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Legacy and emerging contaminants in meltwater of three Alpine glaciers

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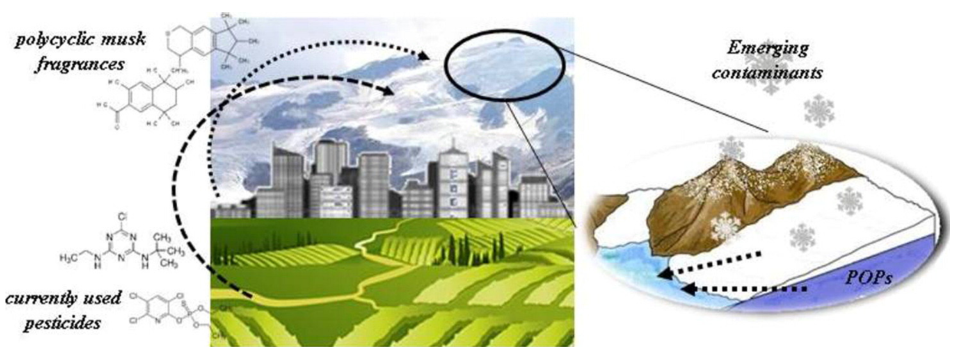
HIGHLIGHTS

- Terbuthylazine and chlorpyrifos in glacial meltwater.
- Influence of anthropized areas on glaciers contamination
- Legacy and emerging pollutants in alpine environments

GRAPHICAL ABSTRACT



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ABSTRACT

Meltwater samples collected in early and late summer from three Alpine glaciers were analysed to determine the occurrence of POPs (Persistent Organic Pollutants: DDTs, HCHs and PCBs) and emerging contaminants (current used pesticides and polycyclic musk fragrances). For legacy POPs, we reconstructed a concentration time series using data from previous surveys in the same areas (starting from 2000). The results suggest a declining tendency of these compounds, probably related to the introduction of international regulations, which has led the strong use reduction and ban of these compounds.
Among the analysed current used pesticides the terbuthylazine and chlorpyrifos were found in all the analysed samples. The experimental results were in line with the prediction of the OECD tool screening model, which was applied to estimate the potential of these substances to undergo regional-scale atmospheric transport processes. Temporal and spatial differences in concentrations for these compounds were related to the timing of applications, weather conditions and crop distribution along the adjacent Po River Plain. Despite model predictions, the herbicide pendimethalin was never detected, probably due to the lower use of this compound in the agricultural practices. Conversely, concentrations of polycyclic musk fragrances galaxolide and tonalide were more homogeneous both temporally and spatially, in agreement with their continuous release from emission sources.

1. Introduction

It is well recognized that contaminants are widely distributed all over the globe and that atmospheric transport is a leading pathway for their diffusion (Harriss et al., 1984). The mechanisms underlying the global atmospheric transport of contaminants were exhaustively explained by Wania and Mackay (1996) and other authors (Finizio et al., 1998; Gouin et al., 2004; Hageman et al., 2006; Scheringer, 2009). As a result of long-range as well as local/regional atmospheric transport, contaminants can be transported in polar regions and mountain glaciers, which are hundreds to thousands km far from their emissions sources (Carrera et al., 2001; AMAP, 2004, 2009, 2011; Wang et al., 2006; Bidleman et al., 2010; Daly and Wania, 2005; Kallenborn et al., 2007; Hung et al., 2010;

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Zhao et al., 2015). According to Grannas et al. (2013), organic contaminants may enter snowpack through wet (snow, rain) and dry (gaseous and particle) deposition processes. The effectiveness of both processes in scavenging contaminants from the atmosphere greatly varies in function of the differences in physical chemical properties among contaminants; this has been largely investigated by means of models (Daly and Wania, 2004; Stocker et al., 2007).

Incorporation of contaminants in snowpack and ice creates temporary reservoir of pollutants. However, once the melting starts due to increased temperature, a re-emission of contaminants back to the atmosphere or release with meltwater to the freshwater systems occurs. Consequently, pronounced concentration peaks of contaminants are common during snowmelt periods (Meyer et al., 2006; Meyer and Wania, 2008; Bizzotto et al., 2009; Bogdal et al., 2010; Grannas, 2011) and this can have strong implication regarding increased exposure of aquatic as well as terrestrial organisms.

According to Blais et al. (1988), temperate-zone mountain regions, which tend to receive high levels of precipitations while being close to pollutant sources, are particularly susceptible to the accumulation of contaminants. In this, the European Alps, which lie across the most populated and highly anthropized regions of Europe, can be particularly at risk. Historically studies on European Alps have been mainly focused on monitoring the presence of persistent organic pollutants (POPs) such as DDTs, PCBs, dioxins, HCHs in glaciers (Villa et al., 2003, 2006a, 2006b; Bogdal et al., 2010; Pavlova et al., 2016) as well as in other environmental matrices (Nizzetto et al., 2006; Tremolada et al., 2008; Villa et al., 2011). However, closer distances of European Alps to local/regional sources of pollutants increase the potential of glacier contamination from other categories of contaminants. For instance, Current Use Pesticides (CUPs), as well as many other emerging contaminants (e.g., PCMs: polycyclic musk fragrances) tend to have much greater polarity and water solubility than 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, CUPs and PCMs have been found in regions isolated from their use and production such as in the Arctic (Hoferkamp et al., 2010; Zhang et al., 2013) or high mountain areas (Zabik and Seiber, 1993; Aston and Seiber, 1997; LeNoir et al., 1999; Hageman et al., 2006; Gouin et al., 2008; Kurt-Karakus et al., 2011; Santolaria et al., 2015). In addition, a few studies highlighted the presence of CUPs and PCMs in snowpack samples (Hageman et al., 2006 and 2010; Villa et al., 2014).

In this context, the aim of this study is to investigate the release of legacy POPs and emerging pollutants (CUPs and PCMs) from the melting of three Alpine glaciers (Lys, Forni and Giogo Alto). This was completed by measuring the concentration levels of the selected compounds in glacial meltwater that was collected in two different monitoring campaigns (summer and late summer/autumn). For legacy POPs, we reconstructed a concentration time series using data obtained from previous monitoring campaigns (Villa et al., 2003; Villa et al., 2006a, 2006b). For CUPs, in consideration of the high number of active ingredients utilized in agricultural practices on the Po River plain, a preliminary screening was performed to select those compounds with a higher potential to reach the glaciers. This was completed by considering both the volume of use (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 the synthetic musk fragrances in the study was made to widen the evidence of their presence in Alpine glaciers and 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 the Ortles-Cevedale group and the Giogo Alto Glacier in the Palla Bianca-Similaun group (Fig. 1). The Lys Glacier is close to France and Switzerland and extends from 4282 m a.s.l. to 2600 m a.s.l., covering an area of approximately 9.58 km^2 (~81% of the total catchment area of the sampling point) (Smiraglia and Diolaiuti, 2015). Further east, the Forni Glacier, in the Ortles-Cevedale group, belongs to the Stelvio National Park. This glacier extends from 3673 m a.s.l. to 2501 m a.s.l. and covers approximately 11.34 km^2 (~88% of the total catchment area of the sampling point) (Smiraglia and Diolaiuti, 2015). Finally, the Giogo Alto Glacier, in the Palla Bianca-Similaun group, is located near the Italian and Austrian borders. This glacier extends from 3260 m a.s.l. to 2760 m a.s.l., covering an area of 0.95 km^2 (~92% of the total catchment area of the sampling point) (Smiraglia and Diolaiuti, 2015), and is located in the area characterized by the lowest precipitation rate of the entire Italian Alpine system (Gabrieli et al., 2011).

The criteria for site 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 to a small extent, whereas Giogo Alto Glacier is exploited as a skiing area. During spring and summer, all of the glaciers receive air masses coming from both 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 et al. (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 that are 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 local hot-spot emissions may cause heterogeneous depositions of pollutants over the Alps.

The monitoring design was defined on the basis of previous experimental works in the same areas (Villa et al., 2001; Villa et al., 2003; Villa et al., 2006a, 2006b; Bizzotto et al., 2009; Villa et al., 2014). Lys Glacier meltwater samples were collected on 25th July 2014 and 3rd October 2014, from the proglacial lake situated in front of the glacier at 2350 m a.s.l. The samples from the Frodolfo stream (that originates from the Forni Glacier) were gathered on 2nd July 2014 and 9th September 2014 near stream source approximately at 2200 m s.l.m. Finally, the Giogo Alto Glacier meltwater samples were collected at 3000 m on 24th July 2014 and 10th September 2014. All samples were collected using aluminium cans (5 and 2.5 L) pre-rinsed with acetone and hexane. The water volume collected for each sample was approximately 10 L. They were kept refrigerated during the transport and stored at −20 °C until analysis.

2.2. Chemical analysis

Analytes included in this study were selected on the basis of the following variables: i) previous experiences of this research group in the studied areas (Villa et al., 2001; Villa et al., 2003; Villa et al., 2006a, 2006b; Villa et al., 2014); ii) pesticide sales data from the Po river plain area; and iii) output of the screening model (see paragraph 2.4). The studied analytes are 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 Musk fragrances (PCMs): galaxolide (HHCB) and tonalide (AHTN);
- Current Use Pesticides (CUPs): terbuthylazine (TBZ), chlorpyrifos (CPF) and pendimethalin (PEN).

Analytical standards were purchased from Dr. Ehrenstofer, GmBH (Augsburg, Germany) and Sigma-Aldrich (St. Louis, USA). All solvents