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# Theoretical and experimental evidences of medium range atmospheric transport processes of polycyclic musk fragrances

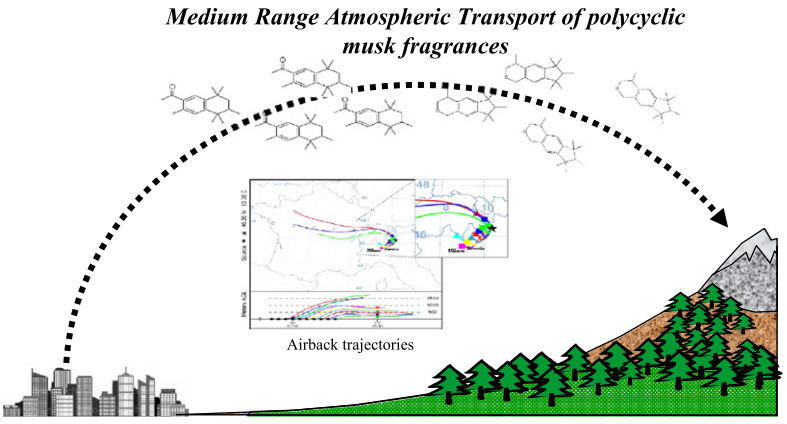
Sara Villa, Marco Vighi, Antonio Finizio *

*Dept. of Earth and Environmental Sciences, University of Milano Bicocca, Piazza della Scienza 1, 20126 Milano, Italy*

## HIGHLIGHTS

- We investigated the atmospheric transport of AHTN and HHCB to Forni Glacier.
- Theoretical models showed possible phenomenon of medium range atmospheric transport.
- AHTN and HHCB were detected in snow and glacial melt water samples.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This study investigates some aspects of the environmental fate of galaxolide (HHCB) and tonalide (AHTN) musk fragrances, paying particular attention to the phenomenon of atmospheric transport of these substances. The problem was addressed theoretically and experimentally. Firstly, the application of a multimedia model allowed the analysis of their potential atmospheric transport. The obtained results argued in favor of a possible phenomenon of medium range atmospheric transport for both substances. These theoretical findings were supported by the experimental results, which showed their presence both in the fresh fallen snow and in water samples taken from the Frodolfo, a glacial stream that originates from the Forni Glacier (Alps, Northern Italy). Furthermore, the analysis of the air back-trajectories highlighted the prevalence of air masses of local origins that reached the sampling area passing through a densely anthropized area of Northern Italy. Finally, the experimental results discussed here gave evidences of accumulation of these two compounds in the glacier.



## 1. Introduction

Synthetic musk fragrances are semivolatile and lipophilic compounds widely used as additives in personal care and household products (Rimkus, 1999; Kang et al., 2010). They belong to a relatively heterogeneous group of substances that can be divided into three classes: aromatic nitro, polycyclic and macrocyclic musk compounds (Sommer, 2004). Their use started in early 20th century with the production of nitro-musks (particularly musk xylene and musk ketone) (Rimkus, 1999). However, concern over their carcinogenic potential, the evidences of their presence in human fatty tissue and breast milk and a correlation between musk xylene concentrations and miscarriage in women (Kafferlein et al., 1998; Schmeiser et al. 2001; Rimkus et al.,

* Corresponding author. Tel.: +39 0264482742; fax: +39 0264482735.
*E-mail address:* antonio.finizio@unimib.it (A. Finizio).

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1994; Liebl and Ehrenstorfer, 1993; Rimkus and Wolf, 1996; Eisenhardt, et al., 2001; Bridges, 2002) led to restrictions and bans on their use in several countries. The production and use of polycyclic musk compounds as substitutes have rapidly increased (Peck and Hornbuckle, 2006a). In 2000, the worldwide use of polycyclic musks was approximately 4000 tonnes (Salvito, 2005). The most widely used polycyclic musk is galaxolide (HHCB) followed by tonalide (AHTN). Production of HHCB and AHTN in Europe was about 1800 tonnes (1427 tonnes of HHCB and 358 tonnes of AHTN, respectively) with a commercial ratio of about 4:1 (OSPAR Commission, 2004). Several studies revealed the presence of high concentrations of HHCB and AHTN in the effluents and sewage sludge of Sewage Treatment Plants (STPs) in European countries and in the United States (Simonich et al., 2002; Artola-Garicano et al., 2003; Gatermann et al., 1999, 2002). Other studies also demonstrated that both substances are only partially removed during wastewater treatments (Bester, 2004; Kupper et al., 2006). Consequently, the remaining fraction is discharged through the effluents into rivers leading to a widespread contamination of water bodies, estuarine and coastal waters as well as of the aquatic biota (Draisci et al., 1998; Moldovan, 2006; Moldovan et al., 2009; Schmid et al., 2007; Sumner et al., 2010; Hu et al., 2011; Villa et al., 2012). The volatilization process during production and use of products containing synthetic musk fragrances, as well as the volatilization from landfills or sewage treatment plants, was recognized to be an important source of these compounds to the atmosphere (Peck and Hornbuckle, 2006b). As reported in the OSPAR and in the ECB reports, the atmospheric lifetime of these substances is sufficiently short to neglect the possibility of long-range atmospheric transport to any significant extent (OSPAR Commission, 2004; ECB, European Chemical Bureau, 2008). However, HHCB and AHTN have been detected in air and snow (Hu et al., 2012; Peck and Hornbuckle, 2006b; Xie et al., 2007; Kallenborn et al., 1999; Peck and Hornbuckle, 2004), which can be seen as an indication of potential atmospheric transport.

This paper is aimed to further contribute to the knowledge on the atmospheric transport of AHTN and HHCB by using both theoretical and experimental approaches. Initially, the potential capability of these substances to be transported in the atmosphere was analyzed by means of the application of multimedia models. In addition, experimental analysis of snow, glacier and non-glacier water samples taken from the Forni Glacier (Northern Italy) in two different monitoring campaigns (summer and late summer/autumn) was carried out.

## 2. Materials and methods

### 2.1. Description of the sampling area

Water and snow samples were taken in an area (Fig. 1) located immediately upstream of the Forni dam (2190 m a.s.l.). The sampling site is located in a pristine area very close to the Forni Glacier (about 1 km), on Ortles-Cevedale group, Italian Alps. The glacier belongs to the "Alta Valtellina" valley and the closest inhabited areas are the municipalities of Valfurva (linear distance from the glacier ~11 km; 2100 inhabitants), Bormio (linear distance from the glacier ~13 km; 4000 inhabitants) and Livigno (linear distance from the glacier ~35 km; 6000 inhabitants). During winter, these villages generally double the population thanks to the presence of several tourist resorts. Due to their proximity to the sampled area, they can be potentially seen as local sources of emission of musk fragrances. In addition, the glacier is about 150–200 km away from very densely anthropized areas and some major cities of the Lombardy Region such as Milano (linear distance from the glacier ~160 km; 1,300,000 inh.), Bergamo (linear distance from the glacier ~110 km; 120,000 inhabitants) and Brescia (linear distance from the glacier ~110 km; 200,000 inhabitants). The glacier area frequently receives air masses coming from these surroundings.

Snow samples (4 replicates) were taken from a 5-cm-deep layer of fresh snow (during the snowfall of 16th of May 2012). Snow was collected using a stainless steel shovel and stored in pre-cleaned aluminum cans. During sampling, attention was paid towards the collection of upper snow layer and also to avoid the mixing of this snow with the older snow layer below. Field blanks (Milli-Q water) were handled in the same manner as the samples.

Water samples (7 replicates) were collected on two different dates (16th of May 2012 and 8th of October 2012). During the first sampling campaign, the water was taken only from the Frodolfo stream that originates from the Forni Glacier (GS: glacial stream) while a non-glacial fed stream (NGS) close to Frodolfo was also sampled during the second campaign. Sampling sites and periods were chosen considering the

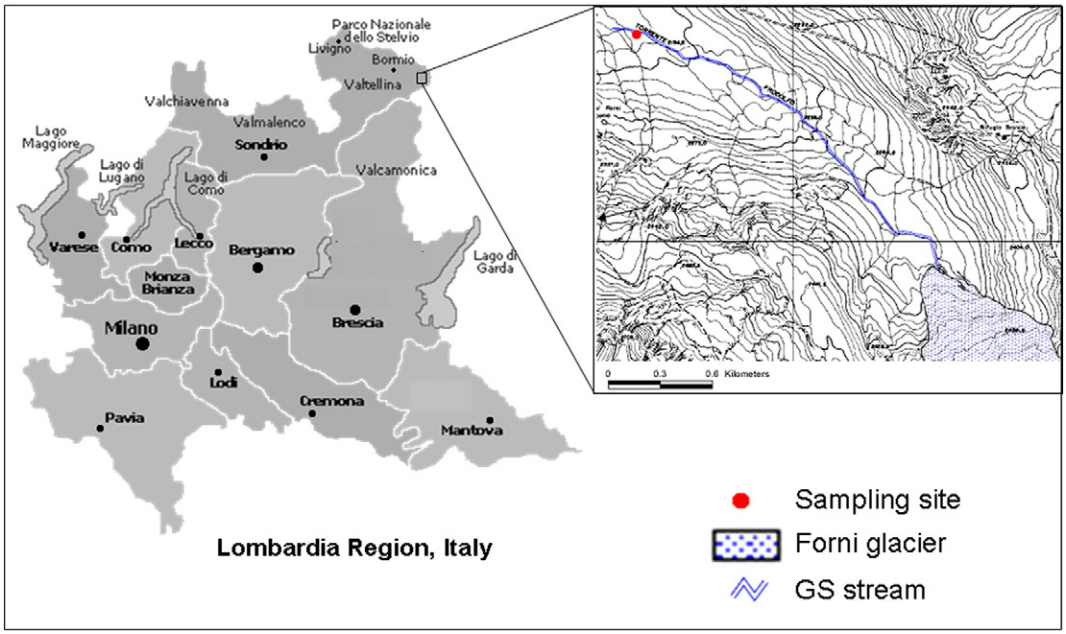


**Fig. 1.** The location of the sampling site on the Forni Glacier; both water and snow samples were taken near the Forni Dam.