

# Atmospheric Scavenging of PCBs, Pesticides and Unknown Compounds in the Snow by GC-Orbitrap

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## 1 Introduction

Persistent Organics Pollutants (POPs) are removed from the atmosphere by wet (snow and rain) and dry (particulate matter and the gaseous phase) depositions. The scavenging of contaminants from the atmosphere is the result of a combination of both processes which vary according to the physical and chemical properties of the contaminants [1]. To this end, it is important to understand (1) the distribution of chemical species between the two phases and (2) the prevailing deposition process as a function of the distribution. Distribution and equilibrium calculations are performed using partition coefficients ( $K$ ) which describe the distribution of chemical species in a two-dimensional coordinate system from air to wet and dry deposition, depending on the temperature [2]. The equilibrium for each compound depends on the pressure of the subcooled liquid-vapor of the chemicals and/or the octanol/air partition coefficient ( $K_{OA}$ ) [3]. Focusing on the samples collected in high altitude and extreme latitude areas, the partition coefficients to be considered for POPs are the snow/air ( $K_{\text{snow/Air}}$ ) and particle/air ( $K_{\text{particle/air}}$ ) valid for  $T < 0^\circ\text{C}$ . Wania et Lei (2004) showed that among all the depositions taken into consideration, snow is the one with the greatest scavenging effect on chemical products [2]. Cold areas such as mountains, the Arctic, and the Antarctica area represent the tank of numerous pollutants that condense here due to low temperatures. In mountain areas, it is mainly concerned with water stored in reservoirs and needed for agricultural, livestock, and even domestic uses. The mountains are representative of large changes in the composition of the ecosystem on a small scale due to the great variability of the climate with altitude. They safeguard an enormous amount of animal and plant species that have found refuge here over time, even following climate change. After atmospheric long-range transport, snow is considered an effective scavenger and deposition medium for atmospheric POPs (gas & particle phase) [2, 4–6]. In this study, a sorbent based on activated carbon fiber (ACF) was used to monitor PCBs and organochlorine pesticides (OCPs) in both ambient air and snow samples in the area of Terminillo Mountain in central Italy. The effectiveness of the sampling was assessed through the R% of the  $^{13}\text{C}$  labeled perdeuterated standards with reference to ISO 16000 13 and 14, EPA TO-4A for air and EPA 1668B and 1699 for snow. In this paper, the scavenging effect of PCBs and OCPs was quantitatively evaluated by the sampling use of the same adsorbent and the sampling of atmospheric air and then snow after a snowfall for two consecutive events with the same adsorbent. It was decided to monitor pesticides that are photosensitive, according to the literature, and for this reason the samplings were performed in the absence of sunlight [7]. Moreover, thanks to the non-specificity of the ACF it was possible to perform a qualitative evaluation of the snow scavenging action on the Unknowns compounds through the GC-Orbitrap analysis.

## 2 Materials and Methods

**2.1 Standard Solutions .** The quantification followed the isotopic dilution method, which involves the use of three standard solutions at a concentration of  $10\text{ pg}/\mu\text{L}$  containing  $^{13}\text{C}$ -labeled and perdeuterated congeners of pesticides and PCBs in different steps of the analysis. The Sampling Standard Solution (SS) included pesticides ( $^{13}\text{C}_6\text{-HCB}$ ,  $^{13}\text{C}_6\text{-PeCB}$ ,  $^{13}\text{C}_6\text{-}\gamma\text{-HCH}$ , D6- $\alpha\text{-HCH}$ ,  $^{13}\text{C}_{12}\text{-}\alpha\text{-HCH}$ ,  $^{13}\text{C}_{12}\text{-p}$ , p-DDE) and PCBs (P-48SS); the Extraction Standard Solution (ES Solution) and the Internal Standard Solution (IS Solution) contained  $^{13}\text{C}_{12}\text{-PCBs}$  (WP-LCS and WP-ISS, respectively); IS solution was added before the GC-Orbitrap analysis. The pesticides were quantified through the labeled congeners of PCBs.

**2.2 Activated Carbon Fiber.** ACF is based on cured phenol-aldehyde fibers that have a specific surface area of about  $2500\text{ m}^2/\text{g}$  and a microporosity uniformly distributed on the surface. The material was already characterized and tested in previous studies [8],[9]. The ACF was prewashed in a Soxhlet with toluene for 24h and dried in an oven at  $120^\circ\text{C}$  under  $\text{N}_2$  flow. The ACF was cut into 102 mm and 47 mm diameter and sandwiched between two Quartz Fiber Filters (QFF): QFF/ACF/QFF.

## 2.3 Samplings and Cleanup

The air-ambient and snow samples were collected in an open field located on Mount Terminillo (Rieti, Italy;  $42^\circ26'43.5''\text{N}$   $12^\circ59'36.2''\text{E}$ ) at 1536 m asl. Two snowfall events were monitored and for each one ambient air (HV) and snow (SN) samples were collected in duplicate. The details are presented in Table 1 and Figure 1. For each event: Two high-volume PM10 samplers were used in parallel at a flow rate of 200 L/min for 24 h. A 102 mm diameter ACF sandwich filter was placed on the sampler head and the SS solution was spiked (100  $\mu\text{l}$ ) before

the sampling started. The ACF sandwich filter was extracted in Soxhlet with toluene for 36 h after adding the ES solution (100  $\mu$ l). Two snow samples were collected with the shovel technique, in two pre-washed 50 L steel barrels. Pre-washed fiberglass blankets were placed on the ground to identify the sampling area to be collected after the snowfall event, following the air sampling. The snow was then melted at room temperature for 24 hours. The melted snow was spiked with 100  $\mu$ L of SS Solution diluted in 1 mL of acetone and the extraction was carried out by sucking the melted snow directly from the barrels through pre-washed Teflon tubes and a holder containing a 47 mm QFF/ACF/QFF sandwich filter, spiked with 100  $\mu$ L of ES Solution. The ACF filter was then extracted in Soxhlet with Toluene for 36 h. The air and snow extracts were concentrated and purified using a basic alumina column and eluted with n-hexane: dichloromethane (94:6 v/v). Blanks followed the same process.

Table 1: Sample collection. For each event, air sampling via High volume (HV) parallel samplings (A and B) and two samples of snow (SN). HV1\_BI and HV2\_BI are ambient air blank collected for each event, as well as FB\_1 and FB\_2 are snow sample field blank.

	Air Sampling	Snow Sampling
Event 1 26-27/02/2020	HV1 A, HV1 B, HV1 BI	Sn1 A, Sn1 B, FB 1
Event 2 07-08/03/2020	HV2 A, HV2 B, HV2 BI	Sn2 B, Sn2 B, FB 2

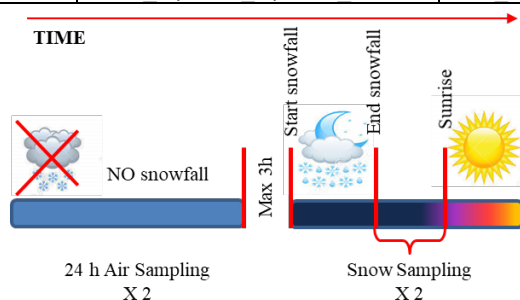


Figure 1: Graphic layout of an event. 2 parallel 24h-ambient air samplings in the absence of snowfall. Start of snowfall at a maximum of 3 h after the end of the ambient air sampling. At the end of the snow event and before sunrise (no UV light), collection from the ground of two snow samples.

**2.4 PCBs, Pesticides Analyses, and Untargeted Screening.** The analyses were performed in HRMS through GC-Orbitrap with Helium at a flow rate of 1ml/min using a DB-XLB column (60 m; I.D. 0.25mm; Film: 0.25  $\mu$ m). Targeted quantification was performed on samples spiked with 100  $\mu$ l of the IS solution by collecting chromatograms in SIM mode setting the resolution at 30000 and the AGC at 5e5. The study of Unknown compounds was performed on “raw” samples, namely injected immediately after the extraction and before the clean-up. The analyses were performed in Full scan mode setting a resolution of 60000, the AGC at 1e6, and a scan range from 50 to 500 m/z. Four batches were created to identify unknown compounds in snow and air, and those that undergo scavenging during the two snowfall events (Event 1 and Event 2). Only the latter two will be discussed in this work. The batches were made up of air and snow samples and the blanks of the same event (i.e. HV\_A, HV\_B, HV\_BI, SnA, SnB and FB). They were processed for “deconvolution” and “Unknown” function with the TraceFinder 4.1 software. The deconvolution processing settings were: TIC intensity threshold of 1000, ion overlap window of 98%, RT alignment of up to 3 s, and SI threshold of 500. After the retention times alignment, every single identification was screened. The “retention index” function was applied and all libraries were included for cross-search. Two levels of reliability have been defined: a) High level: it only includes compounds with a Score > 90% in all batch samples. The Score represents the correspondence between the deconvolved spectrum and the library search and it is expressed in %; b) Medium Level: it includes all compounds with an Average Score (AVG Score %) > 90%. The AVG Score of a compound is the weighted average by the intensity of a compound's match score across the batch. For both levels, the compounds are included in the lists only if detected in all the samples of the batch and absent in the blanks. The identification of a compound simultaneously present in the two parallel air samples and in the two snow samples of the same event (but absent in the blanks) gives the certainty that it was scavenged from the atmosphere through the snowfall. Subsequently, each compound is studied based on the mass spectrum, online databases, and literature searches before compiling the final list.

### 3 Results

**3.1 POPs Data.** Table 2 shows concentrations of all PCBs and pesticide congeners detected in air and snow samples. Data from sample Sn2\_B were discarded since the R% of SS and ES Solutions did not meet the minimum requirements of the methods.

Table 2: Concentrations of OCP, PCBs in air ambient (pg/m<sup>3</sup>), and snow (pg/L) samples. All values <LOD were considered as LOD/2 for the quantitative and identified in bold in the table.

	HV1_A	HV1_B	HV2_A	HV2_B	Sn1_A	Sn1_B	Sn2_A	
	pg/m <sup>3</sup>	pg/m <sup>3</sup>	pg/m <sup>3</sup>	pg/m <sup>3</sup>	pg/L	pg/L	pg/L	
OCPs	PeCB	148	125	103	70	<b>0.0032</b>	<b>0.0036</b>	<b>0.0032</b>
	α-HCH	2.0	1.4	0.91	<b>0.50</b>	141	156	112
	HCB	92	73	55	40	196	174	152
	γ-HCH	10.7	8.3	5.8	1.2	160	261	476
	p,p-DDE	8.8	5.8	2.8	1.8	419	300	228
	o,p-DDT	68	44	21	15	175	78	<b>0.22</b>
PCBs	81	0.32	0.35	0.31	0.30	<b>0.0021</b>	11	<b>0.0033</b>
	77	0.71	1.1	1.4	0.20	<b>0.0032</b>	201	20
	123	0.52	0.31	0.10	0.70	48	30	40
	118	8.7	6.6	4.5	2.8	850	200	100
	114	0.20	0.10	0.11	0.12	<b>0.031</b>	<b>0.030</b>	<b>0.031</b>
	105	1.9	1.5	1.1	2.1	241	310	70
	126	0.90	0.70	0.60	0.40	<b>0.0031</b>	<b>0.0030</b>	<b>0.0031</b>
	167	2.9	2.5	2.1	1.5	<b>0.0030</b>	<b>0.0030</b>	<b>0.0032</b>
	156	4.1	3.2	2.3	1.8	55.3	<b>0.010</b>	<b>0.011</b>
	157	2.8	2.6	2.4	2.1	<b>0.0040</b>	<b>0.010</b>	<b>0.010</b>
	169	0.90	0.70	0.50	<b>0.00022</b>	<b>0.0021</b>	<b>0.0023</b>	<b>0.0031</b>
	189	6.7	6.5	6.3	4.1	<b>0.0022</b>	<b>0.0037</b>	<b>0.0032</b>

**3.2 Unknown Screening.** The chromatogram deconvolution and the retention times alignment of the identifications gave a total of 6769 compounds for the “Event 1” batch and 6813 for the “Event 2” batch. After meticulous processing of each list of compounds, it was possible to cluster the compounds based on their sources. Figure 2 shows the results for the two batches.

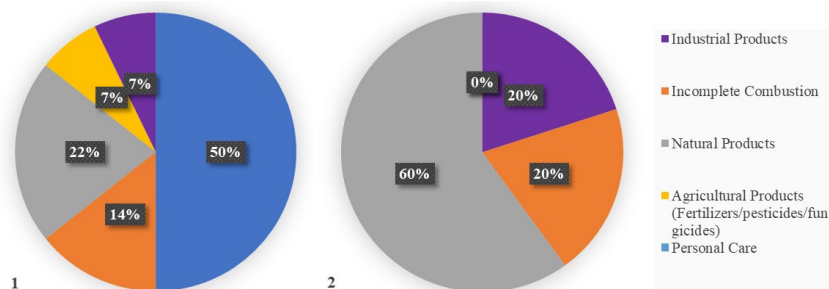


Figure 2: The high and medium levels of identification of each event were considered together. 1) Event 1; 2) Event 2. Main categories/sources = Purple: Industrial products; Orange: Incomplete combustion; Grey: Natural products; Yellow: Agricultural products (Fertilizers/pesticides/fungicides); Blue: Personal Care.

## 4 Discussion

**4.1 POPs Results.** The high OCPs concentrations could be linked to the fact that the samples were collected in winter with a low presence of irradiation and before sunrise, so they underwent limited degradation [10]. However, as far as the concentrations of HCB, p,p-DDE, and o,p-DDT may appear high, they still fall within the ranges found in similarly remote areas [10]. HCB is a compound that does not undergo photodegradation and it is so persistent that in mountainous areas and at high latitudes it tends to accumulate during the winter and resists until summer when it is released by the melting of the snow. Furthermore, the lighter compounds (e.g. α-HCH, γ-HCH, PeCB, and HCB) tend to undergo long-distance transport and it is easy to find them in these regions despite the low values in the air. As regards p,p-DDE, and o,p-DDT, it can be reasonably assumed that they are deriving from the valley in the province of Rieti since strong winds were recorded from the south/east. The concentrations of these compounds detected in the air were significantly lower than those in snow samples, a matrix that tends to be much richer. It can be assumed that time extended air samplings are required to enrich the ACF in the classes under consideration. PeCB is detected in all ambient air samples but not in snow samples. Given the high R% of the <sup>13</sup>C<sub>6</sub>-PeCB of all snow samples, it cannot

be attributed to the analytical method. There are no comparable studies in the literature on this compound and only two events are not sufficient to draw environmental conclusions. As for PCBs, according to Lei and Wania, the snow scavenging ratio is directly proportional to the degree of chlorination as the temperature decreases ( $< 0^{\circ}\text{C}$ ). This justifies the higher relative concentration in the snow samples compared to the concentrations in the air for the congeners 156, 157, and 189 (respectively Hexa- and Hepta-chlorosubstituted) compared to 123 (Penta substituted chlorine). Despite the concentration of PCBs in ambient air samples, snow scavenging was not as efficient as for pesticides; according to the literature, this is due to the greater scavenging action of the particulate concerning the wet depositions in this class [2],[11]. Both PCB and pesticide concentrations agree with the values normally found in these matrices in mountain areas [10],[12].

**4.2 Untargeted Screening.** It was found that all the identified compounds of the final lists fall into some main categories/sources (Figure 3).

Among the industrial products, numerous phthalates (plasticizers) have been identified, mainly related to Event 2 (20% of the total). Apparently, the detected phthalate contamination was specific to Event 2. Indeed, during the study, this class was found in the snow but not in the air of Event 1, which would be explained by the transport of suspended materials during the snowy night. This result assumption is supported by the large number of phthalic acid esters found in Event 2 versus Event 1 across all levels (High and Medium). These data highlight the importance of atmospheric stability, the presence of winds, and vertical mixing as parameters to be considered in the study of the scavenging effect of depositions. Moreover, phthalates, flame retardants, adhesives, and paint additives were identified among the industrial products in both events. Interestingly, two compounds identified used as paint additives in batch Event 2 were: ethyl 4-dimethylaminobenzoate [13] and diethylene glycol acetate propionate [14]. Two days before the start of the ambient air sampling of Event 2, some balustrades were painted not far from the sampling site. This resulted in a positive confirmation of the truthfulness of the data collected, given the absence of such compounds in Event 1. Another category that stands out is that of personal care, equal to 50% of the total Event 1. Two constituents of detergents and household cleaning products have been identified (ex. Methyl 2,4-dihydroxy-3,6-dimethylbenzoate [15],[16]). The (2-methyl phenyl)phenyl-methanone has also been included in this category, even if there are no specific data in the literature, but due to the chemical structure attributable to benzophenones used as UV screens in sun filters [17]. Two Oxy-PAHs were identified among the combustion products, which could have been generated directly in the combustion of e.g. diesel engines [18] or after PAH emission deriving from combustion (anthropogenic or natural) due to reactions in the atmosphere [19].

## 5 Conclusions

An in-depth study of POPs in the atmosphere cannot be limited to the air matrix alone. Dry and wet depositions have a decidedly not negligible scavenging effect on POPs.

The versatility and non-specificity of ACF has given the possibility to study and deepen the knowledge on the scavenging of PCBs and pesticides from the atmosphere through the snow, but above all, it has allowed to expand the study of new classes of contaminants both in the air and in the snow. The next step will be to undertake validation studies to understand whether the adsorption and desorption of these compounds are quantitative and reproducible. In all cases, it is only a preliminary screening as it is necessary to use ad hoc standards to carry out the study of unknown compounds.

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