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POP DISPERSION IN THE ENVIRONMENT: WIND SELECTIVE SAMPLING OF DIFFERENT PM FRACTIONS UP AND DOWNSTREAM THE PREVAILING WIND-LINE OF A POTENTIAL EMISSION SOURCE

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Introduction

Persistent organic pollutants (POPs) are toxic chemicals that negatively affect environment and human health. Since they can be emitted by different anthropogenic activities, like waste incineration and industrial activities, they are nowadays ubiquitously present in our environment. They are persistent and can be transported over long distances by wind and POPs generated in one country can even affect peoples' health and wildlife far from where they were released. For this reason, it is considered that air is the key medium to be sampled in global monitoring programs. Active air samplers' permit to measure POPs selectively according to actual local wind conditions. The environmental impact of a potential emission source can be assessed up and downstream the prevailing wind-line. Used together with a multi-stage impactor, cut points for the particulate fraction at aerodynamic equivalent diameter of 10 µm, 2.5 µm and 1 µm (PM10, PM2.5 and PM1) can be obtained.5, This permits an evaluation of the distribution of dioxins/furans (PCDD/F) on the different size fractions of particulate matter. The use of an aerosol spectrometer permits a higher resolution of the size distribution of particles in ambient air and enables to determine the number, mass and specific surface for different particle sizes. An inside look to specific surface distributions' of the particles helps to explain the migration behaviour of POPs in the environment.

Materials and methods

Directional air samplers were used on the basis of the MONARPOP project, which is the first example of contamination assessment in the Alps regarding persistent organic substances. Directional air samplers allow to differentiate releases according to their origin. They also make it possible to perform distant emission checks of industrial sites or plants otherwise difficult to analyse directly and which, in any case, pose a potential threat of pollution to the environment. One or more directional air samplers are placed in proximity to a potential source of pollutants and collect pollutants on different cartridges according to wind direction. In this way, it is possible to distinguish the contribution of the "source" from that of the "baseline". See figure 1.

In line with wind direction, samples are on three different cartridges, two of which are active according to wind direction and the other in calm wind conditions. Impactors for fine particles that separate the PM10, PM2.5, and PM1 fractions were added to each of the cartridges of the directional air sampler (Genius5-Instruments, Kottingbrunn, Austria). Analysis of meteorological characteristics, underlying release processes concerning the Bolzano municipal waste incinerator and the prevailing wind line, identified the main influenced sites approx. 2 Km of south and approx. 2 Km north of the plant. During the monitoring campaign, one directional air sampler was placed north, one south of the incinerator plant and one was placed in the centre of Bolzano City. Each air sampler was equipped with three cartridges. One cartridge was programmed to sample when the wind was coming from the north, one when the wind was coming from south respectively. The third cartridge of the sampling system collected the air in case of calm wind conditions. At the end of the sampling the dioxin/furan concentration of the collected air was determined according US EPA 1613, using isotope dilution and HRGC HRMS (Thermo MAT 95 XP). The measurement campaign started in 2007 and was repeated in 2009, 2010 and 2015. The instrument used to detect fine particles was an aerosol spectrometer made by Grimm (Ainring, Germany) model 1.108) that classifies the particles size in 15 different size channels from 0,25 up to 20 µm. For the detection of ultra-fine particles a SMPS (Scanning Mobility Particle Sizer) system composed by a condensation particle counter from Grimm (Ainring, Germany) model CPC 5403, coupled to a Vienna-type Differential Mobility Analyser (DMA) 55706 operating within a range from 5.5 and 350 nm. The instrument allows a continuous measurement of the number as well as the mass and the specific surface of the particles, from 5.5 nm until 20 µm.

Results and Discussion:
The measurement results of the sampling campaigns listed in Table1 evidence no significant differences between samplings performed up- or downstream the incineration plant. For example, the obtained measurement results differed in year 2007 at the sampling point "north" from 90 (wind from north) to 79 fg I-TEQ/m3 (wind from south) and at sampling point "south" from 59 (wind from north) to 52 fg I-TEQ/m3 (wind from south).
On the other hand at the sampling point "Bolzano city", located north east of the plant and not in wind-line, at 3 Km distance, significantly higher measurement result of 155 (wind from north) and 259 fg I-TEQ/m3 (wind from south) were obtained. For this sampling point, for technical reasons, we have no measurement result for the calm wind conditions. This is a pity, since calm wind conditions usually lead to the highest measurement results, indicating that small, local emission sources like domestic heating and road traffic are the main source of POP in urban air. The results of table 1 also show us, that starting from year 2007 we do register a significant reduction of the dioxin concentration in Bolzano air. Regardless of the actual wind conditions, continuously lower values are found in 2010 (around 30 fg I-TEQ/m3) and 2015 (around 20 fg I-TEQ/m3). This positive environmental time trend can be related to specific reduction measures, like stricter traffic control, particle filters on new cars, increased use of natural gas for domestic heating and improvement of the energy efficiency of buildings.

Table 1: PCDD/F concentration in the air of Bolzano city in fg I-TEQ/m3 campaigns from 2007 – 2015

Applying multi-stage impactors on the sampling cartridges permits to have a closer look on the distribution of dioxins of different particulate fractions at aerodynamic diameter sizes of PM10, PM 2.5 and PM1. The analysis of PCDD/F of the different PM fractions on the sampling site "south" with wind from north showed that the fraction PM1was of 33 µg/m3 of 44 µg/m3 of PM10, or 75% of the PM10 fraction. On a dioxin basis, 90% are already in the PM1 fraction. Nearly the same findings resulted independently from the wind conditions, with wind from south or calm wind conditions.
The predominant POP content in ambient air particulate is therefore to be found in the PM1fraction, See table 2.

Table 2: PCDD/F in the different PM fraction on the south sampling site of the 2007 sampling campaign

Aerosol spectrometer allow better information on the size distribution of ambient air particles. Beside the much higher resolution, they offer also the possibility to plot the result in terms of number, mass and surface distribution of the different particle sizes. See Figure 2. In terms of numerical distribution, ambient air shows a strong contribution of small and very small particles (<100 nm) to the total particle concentration. In terms of mass distribution particles around or above 1 µm are dominant to the total mass contribution. Particles below 100 nm do practically not contribute to the total mass. But related to the POP dispersion in the environment we should focus on a third way of displaying the results. If we look at the specific surface distribution of the different particle sizes, a strong contribution of particles from 100 to 500 nm (0.5 µm) is clearly visible. POPs (dioxins, PCBs, HCB) have significant vapour pressures already at ambient temperatures, so that an equilibrium between gaseous and solid state is established. If the ambient temperature is cold, equilibrium shifts to condensation, if the temperature gets higher, the equilibrium shifts towards evaporation. The related adsorption or desorption processes are surface related and take place on the surface of the particles. Particles smaller than 1 µm (PM1) have a high specific surface where these processes take place. Figure 2.

Conclusion:
The migration of POPs in the environment is traceable through wind selective sampling. It is possible to measure the impact of a potential emission source like an incineration plant by sampling up and downstream the prevailing wind-line. In the case of the waste incineration plant of Bolzano, the study resulted in no significant differences, indicating that the plant is not a notable source of dioxins. Diffuse, local sources like domestic heating and road traffic do have the greatest impact. The results indicate that wind-transported POPs are mainly bound to the fine particulate fraction (PM1). The study showed

a high contribution of small local emission sources for urban areas (eg. domestic heating, traffic) to the total POP concentration in air. A negative time trend for the last ten years of Bolzano city "dioxin in air" concentration is visible. Reduction measures, like stricter traffic control, particle filters on new cars, increased use of natural gas for domestic heating and improvement of the energy efficiency of buildings, contribute to this.

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Table 1: PCDD/F concentration in the air of Bolzano city in fg I-TEQ/m^3 campaigns from 2007 – 2015

	Wind from north	Wind from south	Calm wind conditions
Year 2007			
Sampling point: north	90	79	89
Sampling point: south	59	52	84
Sampling point city	155	259	N/D
Year 2009			
Sampling point: north	25	26	167
Sampling point: south	41	40	39
Sampling point city	18	25	45
Year 2010			
Sampling point: north	28	30	42
Sampling point: south	18	24	52
Year 2015			
Sampling point: north	16	16	24
Sampling point: south	16	15	16

Table 2: PCDD/F in the different PM fraction on the south sampling site of the 2007 sampling campaign

	PM_{10}		$PM_{2.5}$		PM_1	
		Dioxin		Dioxin		Dioxin
	µg/m^3	fg I-TEQ/m^3	µg/m^3	fg I-TEQ/m^3	µg/m^3	fg I-TEQ/m^3
Wind from north	44	59	38	56	33	53
Wind from south	78	52	70	50	63	47
Calm wind cond.	45	84	39	82	34	77

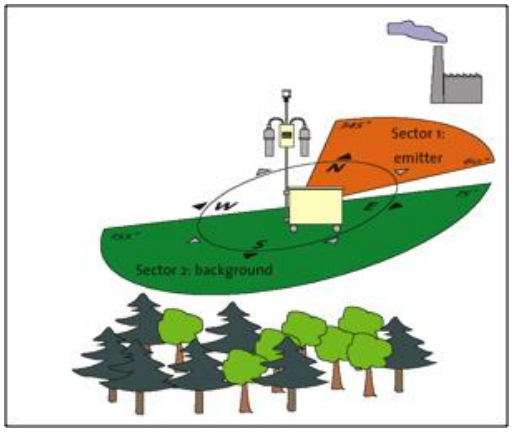
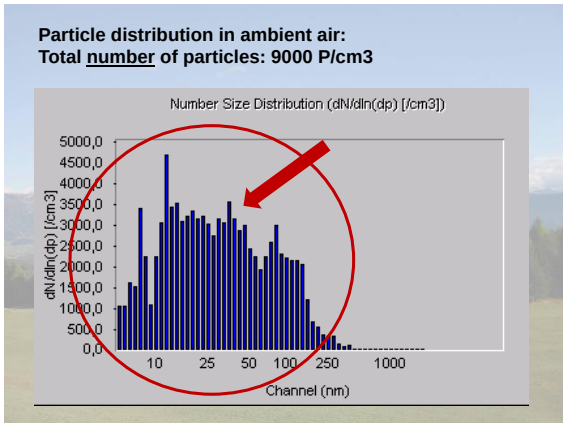
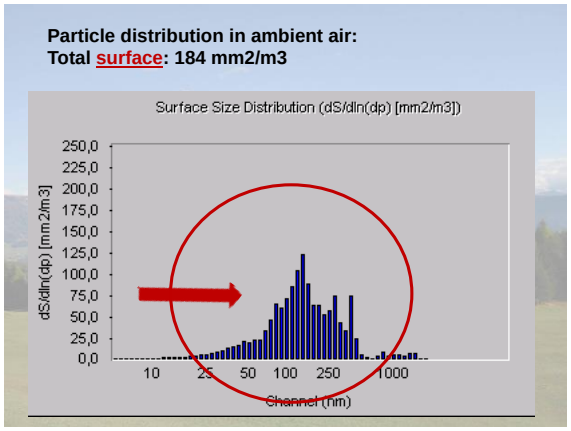


Figure 1: Air sampler placed in the vicinity of a potential emission source





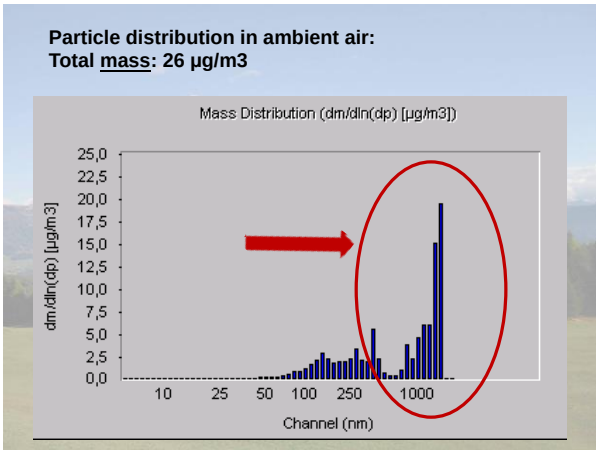


Fig. 2: Number, mass and surface distribution of the different particle sizes