to properties that affect the environmental risk. Despite already proven accumulation in seagulls and other animals (Betts, 2009), the decision on the final assessment of DBDPE has been postponed by the European Chemicals Agency (ECHA) to 2019 due to insufficient data (ECHA, 2016).

Ambient air concentrations at the UFS for DBDPE show strongly increasing tendencies (Fig. 15). In addition, in the deposition at the UFS DBDPE occurs in the highest concentrations of all flame retardants, the emerging pollutant has already overtaken the formerly dominant DecaBDE. The measurements at the UFS give evidence that DBDPE does not degrade appreciably in the atmosphere and undergoes long range transport.

The increase of DBDPE shows that effective restrictions for HFRs of the first generation such as BDE 28 (Fig. 12) have translated into a more intense use of non-regulated HFRs of a second generation with similarly problematic properties. This suggests that a successful chemicals regulation has to encompass both, the forcing of a phase-out of problematic substances and the promotion of alternatives which avoid an increased usage of substitutes which also reveal PBT-properties. In the best case, the promotion of alternatives not only covers a direct substitution by other chemicals but as well a technological shift, which makes the further demand of similar substances superfluous (Science for Environment Policy, 2017).

3.8 Perspectives of chemicals monitoring in the Alps

The results of the ten-year monitoring of PCDD/Fs, PCBs, and OCS show that there are currently higher levels of exposure to compounds, which are produced as undesirable by-products in the combustion of chlorine-containing materials and as well in chlorine-chemical industries. In order to determine whether the sources of these pollutants are located in Europe or in other areas, air masses must be sampled separately for their regional or global origin. Therefore, a pilot study at the UFS is testing whether it is possible to record air masses of the free troposphere separately from regional, ground-level air masses coming from nearby regions (Sig-

Fig. 16: Winterly atmospheric inversion indicated by the low-level clouds in the background. This represents a situation where the UFS is decoupled from lower atmospheric levels. Picture: KF, LfU

mund et al. 2019). The prerequisite for this is a procedure that automatically differentiates two cases: one case, where the atmosphere around UFS is definitely decoupled from the mixing-layer (see Fig. 16) and a second case, where the UFS is located inside the mixing-layer.

Climate change, as a core issue of the 21st century, is also relevant for the environmental risks due to chemicals: the question is to what extent changes in temperature and precipitation will affect the future input of pollutants in the Alpine region. It is also of concern that the use of pesticides in agriculture will likely increase as population in developing and emerging countries continues to grow, and climate conditions may deteriorate in Europe at the same time. In the case of persistent chemicals, this could also affect the cold trapping phenomenon in the Alps. Therefore, for this unique mountain range with its original ecosystems, a global, early commitment to a more environmentally sound economy would be desirable, which also takes into account the environmental and health risks of chemicals.

Another opportunity for the future of chemicals monitoring activities at the UFS may be the combination of continuous measurements of ambient air concentrations of emerging POPs and interval-monitoring of bioaccumulation in wildlife and humans of the surrounding areas. In this way, it would be possible to give evidence of two important characteristics of POPs at the same time: the monitoring at the UFS delivers insights on persistency and long-range transport of chemicals; the monitoring of wildlife and humans allows assessing the level of bioaccumulation under the given deposition rates. For instance, the Partnach-river below the UFS is characterized by karst hydrogeology and is well defined concerning its catchment where the UFS is situated within (Rappl et al., 2010). The accumulation of POPs in brown trout in the Partnach-river (Fig. 17) is therefore directly relatable to the deposition rates which are monitored at the UFS (Freier et al. 2019).

Fig. 17: Brown trout in a pristine alpine catchment is an indicator of background contamination with POP from atmospheric deposition. Picture: © Niklas Winter

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