

Contaminants in alpine glaciers: a never-ending story?

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Abstract

This study is aimed to further contribute to the knowledge of the state of pollution of alpine glaciers, paying particular attention to two contrasting aspects that are contributing to a process that we define as the “*never ending story*” of contamination of the glaciers. On one hand, the temporal trend of accumulation in glaciers of selected POPs (HCHs, HCB, DDTs, PCBs) was verified to be decreasing. On the other hand the possibility of emerging contaminants (currently used pesticides and musk fragrances) to be accumulated in these environments was highlighted. Firstly, the outcomes of OECD multimedia model application argued in favor of a possible phenomenon of medium range atmospheric transport for the most used pesticides in the Northern Italy. These theoretical findings were supported by the experimental results, which showed the presence of chlorpyrifos and terbuthylazine in the glacial melt-water samples (0.1-1.9 ng/L). At the same time evidences of selected fragrances (HHCB, AHTN) accumulation in the glacier were given (0.9-1.8 ng/L).

1. Introduction

Atmospheric transport has been recognized as a major pathway for the distribution of anthropogenic contaminants (Harriss et al. 1984). Concern over the long range atmospheric transport (LRAT) of Persistent Organic Pollutants (POPs) and their detrimental effects in cold ecosystems, such as the Arctic, started in the early sixties with the detection of persistent organochlorinated pesticides (e.g. DDT, dieldrin, aldrin). Later, the detection of other POPs categories (PCBs, dioxins, furans, PBDEs etc) in these areas has increased enormously (Gregor et al. 1989; Stern et al. 1997; De Wit 2002; Herbert et al. 2005). This has led to regulatory concern and, in 2001, to the Stockholm Convention (2001) and to the ban or the strong use reductions of POPs. Wania & Mackay (1996) and other authors (Gouin et al., 2004; Hageman et al., 2006) best explained the mechanisms underlying the atmospheric transport of POPs. Briefly, the combination of some physical chemical properties and persistence of these substances enhances their capability to be transported very far from the emission sources. In 1991, Calamari and coworkers (Calamari et al., 1991) were among the first scientists indicating the mountains as potential “cold condensers” that could interfere

with the global cycles of POPs. Exactly like “remote cold areas”, such as Arctic and Antarctic regions, the mountains can act as cold traps and sinks for these substances (Carrera et al., 2001; Villa et al. 2003; Wang et al. 2006). More recently (Daly & Wania 2005), by recalling previous studies (Wania & Mackay 1993; Wania & Mackay 1996), highlighted the potential of mountains to act as regional convergence zones for selected organic pollutants through a sort of “altitudinal fractionation”.

The effectiveness of mountains to act as cold condensers is depending on several factors such as meteorological conditions (rain and snow precipitation regimes, wind direction, temperature etc.) (Daly & Wania 2005; Vighi et al. in Castro Jiménez, 2007), orographic effects (i.e. the influence of mountain slopes on air flow) (Daly & Wania 2005), presence of vegetation (Nizzetto et al., 2010) and post depositional processes (Villa et al., 2003; Villa et al., 2006; Bogdal et al., 2009). For instance, the extent to which contaminants are transported into mountain regions is clearly dependent by meteorological conditions and orography. Particularly, the presence of the Planetary Boundary Layer (PBL) can have a strong influence on the atmospheric transport of contaminants. Generally, the height of PBL varies from 1000-2000 m a.s.l., in function of the season and location. Areas, which are located below the PBL during the year, are mainly affected by regional or Medium Range Atmospheric Transport (MRAT) of contaminants, which are originated from local sources. On the contrary, mountain sites located above the PBL are more prone to be contaminated from distant sources through LRAT in stratosphere or troposphere layers.

In addition to the above mentioned factors, mountains are in close proximity to emission sources; in fact, whereas the Arctic and especially the Antarctic are located thousand kilometers far from the main industrial and agricultural areas, many mountains are relatively close to these regions. As matter of fact, the most important Earth's mountain systems are quite close to the densely populated and/or agricultural areas. For instance, the European Alps lie across the most populated and highly industrialized regions of Europe. The relative proximity of mountains to source regions has a potential to increase POPs concentrations in air entering in mountain systems to levels, which are higher than those entering the Arctic. As previously reported, this is dependent by the presence of regional or MRAT processes, which can act contemporaneously to LRAT processes. Fortunately, there is some evidence that the ban of POPs is leading to decline of the concentrations of these compounds in several compartments (Holoubek et al. 2007; Brun et al. 2008) and consequently in the atmospheric transport towards mountains.

In a recent study, Arellano and coworkers (2015) evaluated the atmospheric deposition trends (in terms of deposition fluxes) of some organochlorine compounds in four high-altitude European sites. The authors found an increased and constant deposition trends for PCBs and HCB, respectively. However, the same authors observed a significant decline of pesticide deposition from 1996 to 2006 and this was attributed to restrictions on their emissions from primary sources, which reduced the contamination due to MRAT processes. This seems to be quite in agreement with a previous study of Villa et al. (2006). Through the analysis of a firn core drilled on the Lys Glacier (Monte Rosa Group, Italian Alps) in Summer 2000, these authors came to the conclusion that for most of the analyzed POPs, the deposition process on the Lys glacier was more dependent from LRAT than from local emissions. Based on such evidences, the accumulation rates

in glaciers should show a decreasing profile, at least for some categories of POPs. On the other hand, closer distances can increase the potential of glacier contamination from other typologies of contaminants not included in the POP list, because of MRAT processes. For instance, currently used pesticides (CUPs) as well as many other emerging contaminants (e.g. PCP: Personal Care Products) tend to have much greater polarity and water solubility than the POPs and are much more biodegradable. This has led researchers to consider the potential for atmospheric transport of these substances to be quite negligible. In spite of this, evidences of the presence of CUPs in air, rain, pine needles or remote lake waters are growing up (Zabik & Seiber 1993; Aston & Seiber 1997; LeNoir et al. 1999; Gouin et al. 2008; Kurt-Karakus et al. 2011; Santolaria et al., 2015). In addition, there are a few studies highlighting the presence of CUPs or PCPs in snow samples taken at high altitude and in proximity of glaciers (Hageman et al. 2006; Villa et al. 2014).

On this basis, one could argue that there are two contrasting processes leading to what we call a "*never-ending story*" of contamination of the glaciers. On one hand, the ban of POPs and the strong reduction in local sources is having a positive influence in reducing the degree of contamination of these environments. In fact, the contribution of MRAT processes to POP accumulation in glaciers could be significantly decreased during the last years. On the other hand, the proximity of the mountains to the high densely populated areas could have increased the presence of other categories of contaminants and this could be historically underestimated. Since 2000, our research group has been involved in a number of studies aimed at understanding the dynamic of accumulation and release of POPs in Alps glaciers (Villa et al. 2003; Villa et al. 2006). More recently and for the first time, we also measured the presence some musk fragrances (galaxolide and tonalide) both in fresh fallen snow samples (Villa et al. 2014) and in glacial meltwater of Forni glacier. This has led to the hypothesis of possible accumulation of these and other categories of compounds in glaciers, as consequences of MRAT processes. Based on these previous experiences, the experimental work presented in this paper has had a dual aim. The first objective was to verify if a declining trend of POPs accumulation in the Italian Alps glaciers is ongoing. Secondly, we aimed to highlight possible processes of accumulation in glaciers for other categories of compounds such as CUPs and PCPs (polycyclic musk fragrances). This was done by measuring the concentration levels of selected compounds in glacial melt water collected from three different Italian Alpine glaciers (Lys, Forni and Ortis Cevedale) in two different monitoring campaigns (summer and late summer/autumn). For POPs, the measured concentrations were then compared with our historical series to evaluate the trend of contamination. For CUPs, in consideration of the high number of active ingredients utilized in the agricultural practices of the Po River plain, a preliminary screening was made in order to select those compounds showing a higher potential to reach the glaciers. This was done by considering both the volume of uses (sales data) and the results of the OECD Pov and LRTP screening tool model (OECD, 2002; 2004; Wegmann et al. 2009). Finally, the decision to include in the study the synthetic musk fragrances was taken to widen the evidences of their presence in Alpine glaciers and to confirm the data obtained in previous studies (Villa et al. 2014).

2. Materials and methods

2.1 Description of the sampling area and meteorological conditions

The selected sampling sites are located in the Italian Alps: the Lys Glacier in Monte Rosa massif, the Forni Glacier in Ortles-Cevedale group and the Giogo Alto Glacier in Palla Bianca - Similaun group (Figure 1). The criteria for sites selection were based on differences in geographic positions, meteorological regimes (Gabrieli et al. 2010; 2011) and land uses.

Forni and Lys Glaciers are directly influenced by human activities only to a small extent, whereas Gioco Alto Glacier is exploited as skiing area. During spring and summer, all of them receive air masses coming both from the surrounding agricultural and urbanized areas (Gabrieli et al. 2011; Villa et al. 2014). These authors reported a strong link between Po River plain emissions and atmospheric depositions over high altitude Alpine glaciers during spring and summer seasons. In that period, Maggi and coworkers (2006) indicated significant vertical exchanges between the boundary layer and the free troposphere due to the presence of convective storm systems. This phenomenon produces snowfalls highly loaded with chemical substances, which deposit on glaciers (Largiuni et al. 2003). In addition, even though the air mixing within the Po river plain is very efficient (APAT, 2008), the presence of hot-spot emissions may cause heterogeneous depositions of pollutants over the Alps.

The Lys Glacier is close to France and Switzerland and extends from 4,282 m a.s.l. to 2,600 m a.s.l. covering an area of about 9.58 km² (Smiraglia & Diolaiuti 2015). Meltwater samples were collected on two different dates (25th of July 2014 and 3rd of October 2014). Further east, the Forni Glacier belongs to the Stelvio National Park and covers about 11.34 km² (Smiraglia & Diolaiuti 2015). The samples were gathered from the Frodolfo stream (about 1 km from the Glacier) on 2nd of July 2014 and 9th of September 2014, respectively. Finally, the Giogo Alto Glacier is located near the Italian and Austrian borders; it covers an area of 0.95 km² (Smiraglia & Diolaiuti 2015) and is located in the area characterized by the lowest precipitation rate of the entire Italian Alpine system (Gabrieli et al. 2011). Meltwater samples were collected on 24th of July 2014 and 10th of September 2014, respectively.

Previous experimental works in the same areas (Villa et al. 2001; Villa et al. 2003; Villa et al. 2006; Bizzotto et al. 2009; Villa et al. 2014) allowed simplifying the experimental design and reducing the numbers of sampling campaigns. All samples were collected using aluminum cans (5 and 2.5 L) prerinsed with acetone and hexane. The water volume collected for each sample was about 10 L. They were kept refrigerated during the transport, and stored at -20°C until analysis.

Figure 1: Location of the sampling sites on the Lys Glacier, the Forni Glacier and the Gioco Alto Glacier and land use in the surrounding areas in Northern Italy.

According to Jakobi and coworkers (Jakobi et al. 2015), air pollutants are transported towards the Alps by the large scale synoptic air flow and regional and local wind systems. Particularly, these authors indicated that, because of typical cyclonic weather patterns across the Alps, the Weissfluhjoch station (located in the

mid-western part of the Central Alps) receives repeated airflows coming from the Gulf of Genova by crossing the Po Riverplain. This station is not far from both Forni and Giogo Alto glaciers investigated in this study. In addition, previous studies using air masses back trajectory models have shown the presence of local air masses coming from Po Basin and flowing to the Alps (Finizio et al. 2006; Kaiser et al. 2007; 2009; Gabrieli et al. 2011). Particularly, Kaiser et al. 2007 indicated that the northwest corner of Alps (where the Lys glacier is located) is most exposed to the air flow from the Po basin. On this basis, it can be assumed that the investigated glaciers receive a continuous load of contaminants from polluted air masses coming from the Po basin.

2.2. Chemical analysis

Analytes included in this study were selected on the basis of: i) previous experiences of this research group in the studied areas (Villa et al. 2001; Villa et al. 2003; Villa et al. 2006; Villa et al. 2014), ii) pesticides sales data in the Po river plain area and iii) the output of a screening model (see paragraph 2.4). They comprise organic pollutants belonging to three different categories:

- Persistent Organic Pollutants (POPs): DDTs (including DDE, and DDD), α - and γ -HCHs, HCB, PCBs (28, 52, 101, 118, 138, 153, 180 congeners);
- Polycyclic Synthetic Musk fragrances (PCMs): galaxolide (HHCB) and tonalide (AHTN);
- Currently Used Pesticides (CUPs): terbuthylazine (TBZ), chlorpyrifos (CPF) and pendimethalin (PEN).

Analytical standards were purchased from Dr. Ehrenstofer GmbH (Augsburg, Germany), and Sigma-Aldrich (Saint Louis, USA). All solvents (residue analysis grade; Merck Darmstadt, Germany) were checked by gas chromatography (GC) before use.

In order to separate particulate matter, water samples were filtered on a glass fiber filter (0.45 μ m, Whatman, Maidstone, England), before SPE procedure. Prior to the extraction of suspended solid samples, glass fiber filters were cleaned with hexane.

Filtered water samples (divided into 2L fraction) were extracted with SPE cartridges (Oasis HLB, 6 cc/500 mg, LP Extraction cartridge, 60 μ m; Waters Corporation Milford, Massachusetts, USA). The cartridges were pre-cleaned with 5 mL of hexane, conditioned with 3 mL of methanol and 3 mL of deionized water (Milli-Q). Samples were then drawn through the cartridges using a vacuum manifold at a flow rate of 10 mL/min. In order to assess the recovery efficiency, 10 μ L of recovery standard (mixture of PCB 40 and PCB 128 at concentration of 400 pg/ μ L), previously diluted in 3 mL of methanol, were added to each sample. After the extraction, the cartridges were dried under vacuum pressure and subsequently eluted (under gravity) with 6 mL of hexane and 3 mL of ethyl acetate.

Extraction of suspended solid samples was performed via soxhlet with n-hexane for 24 h. The extracts were then concentrated to 2 mL by rotaevaporation. Then 50 μ L of recovery standard (mixture of PCB 40 and PCB 128 at concentration of 400 pg/ μ L), previously diluted in 3 mL of methanol, were added to each

sample. The extracts were then concentrated to 0.5-0.7 mL by a gentle stream of nitrogen. Samples purification were achieved by column chromatography using 0.5 g Supelclean ENVI-carb SPE tubes (Supelco, Bellefonte, PA, USA) pre-cleaned with 10 mL of hexane. Samples were drawn under vacuum through the cartridges at a regulated flow rate of 10 mL/min. After the extraction, the cartridges were dried using a vacuum pump and subsequently eluted (under gravity) with 10 mL of n-hexane, 10 mL of a mixture of n-hexane/ethyl acetate (60:40) and 5 mL of ethyl acetate.

All the extracts were finally concentrated to 0.2-0.3 mL by a gentle stream of nitrogen and transferred into GC micro-vials with 25 μ L of dodecane, as keeper.

Finally, the internal standard (PCB 30) was added for subsequent analysis in GC-MS (Agilent Technologies, Santa Clara, CA, USA), in SIM (Single Ion Monitoring).

The GC identification and quantification was performed with an Agilent Technologies 6890N Series gas chromatograph equipped with a 30-m long, 0.25-mm internal diameter capillary column (Zebtron Capillary GC Column, ZB-Semivolatiles Guardian). Samples were injected by an Agilent Technologies 7683 Series autoinjector, with the injection port at 250 °C in splitless mode. Samples were run in splitlessmode using helium as a carrier gas (flow= 1 mL/min). Transfer line and detector temperature were maintained at 280 °C.

Details on oven program, MS setting and limit of detection are reported in Section S1 of the Supporting Information (SI).

2.3. Quality control

A series of procedural blanks was analyzed contextually to the extraction tests. Field blanks were generated and handled in a manner identical to that of water sample. No CUPs were found in blanks while HCB, PCB p,p'-DDT and musk fragrances were present occasionally. Reported values were then corrected by subtracting the average blank values of HCB (mean concentration about 73 pg/L), p,p'-DDT (631 pg/L), PCB 52 (429 pg/L), PCB 101 (185 pg/L), HHCB (380 pg/L) and AHTN (128 pg/L).

2.4. The OECD Pov and LRTP screening tool model

In this study, the potential atmospheric transport of 12 CUPs highly used in the agricultural practices of the Po River plain (Table SI-2) was estimated by means of the OECD P_{ov} and LRTP Screening Tool software (vers. 2.2 downloadable at <http://www.oecd.org/env/ehs/risk-assessment/oecdповandlrtpscreentool.htm>). A more detailed description of the model is reported in Section S2 of the Supporting Information and in the original papers (OECD, 2002; 2004; Wegmann et al. 2009). It is currently applied as a screening tool for making comparative assessments of environmental hazard properties of non-ionizing chemicals, using metrics of overall persistence (P_{ov}) and long-range transport potential (LRTP) (Öberg & Iqbal 2012). Very recently, it has been also utilized to evaluate the potential of Medium Range Atmospheric Transport (MRAT) of the musk fragrances AHTN and HHCB (Villa et al. 2014). As substance-specific inputs, the

software requires air-water partition coefficient (K_{AW}) and the octanol-water partition coefficient (K_{OW}), as well as the degradation half-lives (DT50) in soil, water and air (Table SI-2).

3. Results and Discussion

The application of the OECD P_{ov} and LRTP screening tool allowed identifying those CUPs to be included in the monitoring campaigns. Particularly CPF, PEN and TBZ were selected. Further information of the obtained results are reported in Section S2 of the Supporting Information.

3.1 Contamination patterns in meltwater samples of the investigated glaciers

An overall picture of the analysed chemicals residues found in the melt water samples collected in the three glaciers is reported in Figure 2 (details in table SI-3). In the Figure 2, data are referred to the sum of concentrations measured in both the dissolved and sorbed phases (Wania et al. 1999; Hageman et al. 2006) and are grouped according the three broad categories of POPs, CUPs and PCMs. Some compounds (o,p'-DDD, p,p'-DDD, o,p'-DDT, o,p'-DDE and PEN) were always below the detection limits.

At first glance, the fingerprint of contamination in the three Alpine glaciers seems to show the same profile. In fact, in all the sampled sites the observed trend is PCMs > CUPs > POPs and PCMs > POPs > CUPs in early and late summer monitoring campaigns, respectively. Changes in the seasonal trends are mainly due to a decrease in CUPs concentrations in the second sampling period. Yet, no statistical significant differences were found between samples collected in July and September (data not reported).

However, going into a deeper detail, it becomes evident that there are some qualitative differences among the sites starting from West towards Est. For instance, among POPs, HCHs isomers are exclusively present in Lys melt water samples. This site is also characterized by the highest levels of TBZ. On the contrary, both compounds are not detected or are present in very small concentrations (TBZ in Forni Glacier) in the other two glaciers.

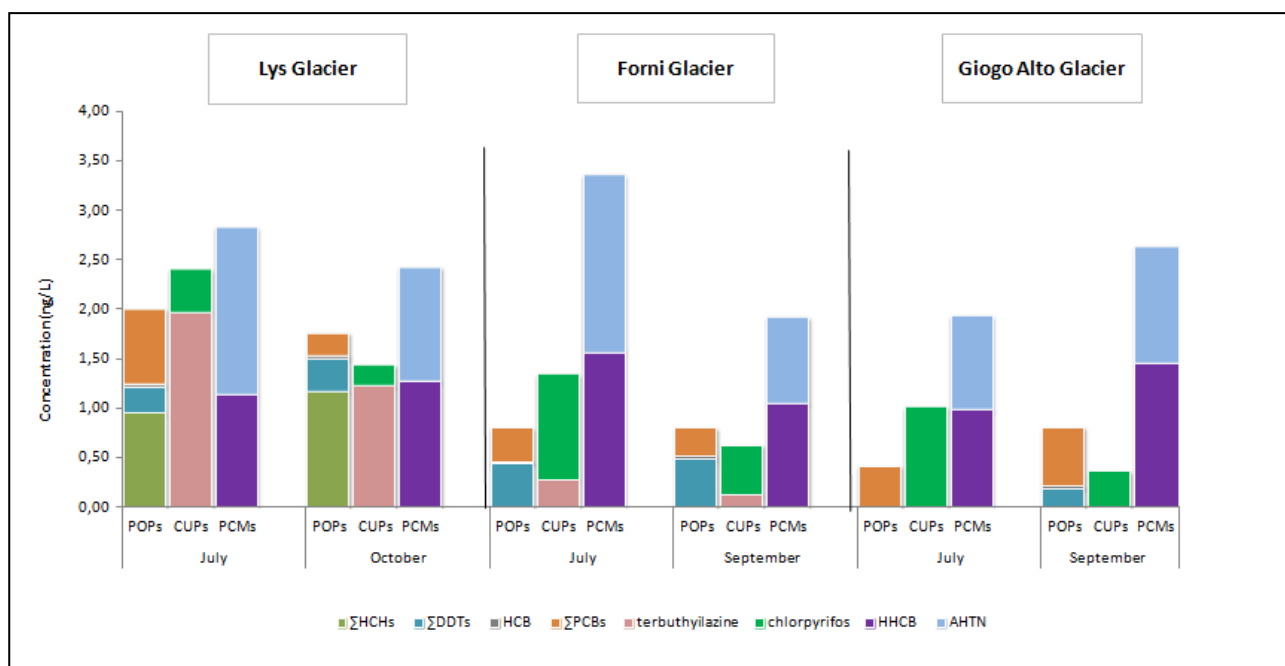


Figure 2: Chemicals concentrations in Lys Glacier, Forni Glacier and Giogo Alto Glacier meltwater samples.

In the next paragraphs, a deeper discussion for each category of the investigated chemicals will be made.

3.1.1 Currently Used Pesticides

As previously described, in this study, the attention was focused on those CUPs showing the highest CTD (TBZ, CPF and PEN) and TE. Two of them (TBZ and CPF) were frequently present in the analysed samples, whereas PEN was always below the detection limit (Figure 2).

TBZ seems to show a decreasing profile from West to East, with the highest measured concentrations in the melting waters of Lys Glacier (1.98 ng/L and 1.23 ng/L in July and September, respectively). TBZ has been frequently measured in air and rainwater samples (Dubus et al. 2000; Mai et al. 2013); nevertheless, there are no evidences of LRAT for this substance, as well as of its presence in snow or glaciers. To the best of our knowledge, the data presented in this study are the first record of TBZ in alpine glaciers. However, it must be pointed out that very recently Santolaria and coworkers (2015) reported the presence of TBZ in a Pyrenean cirque glacial lake (Sabocos tarn) located in the Tena Valley (Spain). In the surface lake water samples, these authors found TBZ concentrations ranging from 2.27 ng/L (July 2011) to 0.32 ng/L (August 2014). This could be an indirect confirmation of potential accumulation of this substance in mountain glaciers.

The potential LRAT of TBZ could be limited by rain scavenging at the lower latitudes. In fact, this compound shows a low value of Henry constant and this could favor its partition into rain. In presence of natural barriers, such as Alps Mountains, the higher precipitation rate could provide an effective sink for this substance, limiting the LRAT process, but enhancing the accumulation of TBZ in mountain glaciers.

In our study, CPF has been detected in all the three investigated glaciers, with concentrations ranging from 0.21 ng/L (Lys glacier in September) to 1.06 ng/L (Forni glacier in July). Contrarily to TBZ, there are a number of studies showing that CPF can undergo to long- and regional-scale atmospheric transport (Muir et

al. 2004). In fact, CPF has been frequently detected in Arctic media (air, water, sediment and biota) (Hageman et al. 2006; Landers et al. 2008; Hoferkamp et al. 2010). The historical reconstructions of CPF concentrations in Arctic ice cores (Hermanson et al. 2005; Ruggirello et al. 2010) suggested its constant presence since 1953.

Highly variable concentrations of CPF, ranging from 0.02 ng/L (Hageman et al. 2006) in Rocky Mountains to 80 ng/L in Arctic samples (Hoferkamp et al. 2010), are reported for snow samples. Based on our results, CPF released from the Italian glaciers into melt waters are in the same order of magnitude of those present in Rocky Mountains. The only available data of the presence of CPF in European mountains are those present in the study of Santolaria and coworkers (2015). These authors reported CPF concentrations ranging from 0.62 ng/L (July 2011 and April 2014) to 0.12 ng/L (August 2014). Even if this data are referred to lake water samples, it must be pointed out that they are in the same order of magnitude of our findings.

Despite model prediction, PEN residues were not measured in all the analyzed samples. The used quantities of this substance could be a possible explanation for this discrepancy. In fact, the sold volume of PEN is two/three times less than CPF and TBZ, respectively (Table SI-2). In the available literature, there are few and contrasting data about the atmospheric transport of this substance. In fact, in two different ice cores drilled in the Svalbard Islands (Norway), PEN residues were not measured or measured sporadically at very high concentration (18 ng/L) in the Holtedahl Fionna and Austfonna ice core samples, respectively (Ruggirello et al. 2010).

From the analysis of Figure 2 and Table SI-3, temporal differences can be also observed. In all the glaciers, the highest CUP concentrations were measured in samples collected in early summer and this can be ascribed to the release of CUPs buried in fresh snow. In fact, as shown by Villa and coworkers (2014), seasonal variations in contaminant concentrations in glacial meltwater is function of the different origins of the sampled waters: in late spring, the predominant source of meltwater feeding glacial stream is the last seasonal snowpack, whereas in late summer the glacial melt is more pronounced. Concentrations measured in meltwater deriving from seasonal snowpacks are the joined result of two factors: the application timing of pesticides and weather conditions. In fact, spring and summer months are the growing seasons and period of intensive use of pesticides. In addition, the transport of ground emitted pollutants to high altitude locations is enhanced by the behavior of planetary boundary layer allowing vertical exchanges (Maggi et al. 2006). At high elevation, the spring/summer snow scavenges efficiently the atmosphere (Lei & Wania 2004) and deposits the contaminants on glaciers, giving rise to highly concentrated spring/summer layers (Largiuni et al. 2003).

Lastly, TBZ and CPF concentrations show different geographic profiles along the Alps (Figure 2 and Table SI-3). The differences in land uses, the presence of natural geographical barriers and/or differences in precipitation regimes could help to explain these results.

In Figure 1, the agricultural land use of the Po River plain is depicted, in relation to the geographic positions of the three investigated glaciers. Historically, maize is the main cultivation of the Northern Italy, and TBZ is applied on this crop as a pre- and post-emergence herbicide. On the contrary, CPF is widely used on vine and

fruit trees (primarily apple trees). These crops are prevalently present in Alps valleys and foothills; the latter are mainly located in the southern edge of the Po River plain. The Lys glacier faces directly to the West side of the Po River plain in an area without geographical barriers. On the contrary, Forni Glacier is separated from the Po River plain by the presence of the Alps foothills (reaching maximum altitudes of 2,500 m a.s.l.), whereas the mountain groups of Dolomites (highest altitude 3,050 m a.s.l.) and the Adamello (max elevation 3,560 m a.s.l.) lie between the Giogo Alto Glacier and the Po River plain. Moreover, the Giogo Alto Glacier is located at the boundary between the Central and Southern European climate regions and differs from the glacial areas of the Western Alps, especially for the precipitation rates and seasonality (Davis et al. 2003).

The lack of geographical barriers and the presence of higher precipitation rates (1100-1300 mm yr⁻¹) are the driving factors, increasing the level of TBZ concentrations measured in Lys Glacier runoff waters. On the opposite, high-elevated mountainous groups (Dolomites and Adamello) represent an area of high scavenging rates (1300 mm yr⁻¹ of rain). This area acts as a barrier and prevent the herbicide to reach the inner part of the Italian Alps: the Giogo Alto Glacier. Finally, among the three investigated sites, Forni Glacier is the closest to the area of high intensive maize cultivation. However, the presence of the Alps foothills and lower precipitation rates (750 - 850 mm yr⁻¹) could reduce the transfer of TBZ. Therefore, the combination of these factors leads to TBZ concentrations, which are between of those observed in Lys and Giogo Alto Glaciers.

The different trend shown by CPF could be ascribed to the spatial distribution of vine and fruit trees. Contrary to maize, which is widespread, these crops show a patchy distribution along the Po River plain. Particularly, they are present in the Alps valleys in an area, which is very close to Forni and Giogo Alto glaciers (less than 40 km in linear distance). Consequently, the higher concentrations of CPF in both site could be due to the very short travelling distance.

3.1.2 Polycyclic Musk Fragrances

The potential for HHCB and AHTN to undergo to a regional atmospheric transport was already assessed in a previous work of Villa and coworkers (2014). Furthermore, these authors confirmed the presence of both fragrances in fresh fallen snow samples and water taken in the area of the Forni Glacier. They hypothesized the potential of these substances to be accumulated in cold environments, near densely anthropized areas.

Present data support this hypothesis; indeed, both compounds were detected, at comparable concentrations, in all the analyzed sites: the averages for HHCB and AHTN were 1.25 ng/L (0.99 - 1.57 ng/L) and 1.27 ng/L (0.86 - 1.79 ng/L), respectively, which are in the same order of magnitude with those previously reported in the study of Villa and coworkers (2014) (HHCB and AHTN mean concentrations: 3.14 ng/L and 3.88 ng/L, respectively). The two investigated fragrances are characterized by a high and constant release in the urbanized areas present in the Po River plain. This can explain the widespread level of contamination of the Alps and the lack of seasonal variability found in this study. Finally, the HHCB/AHTN ratio is much lower than the value of 4:1 estimated from the market volumes of the two substances (OSPAR Commission, 2004). However, the ratio of about 1 substantially confirms those reported by Villa and coworkers (2014) in snow

(HHCB/AHTN ratio = 1.24) and in other remote sites (Xie et al. 2007). The different fate of two musks is probably driven by their half-life in atmosphere. As Aschmann et al. 2001 reported, AHTN is slowly removed by atmospheric degradation, because its atmospheric lifetime is almost twice than that of HHCB, which reacts faster with •OH.

3.1.3 Persistent Organic Pollutants

Table 1 presents a summary of the available data of POPs concentrations measured in glacial melt waters collected in Lys and Forni Glaciers, in different monitoring campaigns (starting from 2000). The reported data, expressed as mean concentrations, are referred to previous studies done by this research group (Villa et al. 2006). To the best of our knowledge, POPs concentrations measured in the glacial meltwater of the Giogo Alto Glacier are the first published data reporting the presence of POPs in this glacier.. Same order of magnitude

Table 1 –Comparison of measured concentrations of POPs in glacial meltwaters (ng/L)

	Lys glacier					Forni glacier						Giogo Alto glacier	
	2000 ^a	2001 ^a	2002 ^a	2014 ^b (July)	2014 ^b (Oct.)	2000 ^a	2001 ^a	2002 ^a	2006 ^c	2014 ^b (July)	2014 ^b (Sept.)	2014 ^b (July)	2014 ^b (Sept.)
HCB	0.03	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.04	n.d.	0.04	n.d.	0.02
α-HCH	1.28	0.82	0.47	0.62	0.74	0.53	0.26	0.21	0.29	n.d.	n.d.	n.d.	n.d.
γ-HCH	1.41	1.33	0.98	0.34	0.44	1.55	0.93	0.71	0.24	n.d.	n.d.	n.d.	n.d.
α/ γ ratio	0.91	0.62	0.48	1.8	1.67	0.34	0.28	0.29	1.23	-	-	-	-
p,p'-DDT	0.14	0.05	0.03	0.23	0.33	0.15	0.01	0.03	0.01	0.46	0.23	n.d.	0.10
p,p'-DDE	0.01	0.02	0.03	0.04	n.d.	0.04	0.01	0.03	0.16 (forse è meglio mettere solo il sito 1 del frodolfo?)	n.d.	0.27	n.d.	0.10
p,p'-DDE/ p,p'-DDT	0.07	0.4	1	0.17	<<1	0.27	1	1	16	<<1	1.17	-	1
ΣPCBs	na	na	na	0.76	0.24	na	na	na	0.212 - 0.006	0.35	0.28	0.43	0.60

na = not available; nd = not detected

Data from: ^a Villa et al. 2006, ^b present study, ^c Σ7-ICES Bizzotto et al. 2009

From Table 1 the following considerations can be made:

- HCB: In this study, the concentration values measured for this compound are of the same order of magnitude of previous studies (Villa et al. 2006; Villa et al. 2006; Bizzotto et al. 2009). In addition, there are not particular differences among the considered glaciers (both in the historical and present data). Our findings are in agreement with the most recent studies on HCB in mountains. In the already reported study of Santolaria and coworkers (2015), the HCB

concentrations ranged from not detected (April 2014) to 0.05 ng/L (August 2014). ABBIAMO ALTRI DATI? In a previous study, a reconstruction of the seasonal deposition trend of HCB was made through the analysis of samples of a firn core drilled on the Lys Glacier (Villa et al. 2003). According to these authors, the concentrations of HCB in the Lys ice core between the 1960s to late 1970s were below the detection limit. After an increasing trend during the 1980s, there was a decline in concentration starting from the early 1990s. (Sara c'è un perché?)

- HCHs: In the considered period, α and γ -HCH isomers seem to show a declining temporal trend. This is particularly evident in the melt water samples of the Forni Glacier. In 2014, both compounds are below their relative detection limits. In general, γ -HCH shows a higher declining rate and this can be seen from the α/γ -HCH ratio. Historically, α/γ -HCH ratio has been largely used to identify the possible HCH source. A ratio >3 , generally, indicates input due to the use of technical mixtures of HCHs (55-80 % α -HCH, 5-14 % β -HCH, 8-15 % γ -HCH, and 2-16 % δ -HCH; (Breivik et al. 1999) and LRAT (Lane et al. 1992). On the contrary, a ratio close or <1 is characteristics of local/regional use of lindane (γ -HCH) and of MRAT processes (Iwata et al. 1993; Willett et al. 1998). During the considered period, the ratio seems to be shifted from values indicating a prevalence of lindane and local/regional sources towards values tending to a prevalence of α -HCH and of a higher contribution of LRAT processes. A possible explanation of this trend can be ascribed to the introduction of new EU regulations concerning the γ -HCH. In 2004, lindane uses with crop protection purposes were prohibited in many EU countries (EU 2004), and since 2009, γ -HCH (together with α -HCH and β -HCH) is listed as POP in the Stockholm Convention (UNEP 2015). Therefore, this could have lowered the accumulation rates of lindane in glaciers as consequence of the decline in the use of this substance in the surrounding areas of the glaciers.
- DDTs: In this study, only p,p'-DDE and p,p'-DDT were detected. In 2014, the measured concentrations of p,p'-DDT were in the same order of magnitude along the monitored sites, with Giogo Alto showing the lowest concentrations in both sampling periods. p,p'-DDT show a fluctuating temporal trend and this becomes particularly evident when the Forni Glacier is considered (however, p,p'-DDT concentrations in Lys Glacier seems to follow the same trend). In Forni Glacier, starting from 2000, there is clear decreasing trend of p,p'-DDT up to 2006, followed by a sudden increase in 2014. Contrarily to p,p'-DDT, its metabolite (p,p'-DDE) seems to have a different spatial pattern of contamination. In Lys melting water samples, in 2014, the levels of this compound were close or below the detection limit, whereas appreciable concentrations of this compound were found in the other two glaciers at least during the second sampling campaign. In addition, concentration of p,p'-DDE seems to be quite constant during the considered period (however, a seasonal variability can be noticed). The differences shown by

the parental and its metabolite (both in concentrations and temporal trends) lead to a variability into the p,p'-DDE/p,p'-DDT ratio trends. In Lys Glacier this ratio is always ≤ 1 , whereas in the Forni this ratio shows a higher variability reaching a peak in 2006. The only available data for the Giogo Alto indicates similar concentrations of the parental and its metabolite (p,p'-DDE/p,p'-DDT = 1). In general the p,p'-DDE/p,p'-DDT ratio is used to estimate the age of DDT contamination, because DDE is the main product of DDT degradation under aerobic conditions in the environment (Wang et al. 2006). A higher ratio reflects an aged DDT source and is mainly related to LRAT processes (due to transformation of p,p'-DDT into its metabolite). On the contrary, a ratio < 1 indicates a fresh input of p,p'-DDT and usually is associated to MRAT processes. In a previous work (Villa et al. 2003), analyzing an ice core sampled at the Lys Glacier (4240 m a.s.l.), found a temporal trend of p,p'-DDT, which was clearly in contrast with the declining trends highlighted by other authors after ban of this substance. In the Lys ice core samples the concentrations of p,p'-DDT were almost constant up to the late 1970s, then slightly grown up to a sharp increase in the mid-1990s. The authors explained this trend as the consequence of continuous emissions from an industry, which used DDT as a precursor of dicofol. The factory was located in the Toce river valley (around 250 m a.s.l.), which is very close to the Lys glacier and the Lake Maggiore. Dicofol production started before the 1970s and was stopped in 1996 after an accidental release, which had serious consequences also on the level of the lake pollution (Toce river is an affluent of the Maggiore lake) (Guzzella et al. 1997). The amount of DDT lost during the accidental episode is not known but, taking into account the severity of Lake Maggiore pollution, a relevant emission (at least in the order of many kg) was hypothesized by Villa and coworkers (data). In fact, eight years after the closure of the industry ordered by the Italian Ministry of the Environment the lake was still heavily polluted (Bettinetti et al. 2005). In a recent study, Jakobi and coworkers (2015) measured the p,p'-DDE/p,p'-DDT ratio in atmospheric bulk deposition samples collected (from 2005 to 2010) in three elevated alpine summits: a) The Weissfluhjoch (WEISS: 2663 m a.s.l.) located in the mid-western part of the Central Alps, b) The Austrian Sonnblick Observatorium (SONN: 3106 m a.s.l.) situated in the eastern Central Alps, and c) The Schneefernerhaus (UFS: 2650 m a.s.l.) in the northern edge of the Alps in Bavaria. These authors found an averaged p,p'-DDE/p,p'-DDT ratio ranging from 0.35 in WEISS, 0.47 in UFS and 0.55 in SONN, respectively (average = 2005-2010 period). The ratio was lower in localities receiving air masses coming from the gulf of Genova and passing from the Po plain region. Consequently, emissions and especially re-emissions due to evaporation from the Po basin and probably from the Lake Maggiore area has affected and is still affecting the Alps. Then the accidental release of p,p'-DDT and the role carried out by MRAT processes can help to explain the presence and the accumulation of this compound in the three glaciers (it is interesting to note that the Giogo Alto, which is the farthest glacier from the Lake Maggiore area, in 2014 shows the lowest level of contamination). However, this does not

help to understand the increased p,p'-DDT concentrations in the melt water observed in the last monitoring campaign. In fact, in 2014, the measured concentrations are about one order of magnitude higher than those recorded in Lys and in Frodolfo glacial streams, in 2002 and in 2006 respectively (Villa et al. 2006; Bizzotto et al. 2009). These increases are in agreement with the trend described for the Silvretta glacier (Switzerland) (Pavlova 2014, Ph.D. thesis). A possible explanation of these increases could be ascribed to the significant retreat of Alpine glaciers and the consequent release of this compound, which has been accumulating in the past.

- PCBs: The Σ PCBs concentrations ranged from 0.24 to 0.76 ng/L (Table SI-3). The PCB congener No. 180, the heaviest considered, was never found above detection limit or background values. On the contrary, the PCB congener No. 52 was present in all samples. The concentrations found in Frodolfo, ranging between 0.28 - 0.35 ng/L, are close to the levels found by Bizzotto and coworkers (2009) in Forni meltwater samples. In 2006 the concentrations of Σ PCBs in Frodolfo were from <0.01 ng/L to 0.3 ng/L. However, in June 2006, these compounds reached extremely high concentrations (12.6-31.7 ng/L). The unexpected pulse in PCBs was explained by the fact that seasonal snow melting was coming to an end during June. Therefore the concentration's peak of these compounds were due to a short but heavy precipitation event that washed out substantial amounts of highly hydrophobic particle sorbed chemicals (Bizzotto et al. 2009). In literature, the concentrations detected in glacial streams in remote areas are about 0.36-0.48 ng/L (i.e. for the Canadian Rocky Mountains) (Lafrenière et al. 2006). The data of the selected PCBs are available also for Alpine ice cores. In particular in firn cores from the Lys Glacier the Σ PCBs concentration range from 0.21 to 0.68 ng/L in the period from 1997 to 2000 (Villa et al., 2006). These levels were comparable to concentrations determined in Fiescherhorn Glacier (Switzerland) in the same years, underlining an homogeneous distribution of these compounds in the Alpine region (Pavlova et al. 2014). Based on the Fiescherhorn ice core, that allowed to cover the entire time period of industrial use of PCBs, the level in 2002 is comparable to the concentration in the 1940s, when PCBs were introduced into the market (Pavlova et al. 2014). Another deposition record of PCBs that covers a long time period, was available from Lomonosovfonna glacier in the Arctic (Svalbard) (Garmash et al. 2013). Generally, PCBs concentrations in the Arctic are approximately by a factor of 100 lower than in the Alps due to longer distance from the sources of these compounds. In addition, the heavier congeners concentrations are lower in the Arctic ice core also because the long-range atmospheric transport to the Arctic is more hampered for these compounds, which are more susceptible to dry and wet particle deposition (Pavlova et al. 2014).

Conclusion

It is widely recognized that mountains play a key role in the atmospheric transport of POPs as they can act as “cold traps” for these substances. Therefore, during the years, glaciers have accumulated consistent quantities of POPs deriving both from long and medium range atmospheric transport processes. The regulatory efforts to decrease the emission of these compounds has been effective in the strong reduction of local emissions and consequently on the importance of MRAT contribution in glacier contaminations. The results presented in our paper seems to confirm the long-term declining trend of these contaminants in Alpine glaciers, however, the study has also highlighted the probability of a remobilization and higher release for some of them (particularly for DDT), because of global warming.

On the other hand, this work aimed to go a step forward and to highlight that MRAT processes are still playing an important role in the contamination of glaciers (probably even higher than LRAT) and that this has been historically under evaluated by scientific research. Until now, there are few evidences of the presence of other typologies of contaminants (e.g. currently use pesticides) in mountains environments such as alpine lakes or snow. The results reported in this paper are perhaps the first experimental evidences of a process of accumulation in Alpine glaciers of a variety of contaminants (CUPS and musk fragrances) and are in support of what we defined the never ending story of glacier contamination.

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