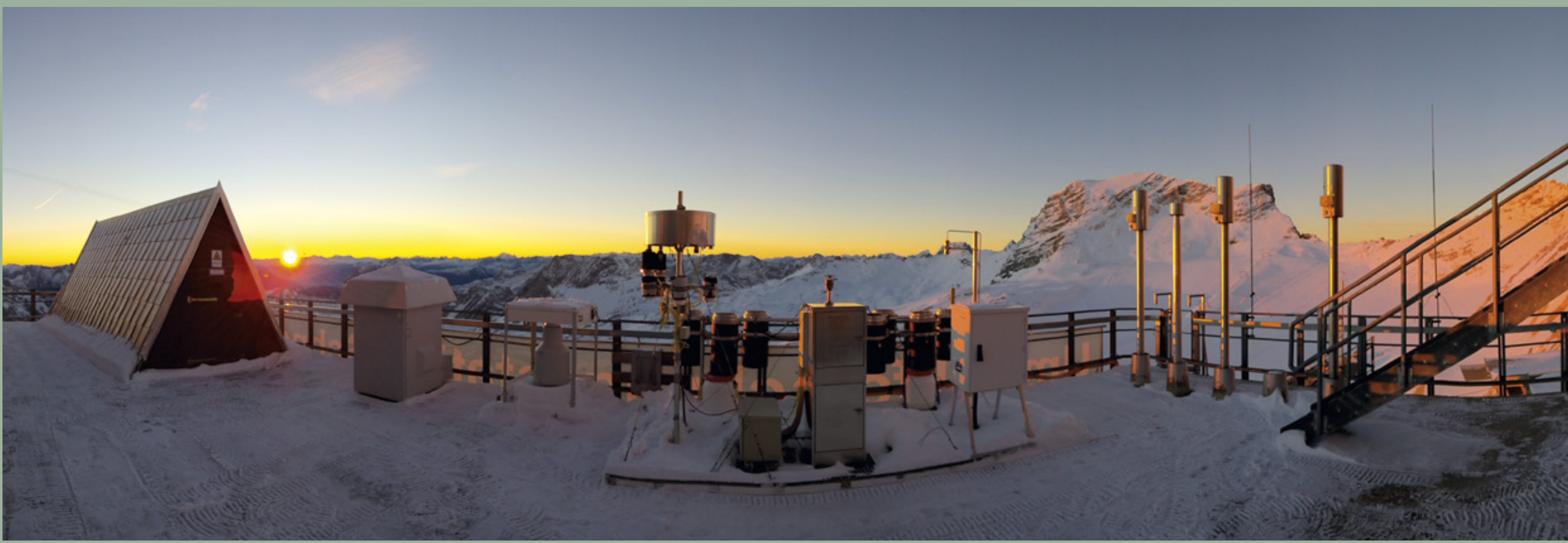
PureAlps

2016 – 2020



Monitoring of Persistent Pollutants in the Alps

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PREFACE

Dear readers,

Chemicals are a constant companion to our advanced lifestyle. They enable progress and serve our prosperity. Nonetheless, some chemicals have the potential to harm the environment and humans, even at trace concentrations. Therefore, relevant pollutants are recorded in the Alps since 2005 by the Bavarian Environment Agency and the Environment Agency Austria.

15 years of successful monitoring of pollutants in the Alps are a good reason for us to document important findings: What is the level of pollution of the Alps with persistent pollutants? How has exposure developed over the years? What regulatory, risk-preventing measures were successful and which ones are necessary in the future to guarantee a continued protection of the Alps as a sensitive ecosystem?

Data from environmental monitoring projects are an important contribution to the regulation of pollutants. Such monitoring projects gather insights about distribution of pollutants. Problematic developments can be identified and regulatory measures can be initiated to minimize risks. Thus, Monitoring projects are an important basis for the further development of international chemicals legislation such as the EU REACH regulation and the international Stockholm Convention. Because only international measures to limit and end the production, use and release of persistent organic pollutants can effectively manage their risks.

In the future, the monitoring of substitutes for already banned pollutants will gain in importance. These substitutes – even though they are engineered to solve problems – can also be problematic for humans and environment. It is our common goal to reduce risks of persistent organic pollutants through national and international measures.

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President of the Bavarian Environment Agency

Monika Mörth, MAS
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SUMMARY

In 2005, the MONARPOP[1] project started monitoring persistent organic pollutants in the Alpine region. Since 2016, the series of measurements has been continued by two projects of the same name, "PureAlps", in Austria and Bavaria. The monitoring continues to this day. Pollutants such as polychlorinated dioxins, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, organochlorine pesticides, halogenated flame retardants, mercury and other novel organic fluorine and chlorine chemicals are being investigated.

The results of the more than 15 years monitoring show that the high altitudes of the Alps are exposed to the input of persistent organic pollutants due to condensation effects: Although air concentrations are many times lower than in urban regions, deposition of pollutants is often in a similar order of magnitude. This means that even remote alpine areas are no longer free from environmental risks due to chemicals.

According to present state of knowledge, the contents of soils and spruce needles in the mountain forests of the Central Alps are usually low compared to those in Central Europe. However, slightly higher concentrations occur at the northern and southern edges of the Alps. Certain pollutants with significant regional sources, such as lindane, from wood building materials, or polycyclic aromatic hydrocarbons (PAHs), from the combustion of wood, are more prevalent in the central Alpine region.

Due to regulations by the European Union (REACH[2]) or the Stockholm Convention[3], some pollutants show a decrease in ambient air concentrations in the Alps. These include the largely banned organochlorine pesticides. In contrast, dioxins have so far been found to have only weak and, in the case of polychlorinated biphenyls, no decreasing concentrations in ambient air. The reasons are still unclear and should be investigated in more detail in the context of the PureAlps projects. Significant increases in the air shows octachlorostyrene - a substance that is an unintended by-product in the production of chlorinated solvents and emits from the combustion of chlorinated hydrocarbons. The flame retardant decabromodiphenylethane (DBDPE), which is used in large tonnages, also exceeded the detection limits of measuring instruments for the first time in 2012 and presently shows the highest concentrations in ambient air of monitored halogenated flame retardants. The goal of the PureAlps projects is to monitor such developments closely and to incorporate the results into the preparation of international measures.

1
MONARPOP: Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants, www.monarpop.at, 04.06.2019

2
REACH: EU chemicals regulation (Registration, Evaluation, Authorization and Restriction of Chemicals), in force since 2007

3
The Stockholm Convention on persistent organic pollutants (POPs) sets internationally binding regulations for protection against POPs. In force since 2004 and since then repeated inclusion of new pollutants. .

Early warning system for the Alps

Top: The environmental research station Schneefernerhaus (UFS) at 2,650 Meters at the Zugspitze/Germany.

Below: The Sonnblick Observatory (SBO) at 3,106 Meters in the Central Alps/Austria.

At the Sonnblick Observatory and at the environmental research station Schneefernerhaus, the inputs of hardly degradable organic pollutants into the Alpine region have been determined for more than 15 years.

Monitoring began in 2005 as part of the MONARPOP project funded by the European Union, in which Italy, Slovenia and Switzerland were involved in addition to Austria and Bavaria/ Germany.
Since then, Austria and Bavaria have continued the measurements together, currently in the PureAlps projects. They thus create the most comprehensive data series on persistent pollutants in the entire Alpine region.

WHY ARE POLLUTANTS ESPECIALLY BEING INVESTIGATED IN THE ALPS?

Viewed from space, the Alps immediately catch your eye: ice-covered peaks stretch from the Côte d'Azur to the Danube basin

In our industrialized world, the unspoiled nature of the Alps and its sensitive ecosystems is no longer guaranteed. Air currents carry persistent organic pollutants (POP) 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 leaches pollutants from the air.

Especially for the Alps with its 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 Alpine region 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.

The aim of the monitoring at the stations in Austria and Bavaria is to control the atmospheric input of chemicals as accurate as possible. In the long term this contributes to a sustainable economy that avoids negative impacts on people and the environment as far as possible.

The environmental monitoring station Schneefernerhaus (Zugspitze, Germany) and the Sonnblick Observatory (Hoher Sonnblick, Austria) are involved in the measurement program for air concentrations and deposition rates. Until 2013, the station Weißfluhjoch, Switzerland, of the Swiss Federal Research Station for Forest, Snow and Landscape (WSL) participated in the measurements.

DETECTION OF TRACE LEVELS

Substances that combine three characteristics are particularly critical for humans and the environment: Persistency, bioaccumulation and toxicity, in short: PBT[4]

PBT substances are emitted into the environment 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 characteristics, which equates to several million tonnes per year of produced quantities [12].

The majority of these chemicals remain where they are used, only a small proportion enters the atmosphere. However, the escape of smallest amounts into ambient air already lead to a globally measurable contaminations. Contaminants from combustion processes, such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F, "dioxins") or polycyclic aromatic hydrocarbons (PAHs), escape directly into the atmosphere.

The distribution of pollutants takes place via air currents and is coupled to the water cycle. In the process, higher concentrations can be measured near sources. However, because of their longevity and long-range atmospheric transport (LRAT), pollutants reach remote areas such as the Alps. There, they can be deposited through increased condensation, especially in cool regions (cold trapping). Therefore, POPs are detected even in areas where they have never been produced or used, such as in the Arctic, Antarctic or in mountain ranges such as the Alps.

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 fat-solubility of these 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 the effect is not subject to a threshold.

For most chemicals, the principle predominantly applies that a harmful effect begins only 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 obtained. To cope with this risk on a precautionary basis, pollutants must already be recorded when they enter ecosystems from the air. At that point, the relevant air concentrations are very low, down to the range of femtograms per cubic meter of air, which means finding a single molecule under a quintillion or 10^{18} others.

4
The Stockholm Convention refers to persistent organic pollutants (POPs). For the sake of clarity, this report uses the term „PBT-Substances" derived from EU-REACH, which also includes the inorganic mercury that is currently being investigated in the PureAlps projects

Deposition sampling devices at the environmental research station Schneefernerhaus/Zugspitze: The pollutants to be investigated are bound to the adsorber within the cartridges used. To assess ambient air concentrations, air is sucked through these adsorber-cartridges. The analysis of substances takes place in accredited ultra-trace laboratories.

Table: Chemicals that are focus of the monitoring

Class of substances	Examples	Sources
Organochlorine pesticides (OCPs)	DDT and derivatives Lindane Hexachlorobenzene Endosulfane	insecticide insecticide and wood preservative fungicide and combustion processes insecticide
Polycyclic aromatic hydrocarbons (PAH)	Benzo[*a*]pyrene Phenanthrene	combustion processes
Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)	2,3,7,8-TCDD (Seveso-dioxin)	combustion processes and by-product of chemical syntheses
Polychlorinated biphenyls (PCB)	PCB 126 (dioxin-like PCB) Indicator-PCBs: PCB 28, 52, 101, 138, 153, 180	plasticizer, flame retardant, insulating oil, combustion processes
Halogenated flame retardants *	Polybrominated diphenyl ethers (PBDE), e.g. DecaBDE, Hexabromocyclododecane (HBCD), Decabromodiphenylethane (DBDPE)	flame protection in plastics and textiles flame protection in building-insulation substitute for DecaBDE
Perfluorinated surfactants and fluorotelomer alcohols*	Perfluorooctanoic acid (PFOA)	water-repellent coatings
Mercury*		small-scale gold mining, chlorine-alkaline electrolysis, combustion of black and brown coal

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

PRECAUTIONARY PROTECTION OF HUMANS AND THE ENVIRONMENT

Special attention must be paid to the precaution towards risks due to pollutant inputs that are irreversible. Therefore, substances that are considered novel pollutants, so-called emerging pollutants, are being investigated as well. Emerging pollutants are only recently observed in the environment and are not yet or only partially regulated. The present monitoring should help to make the risk of these novel chemicals more manageable.

Pollutants of concern, which are globally prevalent, need to be regulated at European or international level, because small-scale approaches have little effect. For this purpose, the measurements at the alpine stations provide an important data basis, for example for the EU Regulation REACH on the Registration, Evaluation and Authorization of Chemicals. For the European Water Framework Directive, PureAlps also provides data for determining background pollution caused by airborne pollutants.

For already regulated substances, it must be verified whether the measures taken are effective and the concentrations decrease. Internationally, most notably the Stockholm Convention serves since 2004 to reduce persistent organic pollutants. The majority of the substances listed therein is subject of the present monitoring. The measured concentrations and temporal trends of these substances are regularly reported to the secretariat of the Stockholm Convention and are published in global reports on the effectiveness of emission limits.

Comparable measurement campaigns to PureAlps exist in the international context for the European lowlands with the EMEP[5] Program, in the Arctic with the AMAP[6] Program and for North America in NDAMN[7] Monitoring. However, due to the uniqueness of the Alps in terms of location and climate, the results of these programs are only applicable to a limited degree. For a mid-latitude high mountain range, the project series from MONARPOP to PureAlps is the only international long-term monitoring worldwide.

5
EMEP: European Monitoring and Evaluation Programme

6
AMAP: Arctic Monitoring & Assessment Programme; international program of arctic states

7
NDAMN: National Dioxin Air Monitoring Network; USA (1998 to 2004)

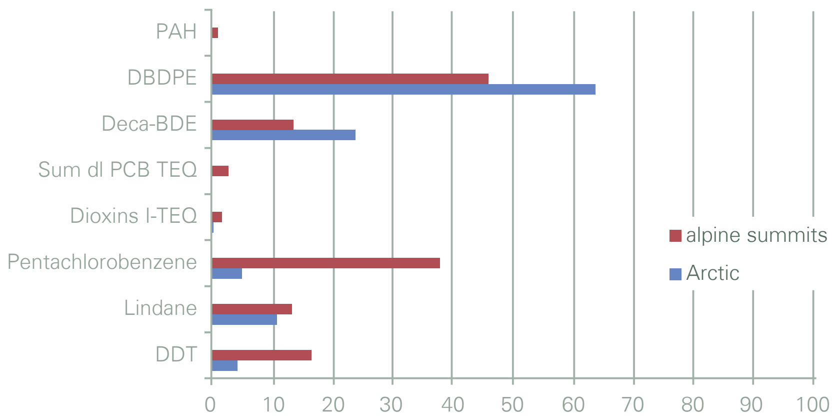
Environmental research station Schneefernerhaus

Cold-trap for air pollutants

The measurements at the alpine stations and in the mountain forests of the Austrian, Bavarian and Italian Alps have detected many persistent pollutants in air, precipitation, soils and plants so far. The measured concentrations are predominantly in a low range and correspond to those in other mountain regions of the earth.

On principle, it can be stated that pollutants accumulate in the Alps in the long term. The Alps no longer correspond to an unpolluted, pristine area.

WHERE DO THE POLLUTANTS ORIGINATE?



Contents of pollutants in ambient air of the studied alpine summits in comparison to emission areas (100%) and the Acrtic

Compared to source regions in Europe and India (for organochlorine pesticides), the concentrations in ambient air of various organic pollutants (DDT, lindane, pentachlorobenzene) at the Alpine peaks are significantly lower. The data for the Alps refer to the averaged medians of the stations at Hoher Sonnblick and Zugspitze. Data Sources [5, 6, 8, 10, 18, 21]

In general, several dozen individual compounds with PBT properties are detected in measurable concentrations at the Sonnblick Observatory and at the environmental research station Schneefernerhaus at Zugspitze[8]. These substances include currently released flame retardants and combustion products.

Also measured are organochlorine pesticides, although these have not been allowed to be used for quite some time at least in Europe. For example, the insecticide DDT and its transformation products 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, as part of the MONARPOP project, only 21 countries worldwide, mainly in tropical Africa and India, used DDT to combat malaria.[17] The ratio of DDT and its transformation products, as determined at the Sonnblick and the Zugspitze, indicates that the substances reach the Alps from sources in Europe as well as from the tropics [8]. This means that transformation products of DDT still escape from the former European areas of application, for example from the soils of the Po Valley in northern Italy. Meanwhile, "fresh" DDT is detected from tropical countries like India.
The measured substances only reach low ambient air concentrations at Alpine peaks. Values in urban or industrial proximities are three to a hundred times higher.[8, 9] Compared to Arctic regions, the concentrations at the Alpine peaks, with exceptions to substances such as pentachlorobenzene and DecaBDE, are of a similar magnitude.
A percentage comparison of the measured air concentrations with those in emission areas is shown for selected pollutants in the diagram to the left.

The pollutants reach the northern and central Alps to one third by air masses from the Mediterranean region and another third from northwestern directions with maritime background (Figure below). About 15 percent of the air masses reach the Alps from the northeast; the remaining air masses cannot be assigned to any exact direction.[8]

The northeast air masses are the most heavily contaminated with polychlorinated biphenyls (PCBs) and chlorinated dioxins (PCDD/F).[9] However, this flow occurs less frequently. Therefore, all source regions, with the exception of direct transport from the Atlantic, contribute approximately equally to the deposition of these PBT substances.

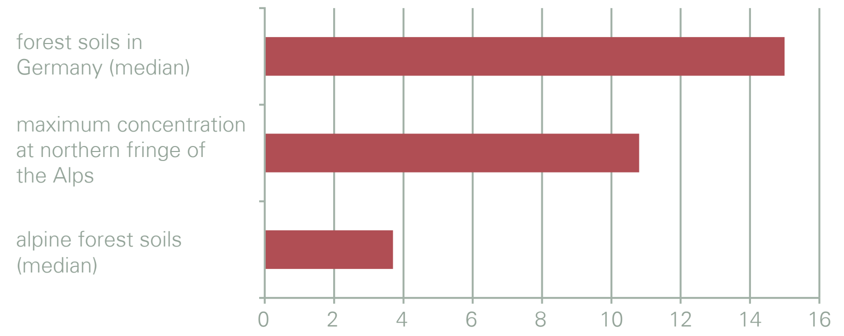
Air masses from the Mediterranean and the Northeast are more heavily polluted with OCPs, especially when compared to Atlantic air masses [8]. These different concentrations with respect to source regions confirm

8
"Measurable concentrations" corresponds to a measurement above the analytical limit of quantification (LOQ), where a substance is not only detected, but also measured in its exact concentration

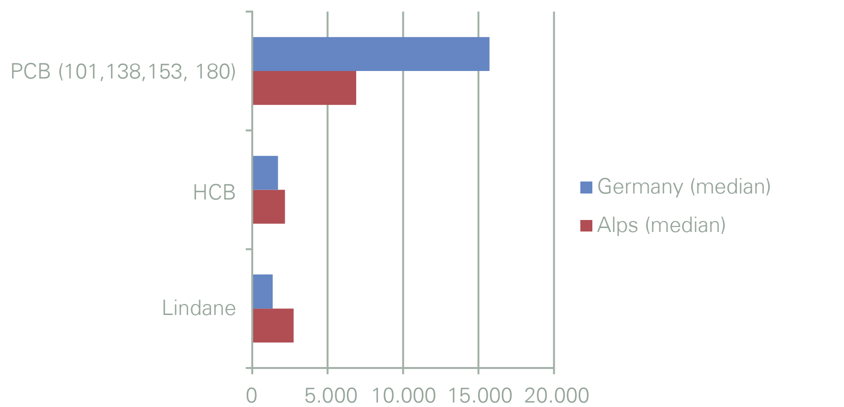
Results from air mass-related measurements: Impact of the Alpine peaks from three dominating directions; as indicated, some direction show higher concentrations of PCB (polychlorinated biphenyls) and OCP (organochlorine pesticides)

that to some extent the transported pollutants are emitted from European sites.

Due to the colder temperatures in the Alps, there is a pronounced deposition of pollutants compared to the rather low air concentrations. This corresponds to the phenomenon of a cold trap, similar to that observed for arctic areas. For example, deposition rates for dioxins are only 10 times lower in the Alps than in the emission areas, even though the air concentrations at the Alpine peaks are 50 times lower.[10] The same can be said for polycyclic aromatic hydrocarbons (PAHs): at the Alpine summits, deposition rates for PAHs are only 10 times lower than in urban areas, even though air concentrations are more than 100 times lower.[10] In the vicinity of the large Alpine valleys, however, the exposure to PAHs is higher due to local sources. For OCP and flame retardants, there is insufficient data on the deposition rates in European emission areas.[7]



Concentrations of dioxins (PCDD/F) in humus layers of forest soils in ng/kg DW (I-TEQ)



Mean concentrations of polychlorinated biphenyls (PCB), hexachlorobenzene (HCB) and Lindane (gamma-HCH) in forest soils in ng/kg DW

Levels of selected PBT substances in the humus of alpine soils compared to soils from other parts of Germany. Data Sources [5, 14, 16]

The phenomenon of the cold trap shows that deposition of PBT substances is a more suitable indicator of the endangering of ecosystems by pollutants than the air concentrations. International agreements should therefore focus not only on air concentrations but also on the amounts of pollutants deposited, which result from the interplay of air concentrations, precipitation rates, temperatures and interactions with aerosols. Otherwise, in cold climates such as the Alps, measuring only very low concentrations in ambient air would seriously underestimate potential risks for ecosystems.

The fact that the Alps are a sink for PBT substances is confirmed by the comparison of levels of dioxins and PAHs in soils with the quantities of these pollutants which are emitted in the Alpine region[1]: The Alps receive significantly more pollutants from the global environment and accumulate them in particular in the humus of the forest soils. This results in a high relevance of international agreements to protect the Alps by constraining emission sources outside the Alpine region at an early stage and effectively.

The alpine humus layers and topsoils always have 10- to 100-fold higher concentrations of PBT substances than spruce needles.[5] The alpine soils accumulate pollutants in the long term and can no longer be regarded as unpolluted. At the same time, the soils represent an efficient filter of PBT substances and thus protect downstream media such as groundwater. As long as the emission of PBT substances cannot be completely restricted on the part of the sources, the protection of alpine soils as pollutant filters is of high relevance, especially in times of climate change.

The contents of PBT substances in spruce needles and in humus top-layers in the Alps are overall in the lower range and are comparable with contents of spruce and soils in other parts of Germany[9] (Figure above). At present, the pollution is therefore principally not alarmingly high. However, there are PBT substances that show significantly higher concentrations in the Alps than in other rural areas (Figure above). For example, the mean value for lindane (insecticide and wood preservative) in alpine soils is twice as high as the mean for soils in Germany.[16] This suggests that local sources and reservoirs in the Alps play a role for lindane, as also evidenced by corresponding higher air concentrations closer to valleys.[11] Hexachlorobenzene (fungicide and combustion residue) is also increased by about a third.[16] In addition, it should be noted that on average low values for the Alpine region do not exclude that there are hot spots with higher levels of pollution: For instance, despite a rather low total amount of dioxins in the soils, the northern Alps in particular are higher polluted compared to the rest of the Alps.

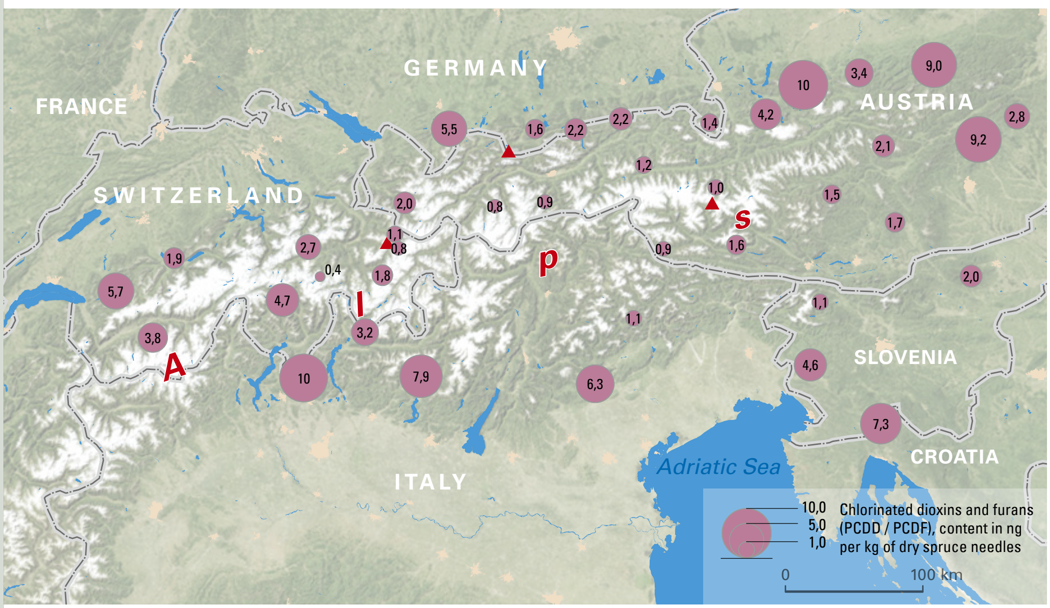
Alpine leptosol: The humic top soils in mountain forests accumulate PBT substances. As a result, the PBT burden of alpine soils increases in the long term, at the same time the soils filter percolating rainwater and thus enable the formation of clean groundwater.

SEASONAL, REGIONAL AND ALTITUDINAL PATTERNS

The measurement sites Hoher Sonnblick and Zugspitze are located in the Central Alps and in the Northern Limestone Alps. Until 2013, the Weissfluhjoch in Switzerland in the western Alps was examined as well. In addition to this, the MONARPOP project also included sampling of soils and spruce needles from more than 50 sites and transects throughout the northern, southern and eastern Alps. As a result, significant insights into the temporal and spatial distribution of pollutants could be acquired over the past 15 years.

Seasonally can be determined, that higher concentrations of dioxins (PCDD/F) and heavier PAHs occur especially in winter. This is associated with their emission by combustion processes in Europe and the entire northern hemisphere. On the other hand, OCPs, which are primarily transported in gaseous form, consistently show higher concentrations in the summer months, which in extreme cases, as DDT and endosulfane II, are more than three times higher than concentrations in wintertime. On the one hand, these higher summer concentrations of OCPs are due to the direct transport from tropical emission areas and, on the other hand, due to regional re-emission of already deposited components (secondary sources). The latter is evidenced by the correlation between high air temperatures and higher air concentrations.

For many substances, deposition depends on the amount of precipitation, which in turn depends on the orography.[5] As a result, the peripheral regions of the Alps with higher precipitation are generally exposed to higher levels of globally transported pollutants. This is demonstrated, for example, by the quantities of dioxins in spruce needles (Figure below).

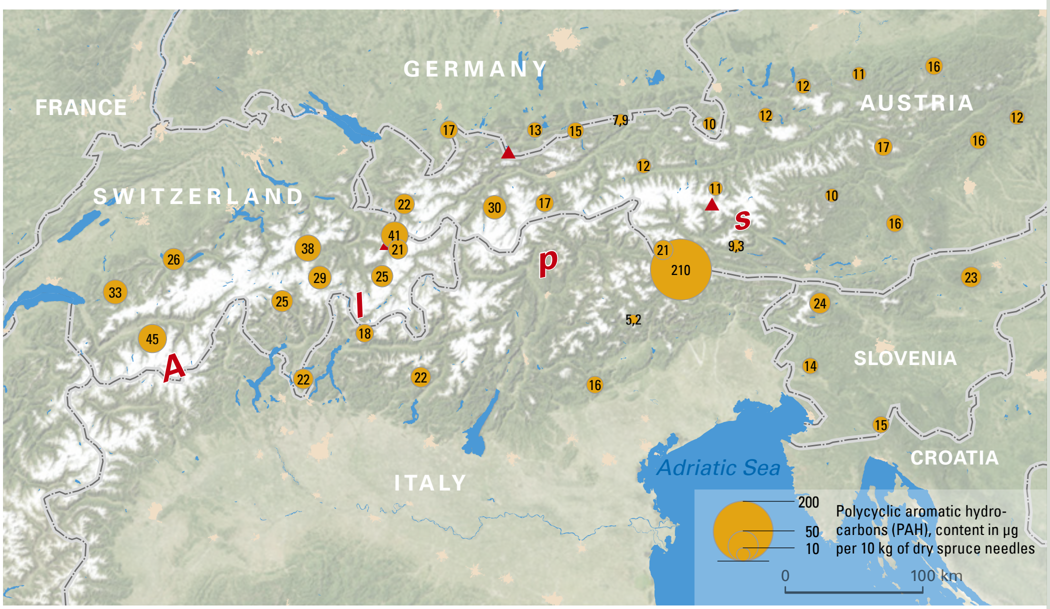


Chlorinated dioxins and furans (PCDD/F) in spruce needles: The size of the circles corresponds to their content. The larger circles in the peripheral areas indicate that above all the periphery of the Alps is affected by the entry of globally transported pollutants

For pollutants, which originate from local sources such as wood burning, a reverse pattern emerges: the levels in spruce needles from the Central Alps, where the tendency to atmospheric inversion is high, are frequently higher than in spruce needles from the Alpine periphery. The figure below shows this exemplary for the sum of 16 PAHs (EPA-PAHs). Additionally, the fact that PAHs in spruce needles and soils decrease with increasing height indicates that near-emissions from alpine valleys are a major emission source of PAHs. Moreover, frequent atmospheric inversion inhibits the exchange with overlying, less polluted air masses.

In contrast to PAHs, the levels of OCPs in needles and humus increase frequently with increasing height and correlate with decreasing temperatures.[5] This suggests the entry by long-range atmospheric transport and proves the cold trapping.

From the seasonal and spatial differences in the distribution of pollutants in the Alps, it can be concluded that the global background concentrations are relevant for a large proportion of PBT substances in the Alps. Only with the group of PAHs, the local emissions can be considered more significant. This indicates that only for the case of PAHs mitigation measures that rely solely on the initiative of the Alpine countries could achieve significant effects.



Sum of the 16 polycyclic aromatic hydrocarbons in spruce needles (according to the method of the US EPA): The size of the circles corresponds to the concentrations. Local combustion processes and atmospheric inversion during winter presumably cause higher levels in the central Alps.

Solved and unsolved issues

Meanwhile 15 years of pollutant monitoring in the Alps proves the partly successes of European and international regulations of PBT-substances by giving evidence for the decline of some compounds. However, it clearly shows that regulation for many known pollutants should be reviewed furthermore and novel pollutants are emerging.

EFFECTIVE INTERNATIONAL AGREEMENTS

The high quality measurements, the coordinated approach between Austria and Bavaria, and the regular sampling enable the detection of long-term changes in pollutant exposure in the Alps. This allows identification of trends and determines whether international agreements are fulfilling their objective of reducing the input of PBT substances into the environment.

Significant decreases in air concentrations for the period 2006 to 2015 can be reported for about one-third of organochlorine pesticides (see table below). 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.

Even the major components of technical DDT (4,4'- and 4,2'-DDT), which is only partially forbidden globally, shows a decline in the period from 2006 to 2017, by over 60 percent. A distinct decline of over 96 percent was observed between 2006 and 2017 for the insecticide endosulfane which has been included in the Stockholm Convention since 2011, but has been banned in the European Union since 2005 (Figure below). This decrease demonstrates that, even before the entry into force of a global ban, a restriction at the level of the European Union can reduce air concentrations to a relevant extent.

A tendency for decreases in ambient air concentrations – probably due to EU legislation – is also visible for 2,4,4'-tribromodiphenyl ether (BDE 28), most volatile component of the technical Pentabromdiphenylether used as flame retardant (see Figure below). Penta- and octabromodiphenyl ethers have been banned in new products in the EU since 2004. The use of decabromodiphenyl ether (DecaBDE) has been severely restricted in electrical and electronic equipment since 2006.[4] However, the measurement series from 2012 is still too short to be able to derive statistically reliable statements.

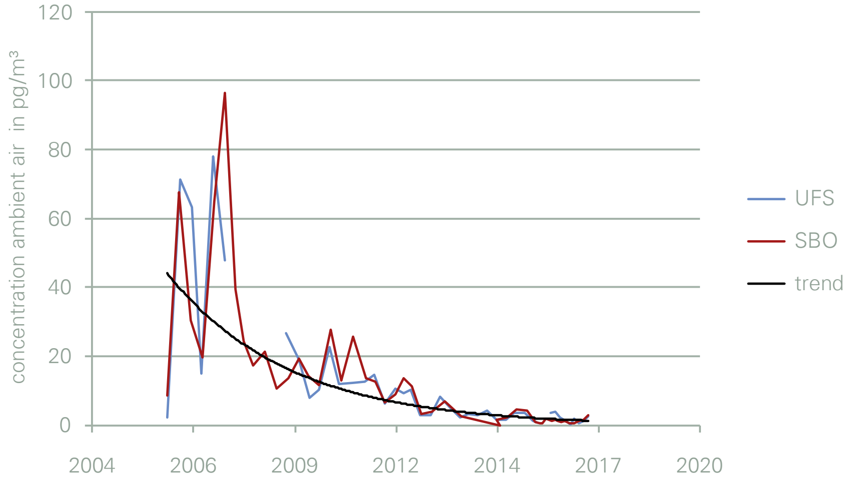
Similar can be said for the deposition of BDE 209, the main component of DecaBDE, which was included by the European Union in the candidate list of substances of very high concern (SVHC) under the REACH Regulation in 2012. Since May 2017, DecaBDE is also part of the Stockholm Convention. Between the first measurements of BDE 209 in the deposition at the Zugspitze in 2008 and the last evaluated data from 2016 there is a decrease of about 90 percent.[18]

The table shows pollutants for which a reduction in concentrations can be observed (statistically significant): „Current concentration level" corresponds to the median of the 2012–2017 measurements of Sonnblick and Zugspitze.

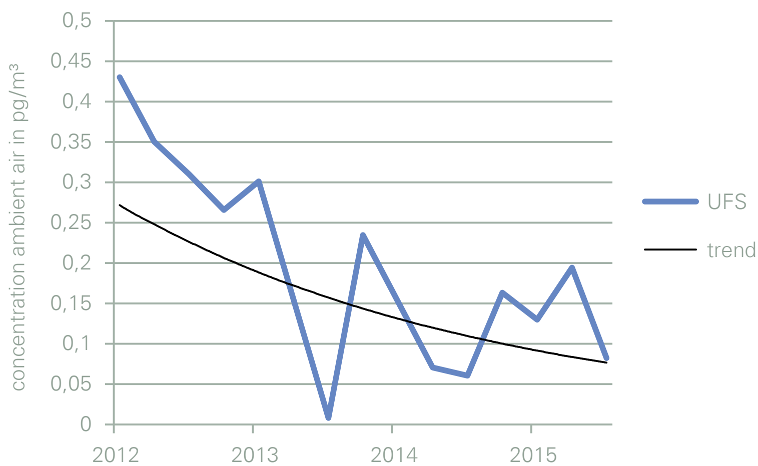
** For BDE 28, only measured values are available at the Zugspitze from 2012 on – therefore the percentage decrease refers to the years between the end of 2012 and mid-2016.*

Substance/Class of substances	Decrease 2006–2017	Current concentration level in Alpine ambient air [picogram per cubic meter of air]
α-HCH	-63 %	4,3 (n = 50; min 1,7 to max 13,7)
lindane (γ-HCH)	-61 %	5,9 (n = 26; min 1,2 to max 16,2)
pentachlorobenzene	-34 %	36,7 (n = 50; min 19,3 to max 67,7)
pentachloroanisol	-37 %	6,6 (n = 50; min 3,5 to max 15,5)
DDT (4,4' + 2,4')	-61 %	0,9 (n = 50; min 0,4 to max 2,3)
chlordane (*trans* + *cis*)	-44 %	0,8 (n = 50; min 0,4 to max 1,5)
cis-heptachlorepoxide	-45 %	1,0 (n = 50; min 0,4 to max 1,8)
endosulfane-I + II	-96 %	2,3 (n = 50; min 0,5 to max 12,1)
2,4,4'-tribromodiphenylether (BDE 28)	-64 %*	0,2 (n = 16; min 0,008 to max 0,4)

Decrease of endosulfane I +II of more than 96% between 2006 and 2017



Decrease of BDE 28



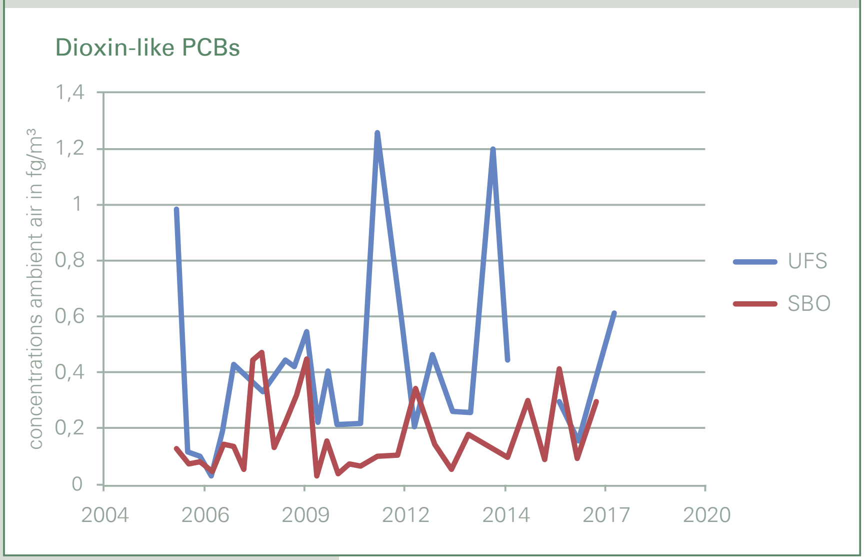
The success of European and global regulation of chemicals from 2011 onwards can be demonstrated by the significant decrease in air concentrations of endosulfane at the alpine peaks (the sum of endosulfane I and endosulfane II is shown).

SBO = Sonnblick Observatory, UFS = Environmental Research Station Schneefernerhaus (Umwelt-Forschungs-Station)

Only since 2012, with the start of the EMPOP project on the Zugspitze, the air concentrations of brominated flame retardants have been measured. A clear decline for BDE 28 is becoming apparent.

PROBLEMATIC CASES DESPITE INTERNATIONAL AGREEMENTS

The air concentrations of polychlorinated biphenyls (PCB in toxicity equivalents TEQ) show strongly fluctuating concentrations in the Alps with a slightly increasing trend.



Substance/Class of substances	Current concentration level in Alpine ambient air
dioxins (PCDD/F)	0,39 fg TEQ/m³ (n = 20; Min 0,06 to max 1,1)
dl-PCB (dioxin-like polychlorinated biphenyls)	0,27 fg TEQ/m³ (n = 19; Min 0,1 to max 2,2)
indicator PCB	9,0 pg/m³ (n = 20; Min 2,9 to max 27,5)
pentachlorobenzene	36,7 pg/m³ (n = 50; Min 19,3 to max 67,7)
hexachlorobenzene	93,9 pg/m³ (n = 50; Min 53,6 to max 134,7)
hexachloro-1,3-butadiene	991 pg/m³ (n = 35; Min 541 to max 1628)

Dioxins (PCDD/F) are highly toxic substances with PBT properties. Dioxins are formed as unwanted by-products in various chemical processes and combustion, especially by burning materials containing chlorine such as PVC (polyvinyl chloride). With the beginning of the 1990s, the installation of appropriate exhaust gas filters in waste incineration and industrial plants reduced dioxin concentrations in metropolitan areas by about 80 percent [14]. Since 2004, dioxins have also been part of the Stockholm Convention.

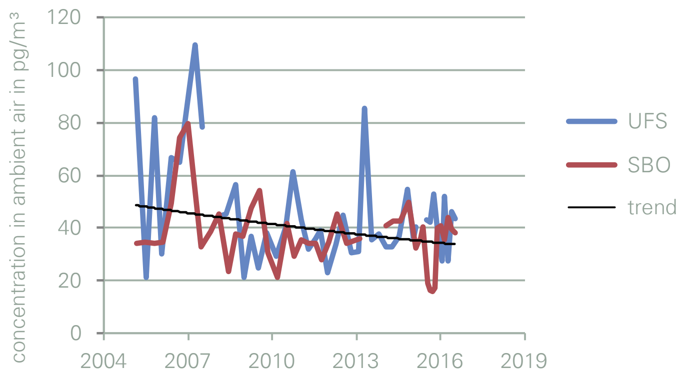
For the alpine air it was found that for the period from 2006 to 2018 the dioxin concentrations tend to decrease, but are subject to larger fluctuations. The same pattern is given for the deposition of dioxins by dust and precipitation: Currently, the deposition is similar compared to measurements in 2005/2006. Overall, until 2018, only weak tendencies of a decrease could be detected. Moreover, additional peak loads exist that are four times higher than the usual entry rates. The underlying causes of these peak loads could not yet be clarified.

The PCBs (polychlorinated biphenyls), which are also regulated by the Stockholm Convention, give a similar picture as dioxins. PCBs are formed to a limited extent in combustion processes, but mainly were used in large quantities as softeners and insulating oils until the end of the 1970s. Up to now, they therefore still evaporate from building materials (joint sealants, paints) and due to improper disposal of transformers and capacitors.

The table shows pollutants that are internationally regulated, but which show no decline in their environmental concentrations or which show relatively high concentrations. Values are medians from the concentrations of Hoher Sonnblick and Zugspitze between 2013 and 2017.

The air concentrations of the dioxin-like PCBs have fluctuated since measurements began and even show significant increases for certain congeners (figure above; the same applies to the deposition by dust and rainfall. The extent to which living beings in the Alps are burdened by these entries is currently being investigated in the PureAlps projects.

Overall, dioxins and PCBs continue to enter the Alpine ecosystems, with no tendency towards a visible decline. For this reason, it must be clarified globally, where similar effects can be observed, what causes the observed air concentrations, and whether further action is required on an international level.



A decline in the concentrations of pentachlorobenzene has been observed since 2006, but the pollutant can still be measured in concentrations five to ten times higher than comparable substances. Since approximately 2010 ambient air concentrations are stagnating

Other pollutants that are indeed regulated internationally but which are measured at relatively high concentrations at the Alpine peaks are pentachlorobenzene, hexachlorobenzene and hexachloro-1,3-butadiene. These substances occur in comparison to other organochlorine pesticides in five to hundred times higher concentrations. Pentachlorobenzene was used until the 1990s for the production of pesticides and disinfectants; hexachlorobenzene was applied as a fungicide and disinfectant; hexachlorobutadiene was used as hydraulic fluid and pesticide. All three substances, similar to dioxins and PCBs, can also be formed by combustion processes, for example in the case of improper disposal of waste. In the production of chlorinated solvents, pentachlorobenzene, hexachlorobenzene and hexachlorobutadiene are formed as unintentional by-products [19, 22]. Although between 2006 and 2015 a decline of pentachlorobenzene has been recorded, the decline (Figure top) implies that concentrations in the air settle at a relatively high level. For penta- and hexachlorobenzene as well as hexachlorobutadiene it should therefore be clarified where the currently relevant emission sources are and which processes underlie their entry into the atmosphere.

UNCLEAR TRENDS REQUIRE DEEPER UNDERSTANDING

For many organochlorine pesticides, no statements about increases or decreases are currently possible Indicated concentration levels are medians of SBO and UFS from 2012 to 2017.

Substance/Class of substances	Current concentration level in Alpine ambient air [picogram per cubic meter of air]
β-, δ-, ε-HCH	in sum 0,2 (n=50; min 0,07 to max 1,2)
trans-Heptachlorepoxid	0,06 (n = 31; min 0,02 to max 3,4)
Aldrin	0,02 (n = 31; min 0,007 to max 0,14)
Methoxychlor	0,10 (n = 33; min 0,01 to max 0,6)
Mirex	0,08 (n = 50; min 0,03 to max 0,3)

Many of the substances measured at Hoher Sonnblick and Zugspitze show no clear trends. In part, this is due to relatively short time series, as given for example for many brominated flame retardants. However, even substances that have been part of the measurement program since 2005 show no statistically significant trends. These include some organochlorine pesticides, although they are regulated by the Stockholm Convention and their reduction is intended on an international level (Table below).

The picture is unclear as well for polycyclic aromatic hydrocarbons (PAHs). Some PAHs show significant decreases in air concentrations, others stagnate, still others even increase significantly (see table below). Therefore, little can be said about global trends for the PAHs as a whole, since regional sources also play a role.

When looking at the complete datasets of Zugspitze and Hoher Sonnblick it is striking that in the case of depositions by dust and precipitation a significantly decreasing trend is rarely observed. The unclear situation in the deposition on the one hand is due to the extremely fluctuating precipitation rates that occur from measurement period to measurement period (each three months). On the other hand, complex processes play a role in scavanging PBT substances via water, ice and dust from the air, which are additionally increasing the variability.

Efforts to limit potential emissions primarily affect concentrations in the air. Since deposition is the more relevant factor for the contamination of ecosystems with PBT-substances, statistically proof changes can only be detected with very long time series, where even more than ten years are not sufficient, as the present data shows.

Substance	Tendency of air concentration	Current concentration level in Alpine ambient air [picogram per cubic meter of air]
Naphthaline	↘	2.964,0 (n = 49; min 857 to max 12.578)
Acenaphthylene	↘	4,3 (n = 39; min 0,4 to max 15)
Acenaphthene	↘	69,0 (n = 49; min 11 to max 405)
Fluorene	↘	269,0 (n = 48; min 116 to max 760)
Phenanthrene	↘	152,0 (n = 49; min 54 to max 672)
Anthracene	↗	10,0 (n = 33; min 2,8 to max 50)
Fluoranthene	↘	49,0 (n = 49; min 22 to max 162)
Pyrene	↘	20,0 (n = 49; min 8,7 to max 188)
Benzo[*a*]anthracene	~	2,7 (n = 37; min 0,6 to max 15)
Chrysene	↘	5,7 (n = 40; min 1,3 to max 15)
Benzo[*b*]fluoranthene	↘	5,9 (n = 31; min 1,2 to max 14)
Benzo[*k*]fluoranthene	~	4,6 (n = 36; min 1,4 to max 9,5)
Benzo[*a*]pyrene	~	3,8 (n = 42; min 0,7 to max 16)
Indeno[1,2,3-*cd*]pyrene	~	6,0 (n = 30; min 2,0 to max 15)
Benzo[*g,h,i*]perylene	↗	7,1 (n = 34; min 1,6 to max 24)
Dibenzo[*a,h*]anthracene	~	1,0 (n = 25; min 0,1 to max 3,9)

The table shows the current air concentrations (median, averaged from Sonnblick and Zugspitze between 2012 and 2017) and trends of the 16 recorded polycyclic aromatic hydrocarbons (EPA-PAK) between 2006 and 2017.

INCREASING CONCENTRATIONS OF NOT YET REGULATED SUBSTANCES

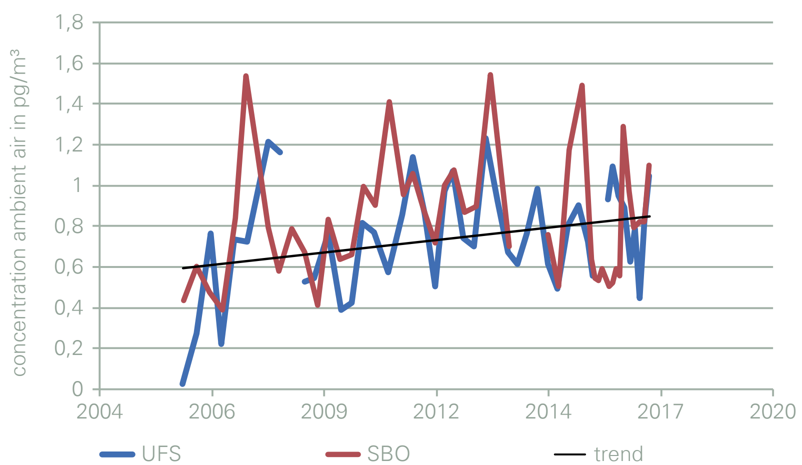
Concerning the abundance of chemicals produced by humans, the monitoring at Hoher Sonnblick and Zugspitze is suited to identify novel problematic substances. However, due to the high demands on the chemical analysis, it is necessary that at least initial information is available, so that the substances can be specifically analyzed.

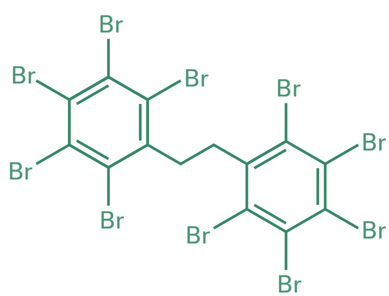
From the group of organochlorine pesticides, octachlorostyrene (OCS) can be identified as possibly problematic case. OCS is a substance that has hitherto been neither nationally nor internationally regulated. Since the beginning of the program, ambient air concentrations of OCS at the incorporated summits are steadily increasing (Figure left): The increase of 30 percent since 2006 is statistically significant at Zugspitze. OCS is classified as a PBT substance[15] and is also suspected of acting as a hormone for certain organisms.[20]

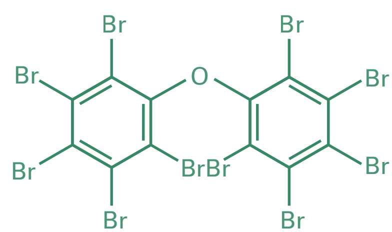
OCS originates from the extraction of aluminum and magnesium in chlorine chemistry and the combustion of plastics containing chlorine. Concerning the deposition in the alpine area, it is currently completely unclear, from which sources the OCS originates. The simultaneous measurement of high concentrations 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.[19, 22] Therefore, it would be desirable for OCS to record the main sources and quantities emitted internationally in order to possibly develop measures to prevent further increases in ambient air concentrations.

Octachlorostyrene has been measured since 2006 in significantly increasing concentrations

Increase of octochlorostyrene of more than 30% between 2006 and 2017







Structural formula of Decabromodiphenylethane, DBDPE (left) and the previously used, meanwhile banned decabromodiphenyl ether, DecaBDE

Increasing demands on a low inflammability of materials and at the same time increasing production volumes of plastics lead to a worldwide increasing use of emerging halogenated flame retardants. Many of these are regarded as PBT substances,[13] but so far are neither nationally nor internationally regulated. Therefore, emerging halogenated flame retardants are also monitored at Hoher Sonnblick and Zugspitze. A total of eight of these have already been detected in the air, seven also in precipitation.

Particularly striking is decabromodiphenylethane (DBDPE). Several thousand tons of this flame retardant were introduced into the EU back in 2001, and since the bans and restrictions on older brominated 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 (Figure above). This similarity however extends to properties that affect the environmental risk. Despite already proven accumulation in seagulls and other animals[2], the decision on the final assessment of DBDPE was postponed to 2019 due to insufficient data from the European Chemicals Agency ECHA[3] and was not available until the editorial deadline for this publication.

DBDPE occurs at Zugspitze in ambient air in the highest concentrations of all measured halogenated flame retardants; its concentrations are meanwhile 3.5 times higher compared to the previously dominant DecaBDE. The deposition for the Sonnblick and the Zugspitze is of the same order of magnitude as DecaBDE. The measurements at the Hoher Sonnblick and at the Zugspitze show that DBDPE does not degrade appreciably in the atmosphere and is entered in ecosystems that are far from the emitting sources.

Substance	Tendency	Current concentration level in Alpine ambient air [picogram per cubic meter of air]
Octachlorostyrene	significant increase by 30 % between 2006 and 2017	0,8 (n = 50; min 0,5 to max 1,4)
Decabromodiphenylethane	uncertain	1,0 (n = 15; min 0,14 to max 4,5)

PBT substances for which there exist no international regulations.

For a save future

The entry of novel PBT substances into the Alpine region shows that the precautionary regulation of environmental risks emanating from chemicals has not yet fully matured.

Given the global dynamics of economic development, population growth and global environmental changes, monitoring at Sonnblick and Zugspitze should contribute to protecting the ecosystem services and biodiversity of the Alps.

TURNING THE INVISIBLE VISIBLE

The observation period of meanwhile fifteen years now enables well-founded knowledge on trends in pollutant concentrations. Thus, the monitoring could prove the effectiveness of international agreements, as in the case of some organochlorine pesticides. However, there are many substances that should be monitored further on. This is shown by the steady concentrations of chlorinated dioxins and furans (PCDD/F) and polychlorinated biphenyls (PCBs).

The comparison of air concentrations and precipitation records confirms the thesis of the cold trap at high altitudes in the Alps: Deposition loads in the ecosystems cannot simply be deduced from the air concentrations of the pollutants. In fact, the deposition loads in the Alps are significantly higher than the low air concentrations give reason to expect. Of great importance for the pollution are therefore not only the air concentrations but also the cooler temperatures and the sometimes high precipitation rates. International agreements, which focus solely on ambient air concentrations of pollutants as the basis for assessment, would underestimate these potentially higher inputs.

The monitoring shows that the Alps are no longer an area that is free of the burden of pollutants. In addition to determining the levels of PBTs in air and precipitation, measurement activities therefore also serve to assess the societal intercourse with environmental risks posed by chemicals. Even beyond civilization, man leaves a clear footprint.

Continuous monitoring makes it possible to detect novel pollutants relatively quickly. As soon as chemicals are known as candidates for long-range atmospheric transport and persistency, they can be included in the monitoring, as long as an appropriate measurement technology is available. In the case of decabromodiphenylethane (DBDPE) and octachlorostyrene (OCS), monitoring currently indicates two emerging substances for which a thorough risk assessment should be carried out.

Currently, the PureAlps projects investigate the background levels of PBTs in wild fish such as brown trout.

OPEN QUESTIONS

While the monitoring can prove LRAT and the persistency of emerging pollutants so far, little is known about the enrichment in the alpine food chain. Therefore, the question of whatever the pollutant inputs are linked to bioaccumulation in organisms is investigated in the ongoing PureAlps projects in Bavaria and Austria. Here, the focus is on trout and chamois as representatives of animals living in the water and on land. Also predators such as fox, birds of prey or fish-eating birds are investigated. As an additional element, insects come into focus, since in this class of animals currently the greatest losses in biodiversity are being recorded, the causes of which are not yet entirely understood for the case of nature reserves.

In addition to extending monitoring to bioaccumulation, PureAlps has also expanded the range of studied substances. In particular, substances have been recently included in the monitoring that are under the watch list of the European Water Framework Directive; these include mercury and perfluorinated chemicals. Currently, there is insufficient data available on the behavior and long-term development of these substances in the Alpine region.

As the results of the 15-year monitoring of dioxins, PCBs, penta- and hexachlorobenzene and octachlorostyrene show, there are currently still relatively high levels of exposure to compounds, which are also produced as undesirable by-products in the combustion of chlorinated materials and in chlorine chemistry. In order to determine whether the sources of these pollutants are located in Europe or in remote areas, air masses must be sampled separately for their regional or global origin. Therefore, it was additionally verified in PureAlps in a separate study that it is possible to record air masses of the free troposphere separately from regional, ground-level air masses.[23]

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. There is the risk that the use of pesticides in agriculture will 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 Alps as a cold trap. Therefore, for this unique mountain range with its unique ecosystems, a global, early commitment to a more environmentally sound economy would be desirable, which also takes into account the environmental risks of chemicals.

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ABBREVIATIONS

LfU:	Bavarian Environment Agency (Bayerisches Landesamt für Umwelt)
LRAT:	long-range atmospheric transport
MONARPOP:	Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants
OCP:	organochlorine pesticides
OCS:	octachlorostyrene
PAK:	polycyclic aromatic hydrocarbons
PBT/PBT-substance:	persistent, bioaccumulative and toxic substance
PCB:	polychlorinated biphenyls
PCDD/F:	general „dioxins", in technical terms polychlorinated dibenzo-p-dioxins and -furans
REACH:	EU Chemicals Regulation (Registration, Evaluation, Authorizationand Restriction of Chemicals)
SBO:	Sonnblick Observatory, Hoher Sonnblick, Austria
UFS:	Environmental Research Station Schneefernerhaus, Zugspitze, Germany
WEI:	Measuring station at Weißfluhjoch, Switzerland

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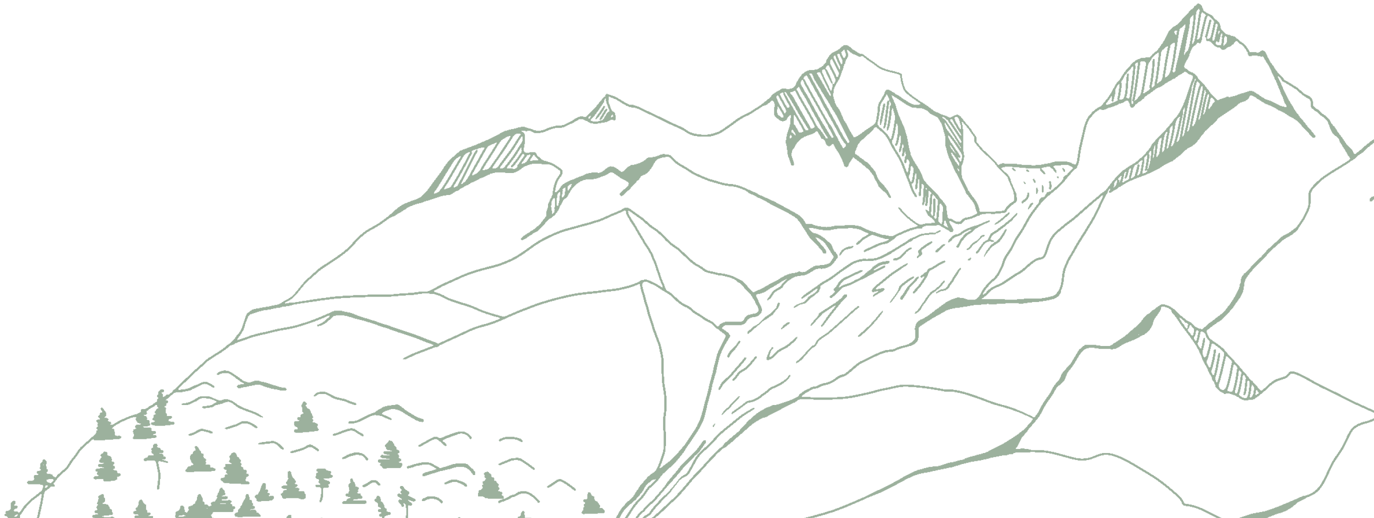

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