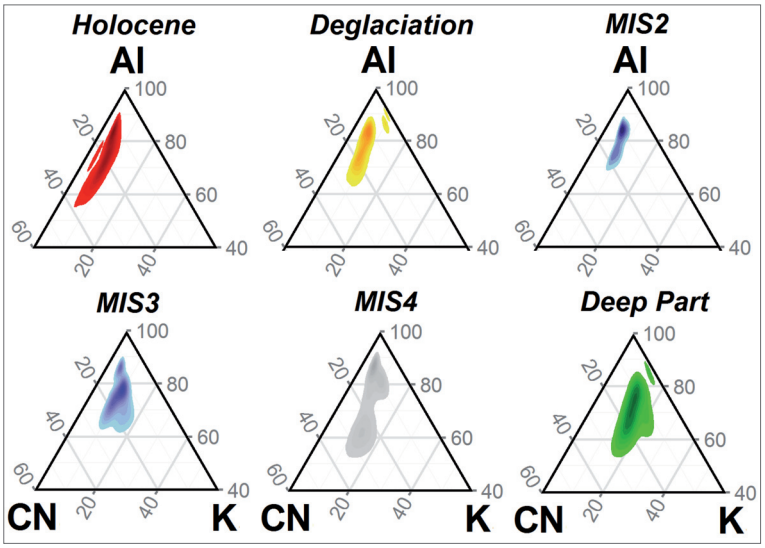
Aerosols in snow and ice. Markers of environmental pollution and climatic changes: European and Asian perspectives



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Cover page: Scatter plots relative to different climatic periods from ice core samples (courtesy V. Maggi et al. - unpublished).

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*These authors presented the scientific reports collected in this book at the workshop held in Rome (Italy) on September 7-8, 2017.

Papers presented at the Italian and Chinese bilateral workshop “Aerosols in snow and ice. Markers of environmental pollution and climatic changes: European and Asian perspectives”

Rome, Italy September 7-8, 2017

Organized by Istituto Nazionale di Fisica Nucleare and Università Milano Bicocca

With the patronage of Ministero degli Esteri e della Collaborazione Internazionale (MAECI)
With the patronage of Regione Lazio
With the patronage of Consiglio Nazionale delle Ricerche (CNR).

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Preface

This book collects the contributions presented at the bilateral workshop «Aerosols in Snow and ice: markers of environmental pollution and climatic changes: European and Asian perspectives».

The event, which took place on September 7-8, 2017, met Chinese and Italian researchers involved in climatic and environmental researches based on dust and aerosols collected in ice cores and in the atmosphere. It was held in Rome and hosted by *Accademia Nazionale delle Scienze*, also called *Accademia Nazionale dei XL (The Academy of the Forty)*, the leading scientific Italian Academy. It was the first event of this type organized in collaboration between the most important Italian and Chinese institutions involved in this field: an interdisciplinary, modern and strategic research field looking at the climate and the pollution on a local and global scale.

The event received the patronage of the Italian Minister of Foreign Affairs and International Cooperation (MAECI), the Region Lazio and the Italian National Research Council (CNR). It was organised by by University of Milano-Bicocca (UNIMIB) and Italian Institute of Nuclear Physics (INFN) and promoted by the Italian Scientific and Technological Office of the Italian Embassy in Beijing. It was made possible thanks to the contribution of important Chinese institutions, many of which belonging to the Chinese Academy of Sciences (CAS).

As chairpersons of this initiative, we have to underline the following matters of fact.

The meeting was organized in thematic sessions that followed one to the other. Thus, each participant was made aware of all the new developments occurring in his own as well as in the closely related research lines. The present proceeding followed the same strategy, thus the entire book can split in subheading related to one subject and yet interrelated one to the other.

Consequently, thanks to the efforts of two among the most important and recognised, scientific communities involved in these researches, all contributions, taken together, represents parts of a unique fundamental puzzle that we tried for the first time to assemble and integrate.

Both the meeting and the book represent a great opportunity to promote the collaborations among Italian and Chinese institutions and researchers in the study of mountains and polar glaciers and of the cryosphere in general. They make up an extraordinary climatic and environmental information archive on a matter that is seriously at risk because of the increasing temperatures on the Earth.

In addition to the existing joint researches presented in this book, we intend to stimulate new experimental programs and collaboration agreements among Italian and Chinese organizations and try to define guidelines for exploration and perforation of glacial areas. The Italian scientific community in this field is already involved in

important projects in Italy and in the polar areas. However, the meeting in Rome is only the first of a series to be continued, both in Italy and in the P.R. China, in that it represents a unique opportunity to compare our knowledge, and skinless with one of the largest scientific community working in this field.

Valter Maggi and Augusto Marcelli

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Mineral dust and Mediterranean Climate Reconstructed from European Alps Ice Cores.

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Keywords: ice cores, mineral dust, European Alps.

Glaciers are one of the best archives of atmospheric data, but the fragility of their environment can generate troubles on data sequences and completeness. Despite glaciers are distributed at all latitudes, the availability in terms of information preservation and ice core drilling is not the same everywhere. Summer melting or winter wind erosion can reduce or cancel the information stored in the ice. Only glaciers (or parts of them) in cold conditions, with ice at temperatures well below the melting point of water, can be used for this kind of studies. One typical example are glaciers located at high altitude inside mountain chains. In the European Alps, with few exceptions, an altitude of 3800-4000 m asl seems to be the lower limit for this kind of work. In the Himalaya-Karakoram chain, one needs to reach 5-6000 m asl or more to find glaciers suitable for ice coring.

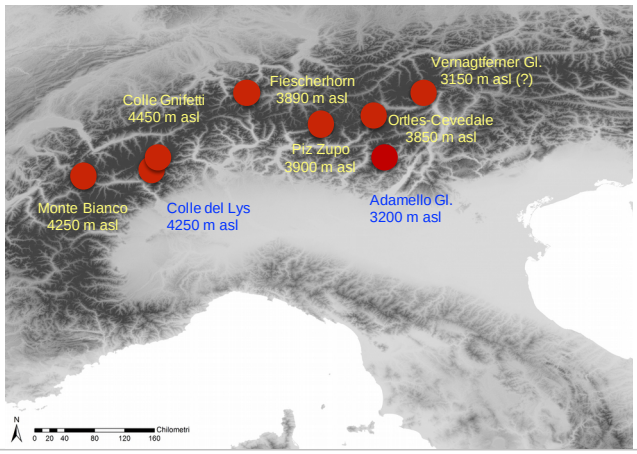

Figure 1: In the picture, the main ice core sites in the European Alps.

A major problem is that Alpine cold glaciers (or part of them) are located in just a few high mountain massifs (Monte Bianco, Monte Rosa, Swiss Oberland) leading to serious difficulties to extrapolate the information to other parts of the Alpine region. For this reason, despite larger difficulties in data interpretation, new ice coring activities were conducted at altitude below 4000 m (i.e., also also in the percolation zone) in order to extend the geographic distribution of the climate and environmental information.

In the Alpine area, at least 7 sites and 44 ice cores were drilled from the 70's (as indicated by the available literature), in general reaching the glacier/rock interface. The ice core records for the Alpine area cover the entire Holocene and part of Younger Dryas (around 13.000 BC), but most records span the last centuries, with special emphasis on the last 70-100 years.

Oxygen and hydrogen stable isotopes as well as fine particle records were measured for climatic reconstruction purposes, and major and trace chemical compounds measurements were performed for environmental characterization [1].

Dust concentration (both microparticles and Calcium records), mainly related to transport from North Africa and from local background, apparently displays a common feature along the Alpine chain: The period between 1970 to 2000 seems to be related to high dust concentration, while the previous decades and the first 15 years of the XXI century display lower dust levels.

The size distribution is strongly related to the wind strength, with the particle size distribution peaking on diameters between 1 and 2μm during background transport, mainly from areas close to the drilling site, and between 4 to 5μm for extreme Saharan dust events that represent transports from distances larger than 2000 km.

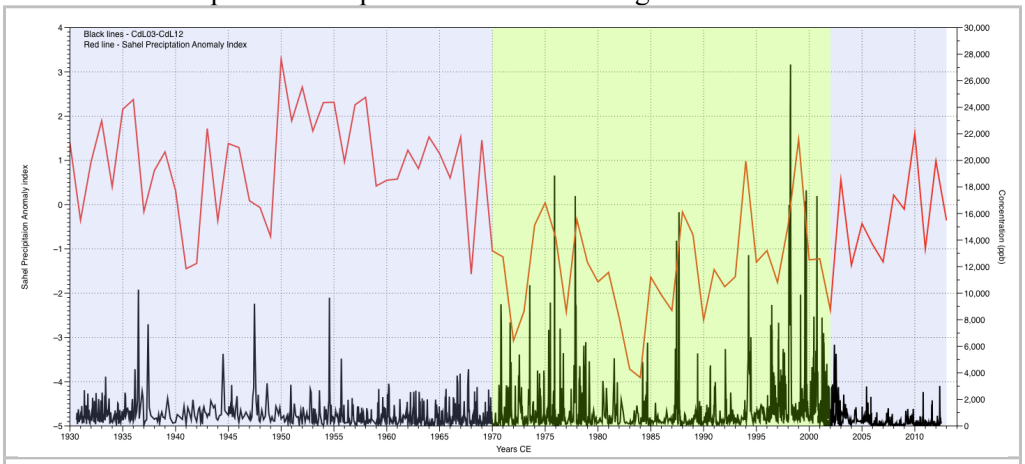

Figure 2: "Colle del Lys" mineral dust record together with the Sahel Precipitation Anomaly index. An antiphase between the two sides of the Saharan desert emerges.

To date, there are few analyses on the mineral composition of the dust reaching the Alpine area, especially for the long range transport, owing to the very low amount of dust and for the small size distribution. Recently, work done using synchrotron x-ray facilities provided interesting information on the Fe coordination on the dust, that is strongly related to the mineral typology [2].

Despite the difficulties in interpreting these data, generated by the fact that transport from North Africa across the Mediterranean relies upon different baric mechanisms, it was anyway possible to identify a relationship between the north/northwestern and the south/southeastern parts of the Saharan desert (Fig. 2).
In the framework of the Italian Project of Strategic Interest NEXTDATA, funded by Italian Ministry of Education, University and Research (MIUR) and coordinated by the National Research Council (CNR), a reconstruction of the climate in the past 2000 years in Italy (Italy 2K) will be obtained using different records, such as paleovegetation (mainly pollen), dendroclimtology and, for the Alpine high mountain areas, ice core records.

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Atmospheric Pollution and Cryospheric Change (APCC) over Third Pole: Current Status and Future Prospects.

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The Himalayas and the Tibetan Plateau (HTP) as a whole is concerned for accelerated cryospheric degeneration and related shifts in hydrological cycles that affect Asian water supplies. While atmospheric pollutants contribute to climatic and cryospheric changes via mediating solar radiation and albedo of snow/ice surface, their fates and cycling within cryosphere and relevant environmental impact are raising concerns. Integrated investigation that link atmospheric pollutants and cryospheric changes (APCC) remains a paucity. To address these issues, we have established a coordinated APCC monitoring network consisting of 26 sites spanning vast HTP regions and beyond. Total Suspended Particle (TSP) samples are periodically collected every 3-6 days, real time black carbon and trace gases are observed continuously at selected sites. Meanwhile, benchmark glaciers and snow cover sites are investigated for sample collection and in-situ measurement of surface albedo. Samples are quantified for carbonaceous species, toxic chemicals, and other auxiliary variables. With intensive sampling, monitoring and systematic lab measurement and data analysis, we aim to quantify the composition, distribution, and transport pathway of atmospheric pollutants and assess their effects on cryospheric changes. In this paper we will also briefly review the recent progresses and achievements in relation to the APCC monitoring network and propose future research priorities. We are planning to extend the APCC monitoring network that will include several pioneer sites in the two polar regions to attempt to expand the APCC program to a global scale. The ongoing APCC monitoring network over HTP facilitate the most comprehensive coupled studies on atmosphere-cryosphere interactions and contribute to earth system science in a global perspective.

A comprehensive geochemical characterization of atmospheric dust and impurities in snow and ice from past and recent times: Antarctic and Alpine perspectives.

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Keywords: snow, ice core, atmospheric mineral dust, cryoconite, neutron activation, elemental characterization, radioactivity

Thanks to recent advances, the geochemical investigation of snow and ice from polar and continental glaciers has become well established. Important climatic and environmental information is obtained through such analyses. But if the determination of selected isotopic ratios and elemental concentrations in ice and snow samples are well established, we can't say the same with respect to wider studies, which apply a multi-analytical approach. This is mainly related to the low availability of similar samples, in particular ice core ones, whose availability is strictly limited. With the development of dedicated procedures for the preparation of samples [1,2], it is now possible to extract few micrograms of dust from snow and ice in clean conditions and applying to them many techniques with a minimal use of the original material. Following such an approach, new and original information about dust geochemistry is obtained [3]. This is essential to better understand the relationships between climate, the atmospheric dust cycle, biogeochemistry, the cryosphere and the impact of human activities. Focusing on different contexts, these themes are investigated with multiple perspectives. Here we present our last results about the geochemical investigation of dust extracted from Antarctic ice core samples, Alpine snow and ice and of cryoconite.

1. Antarctica. Thanks to its remoteness and to the length of climatic records obtained from ice cores here collected, the white continent allowed obtaining the longest climatic records using ice samples. In this context we have been studying for several years the atmospheric dust record constructed exploiting the TALDICE ice core, drilled in a peripheral area of the East Antarctic Plateau (Talos Dome, East Antarctica, Ross Sea sector). We will present our new results concerning the elemental composition of dust deposited in this Antarctic sector during the last climatic cycle. Comparing the composition of dust, its concentration and size with other climatic records related to

climatic variability (stable isotopes), the complex mechanisms linking the dust cycle and climate will be investigated, with a focus on the different response of local and remote dust sources to climatic variability [4,5]. Given the different geographical and environmental features of local Antarctic dust sources and the Southern American ones, their activity responds differently to climate, both with respect to long-term variability and to higher frequency oscillations. A second important result concerns the definition of the first reference for multi-elemental deposition fluxes in Antarctic remote areas, which will be here presented. It was possible to define two references, one for the Holocene and one for the last glacial maximum, when the dust regime was completely different. This is an important result in order to make quantitatively assessable the current impact of human activities on the biogeochemistry of the most remote region of Earth.

2. High Altitude Alpine glaciers. Analyzing snow and ice cores collected from the few cold glaciers of the Alps, complementary climatic and environmental information can be obtained with respect to polar areas. The position of Alpine ranges, in the middle of Europe, makes them an extraordinary playground in order to understand the impact of human activities on glacial environments [6]. The typical features of small continental glaciers, i.e. high snow accumulation rates and fast dynamics, are responsible for the preservation in these glacial bodies of relatively short records, in the range of few decades-centuries, with a high temporal resolution, often seasonal. Therefore the analysis of Alpine snow and ice cores it became possible to study at high spatial and temporal resolution natural and anthropic processes [7]. It will be shown that in this context the dust cycle is deeply affected by the arrival of Saharan dust plumes, but also by atmospheric human emissions, even at the highest Alpine glaciers. It seems that dusty and polluted air masses interact with each other during the atmospheric transport [8]. In accordance to our hypothesis specific elements, as Sb, As, Hg and other heavy metals presenting a relevant volatile behavior, are adsorbed on mineral particles and finally deposited on glaciers, where they are temporarily stored with other anthropic substances [9]. A detailed presentation of this picture will be given, focusing on the results concerning an ice core obtained from the glacial saddle Colle del Lys (4250 m, Monte Rosa massif).

3. Cryoconite. The behavior of pollutants in glacial environments is definitely complex. Different substances, presenting affinities for different environmental matrices, are fractionated and transported in different ways, also when considering little ecosystems as Alpine glaciers. After having demonstrated that many pollutants arrive on glaciers in association with dust, we will show that cryoconite, the dark sediment found on the ablation surface of worldwide glaciers [10], plays another essential role in determining the environmental fate of these substances. Focusing on radioactive and selected elements we unexpectedly found extraordinary high concentrations, in some cases the highest ever observed if nuclear accident sites or heavily contaminated areas are excluded. Cryoconite can thus be definitely considered an extremely efficient, but temporary, sink for many substances. A first detailed analysis of these mechanisms will be presented, in relation to what we observed on the Morteratsch glacier (Bernina range, Switzerland [11]).

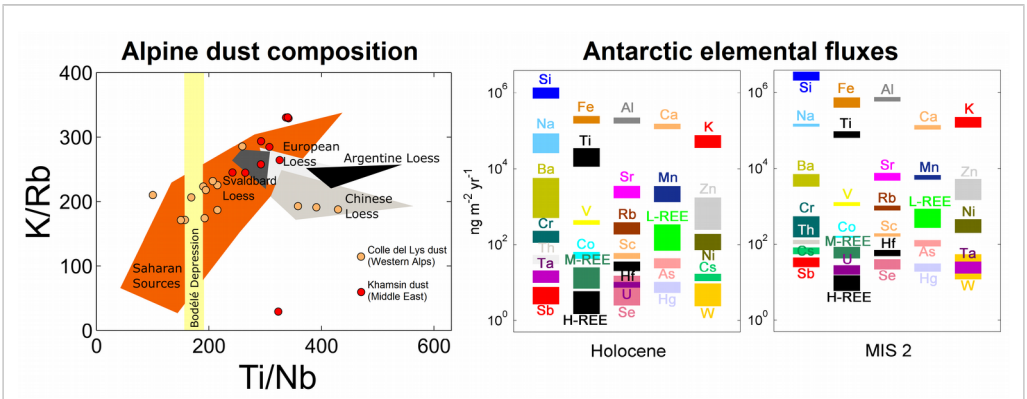

Figure 1: Selected elemental ratios used to identify the provenance of mineral dust deposited on Alpine high altitude glaciers (left). A comprehensive list of elemental depositional fluxes in Antarctica during the Holocene and the last glacial maximum (right).

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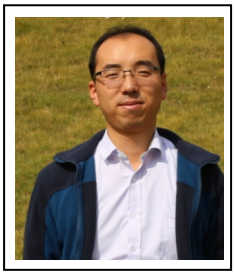
Identification of sources of iron in mineral dust (aerosol) from Western China, Arctic and East Antarctica regions by chemical speciation using X-ray absorption near-edge structure (XANES) spectroscopy



Zhiheng Du[a*], Cunde Xiao[b,a], Augusto Marcelli[c,d], Giannantonio Cibin[e], Giovanni Baccolo[f], Salvatore Macis[g], Wei Xu[h], Alessandro Puri[i], Valter Maggi[f], Shiwei Liu[a], Yingcai Zhu[h]
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Keywords: Glacier, Desert, snow/ice, Arctic, Antarctica, iron speciation and XANES

In this study, snow samples were collected from Western China (Laohugou glacier), Arctic (Ice stations, Svalbard and Barrow), and East Antarctica (Zhongshan-Dome A transect), the mineral dust samples were extracted with 0.2 μm filter (Teflon and Polycarbonate).

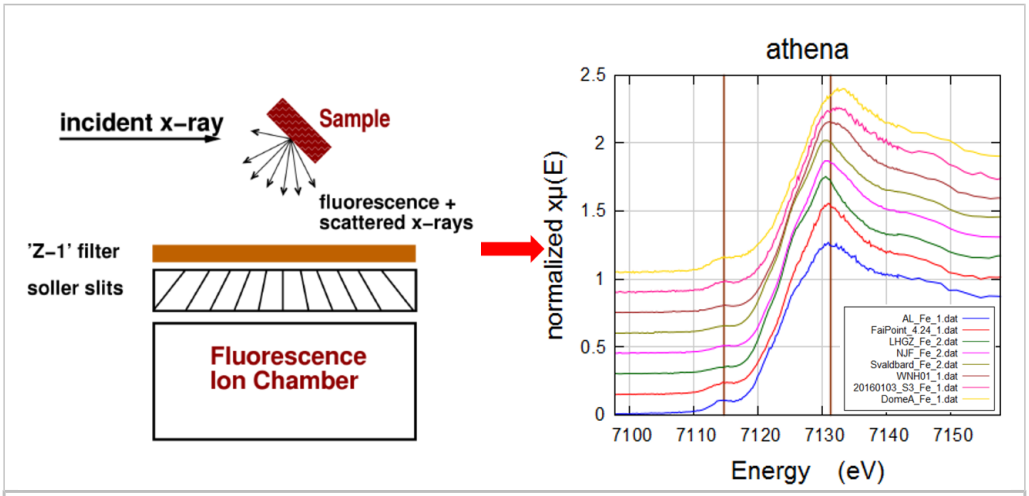

Figure 1: Experimental set-up for Total X-Ray Reflection Fluorescence and Absorption spectroscopy experiments.

Aerosol samples were collected at three sites (Beijing, Barrow and Indonesia) using the multi-stages MOUDI aerosol sampler (Tish). Sand samples (including loess) from these potential sources were sieved with the diameter of a 73 μm sifter. These samples were determined the iron speciation using synchrotron radiation-based techniques, such as X-ray Absorption Near-Edge Structure (XANES) spectroscopy and microscopic X-ray fluorescence measurements at the European Synchrotron Radiation Facility (ESRF) in France. The preliminary Fe K edge and XRF data results indicate that they are taken as the good indicators tracing the variability of mineralogy on snow, ice and aerosol dust samples with different provenances.

10-year record of atmospheric aerosol composition in the high Himalayas

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Keywords: aerosol properties, Himalayas, aerosol deposition

Since the end of the 20th Century, field experiments and satellite observations identified in the South Asia a thick layer of atmospheric pollutants extending from the Indian Ocean up to the atmosphere of the Himalayas: the Atmospheric Brown Cloud. This cloud over the Indo-Gangetic Plain and its transport to the Himalayas was studied during 10 years of activities carried out at the Nepal Climate Observatory-Pyramid in the Nepal high Himalayas (5079 *m asl*), one of the 31 Global Stations of the Global Atmospheric Watch program of WMO.
Under well-developed upvalley wind, high concentrations of BC, PM1 and other pollutants, as well as high values of aerosol scattering coefficient significantly greater (orders of magnitude) than seasonal background values were found at the Observatory.
Basing on different methods to estimate the uncertainty range of BC dry deposition over the southern Himalayas during pre-monsoon period (March- May 2006) and using ice surface roughness and NCO-P observation of eqBC, particle size and meteorology, the averaged BC dry deposition rate was estimated as 2089 μg m^{-2} day^{-1}, providing 266 μg $m^{-2}$for the pre-monsoon season. Under dry and highly polluted conditions (like pre-monsoon), aged snow and sulfate coated BC are expected to possibly reduce visible albedo by 4.2-5.1%. Previous investigations indicated that a 2-5.2 % snow albedo reduction would imply 70-204 mm runoff increase from a typical Tibetan glacier (24 % of the seasonal runoff) [1].
Considering 10-year record of atmospheric aerosol observations in the high Nepalese Himalayas, main results can be summarized as follow:
(i) Atmospheric composition and aerosol variability in high Himalayas are characterised by an evident seasonality, with pre-monsoon season able to favor the transport of ABC to high altitude [2].
(ii) During this period, acute pollution events of BC with concentrations greater than 500 ng m^{-3}, were systematically observed at NCO-P. On average, these "acute" pollution events were characterised by dramatic increases of BC (352%) and O_3 (29%) levels compared with the remaining days [3].
(iii) Himalayan valleys represent a "direct" channel for aerosol transport to high Himalayas, also triggering new particle formation events.

(iv) Open fires in South Asia appeared to have a significant role in affecting the occurrence of pollution events.
(v) The transport of aerosols to high Himalayas affects the surface radiative forcing and snow/glacier albedo with severe implication for cryosphere.

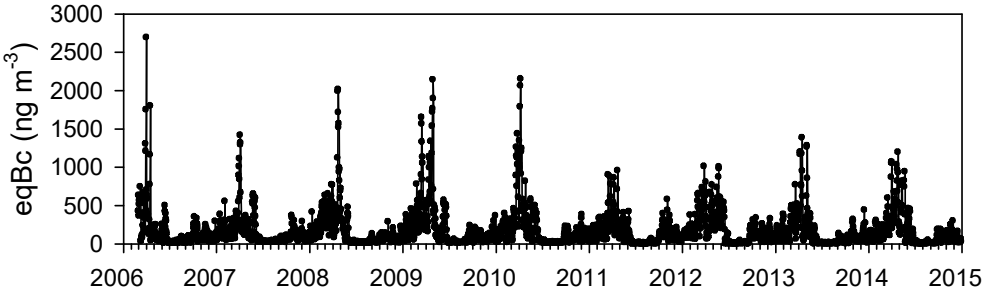

Figure 1: Variability of eqBC at the NCO-P from 2006 to 2015 (daily averages).

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Progresses of study on mercury geochemistry over the cryosphere of the Himalayas and Tibetan Plateau.

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Keywords: Mercury geochemistry; Study progresses; Cryosphere; Himalayas and Tibetan Plateau

Mercury (Hg) is a global pollutant that can be transported over long distances and bio-accumulated through food webs, which cause adverse ecological and health impacts in the environments. Western China, particularly for the Himalayas and Tibetan Plateau, is the most cryosphere concentrated region at low- and mid-latitudes and there landscapes mainly consist of glaciers, permafrost, lakes, and snow cover. Hg in the cryospheric environment of Western China is generally elevated compared to other remote regions (e.g., polar regions) in the world. This review presents research progresses on the temporal and spatial characteristics of Hg from different environmental matrices (atmosphere, snow/ice, precipitation, lake/stream/river water, soils/permafrost, sediments, aerosols, etc.) as well as the mechanisms of Hg transportation, deposition and transformation processes in various cryospheric environments over Western China. Furthermore, historical variations of the atmospheric Hg deposition over Western China during the past 500 years, has been reconstructed using ice core and lake sediment records. Our research will not only fill the gap, which exists in our knowledge on the geochemistry of Hg over the highest cryosphere in the world, but also provide critical insights for understanding the Hg biogeochemical cycling on a regional/global scale.

Transport and impacts of mineral dust: an Earth system model perspective

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Keywords: mineral dust, global Earth system models

Changing climate conditions affect dust emissions and the global dust cycle, which in turn affects climate and biogeochemistry. Snow and ice can act as a natural archives preserving the pristine dust input from the atmosphere. This allows to determine physical and chemical properties of dust aerosol and to reconstruct its past deposition history. While the coherent analysis of mineralogy, size, and isotope geochemistry can provide fundamental constraints on source-to-sink relations through time [1], only the coupling of this kind of information with models allows for a complete understanding of the transport dynamics. In this respect, we discuss how models can help the interpretations of paleodust records [2, 3].

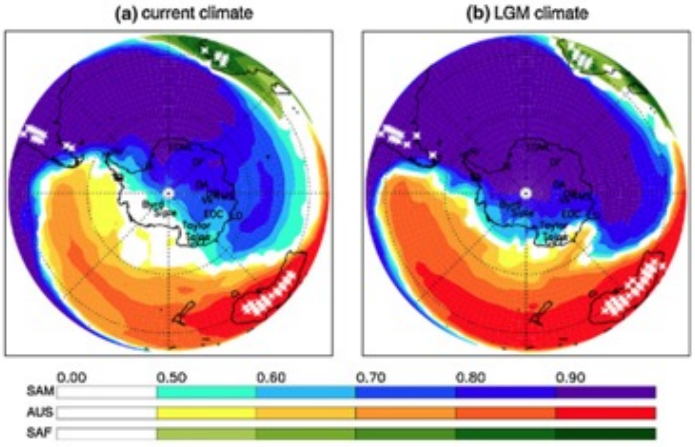

Figure 1: Maps for source apportionment in dust deposition, represented by the relative fractions to the total deposition flux, of dust originated from Southern Hemisphere major sources [2].

On the other the analysis of dust trapped in snow and ice can provide high-quality observational constraints on dust physical properties [4] and deposition rates that are of

great interest to the modeling community [5]. We show examples of how models that are improved by adequate observational constraints can then be used to reconstruct the global dust cycle and simulate dust impacts on present and past climates [5, 6].

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Mineralogy of dust and aerosols: status and perspectives of spectroscopic methods as novel ice cores proxies and for climatic and environmental applications.

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Keywords: XAS, XRF, ice core, dust, aerosols

Investigations on the insoluble components in ice report measurements of dust concentration, dust grain size, dust elemental and isotopic composition, mineralogy and magnetic properties. In ice cores the amount of mineral materials is generally around 10-100 *ngr/gr* (i.e., in the *ppb* range). Therefore, ice core handling and decontamination along with sample preparation for high-resolution analytical techniques is challenging and prone to external contamination.

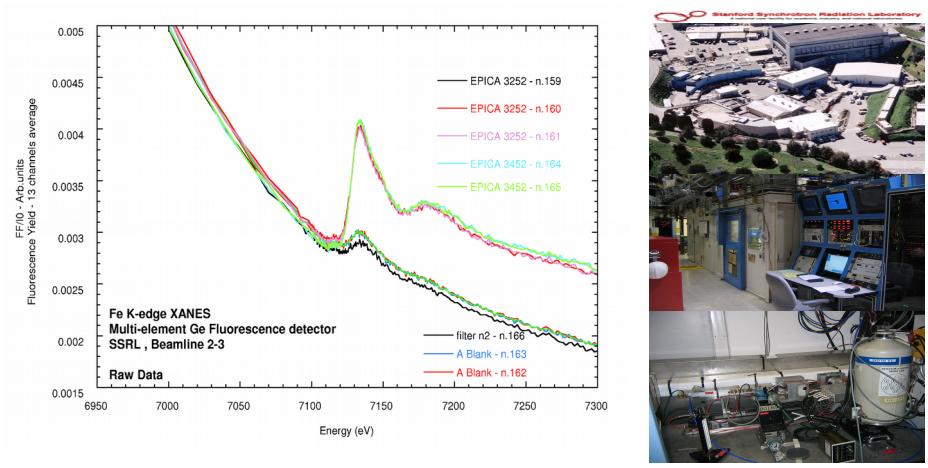

Figure 1: The really first Synchrotron Radiation X-ray Absorption Spectra collected in 2006 on mineral particles extracted from Alpine and Antarctic ice cores, dating back 160 kyrs. Experiments were performed with the support of the Italian National Institute for Mountains (INRM) at the beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL).

We demonstrated that an evaluation of the dust composition contained in limited sections (~1-2 m) of deep ice cores is possible exploiting the unique capabilities offered by X-Ray Absorption Spectroscopy (XAS) spectroscopy combined with X-Ray Fluorescence

(XRF) measurements and analysis. In line with the expected continental origin: Si, Al, Fe, Ca, Na, Mg, K, and Ti are the main constituents of the dust present in ice core samples. Comparison of X-ray absorption spectra (see Fe K edge in Figure 2) with rock and soil from possible source areas, from literature and other experimental analysis points out clearly that, using the same sample procedures, a convergence between different techniques such as PIXE and XAS occurs. Moreover XAS spectra show that a clear difference between different paleoclimatic periods emerges. In addition to Fe K edge XANES spectra other spectra can be collected such as S, Ca or Ti K edge spectra, the latter allowing discrimination among oxides and silicate phases. Combining XRF data and several XAS edges the mineralogical analysis is now possible.

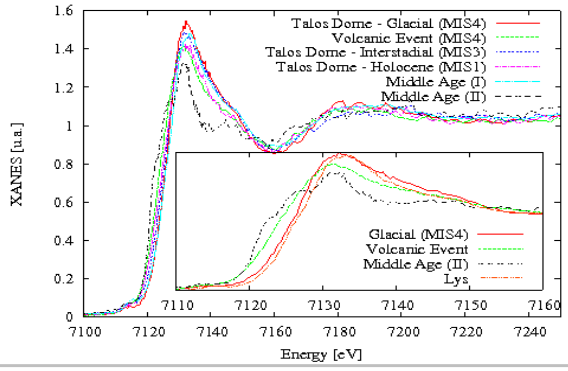

Figure 2: Comparison of Fe K-edge XAS spectra from ice cores sections from different climatic periods. In the inset the edge region where clear differences occur. The Lys spectrum refers to a sample from a ice core from Italian Alps.

A combined analysis of XRF, XAS and also X-Ray Diffraction (XRD) data allow detecting reliable composition variations vs. time and a strong support to studies showing also how the air circulation patterns have been changing during climate transitions. We have already demonstrated for the first time the unique role played by XAS in this field but improvements in both the analytical procedures and in the time resolution of deep ice core studies may offer soon new unexpected surprises.

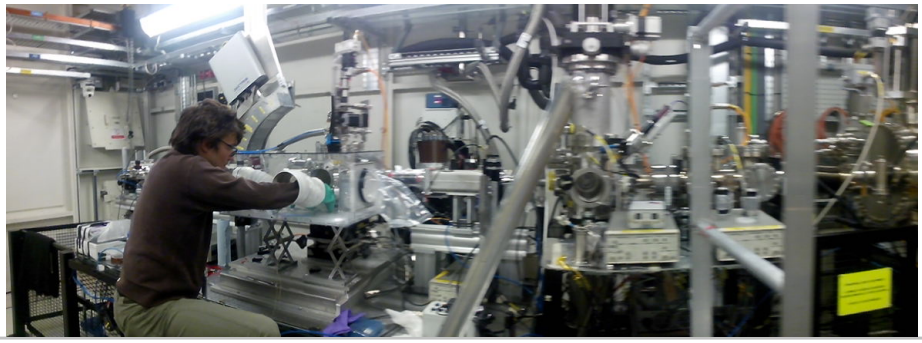

Figure 3: Photographs of the XAS/XRF/XRD station available at Diamond (beamline B18) where mineralogical studies of inorganic components from ice cores have been performed.

Mineral aerosols affect climate directly by scattering and absorption of shortwave and longwave radiation. Indirectly, they also interact with clouds and by supporting heterogeneous chemistry reactions. In addition, they affect climate by altering the albedo of surface snow and by modifying the main biogeochemical cycles. A substantial improvement in the study of the physical and radiative characteristics of dust particles and in climate models has occurred in order to reliably predict their impact on climate. However, key properties of mineral particles are still poorly known so that global dust cycle simulations are still poor. One of the main goals of these studies, in next years also in collaboration with Chinese researchers, is to understand the balance between positive feedback components such as greenhouse gases and negative feedback components like mineral dust. Indeed, the most precise information on Earth's climate variation can be extracted from ice cores. Within this framework, the investigation on high altitude air circulation and the characterization of low concentration of airborne particles in natural ice and snow although challenging, is strategic.

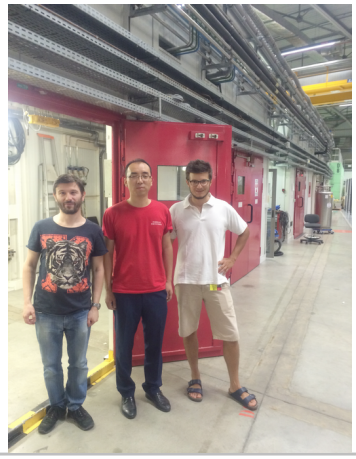

Figure 4: Photograph at the LISA beamline (ESRF) during the 2nd experimental run (July 2017) on aerosols stored in snow and ice-cores from Western China and Arctic.

Portions of this research were carried out in the framework of proposals 90U5 and 3082M at SSRL, of the Long Term proposal NT1984 at Diamond and the Long Term proposal 08-01.1031 at LISA the Italian CRG at ESRF. Acknowledgement is also due to *Italian Presidenza del Consiglio dei Ministri* (DARA) through the MIAMI project.

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Trace element and their specification in environmental sciences via X-ray Fluorescence and X-ray Absorption spectroscopy: status quo and perspectives in BSRF and BAPS.

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Keywords: XRF, XANES, BSRF, Environmental sciences, Beijing Advanced Photon Source

The environmental and energy are two critical issues in nowadays world. To protect the environment on this planet while providing sufficient energy to the human species, almost every country in the world has deployed strategic and strict roadmaps for developing sciences and technologies surrounding issues such as environment recovery and energy recreation.
Synchrotron radiation methods such as X-ray fluorescence spectroscopy (XRF) and X-ray absorption spectroscopy (XAS) enables people to identify the trace element down to ppb level and allows one to identify the atomic bonds that could exist in the complex environmental markers, such as aerosols, fly ashes, foods, soils, water and air.

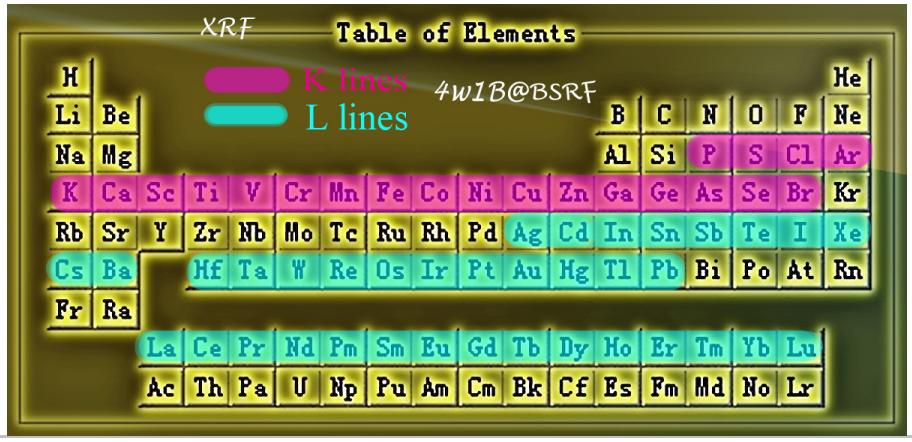

Figure 1: The elements that 4W1B of BSRF could cover for X-ray Fluoresecence spectroscopy.

At Beijing Synchrotron Radiation Facility (BSRF), several beamlines can provide the aforementioned techniques for investigations on environmental markers. The beamline 4W1B, is dedicated to microscopic X-ray fluorescence spectrograph techniques, which was employed extensively in investigating the plants, soil, aerosols, mineral inclusions, etc. The beamlines 1W1B and 1W2B are XAS beamlines covering energy over 4-29 keV that could be employed to study the specification of toxic elements such as As, Hg, and Pb. Furthermore, the beamline 4B7A provides XAS techniques for tender X-ray energy over 2-5 keV, which could be tuned to measure the *K*-edge absorption spectra of S, P, Cl, K, and Ca etc.
Starting early in 2013, collaborations between Chinese and Italian scientists have been established on the investigation of aerosols in snow and ice using advanced synchrotron techniques. In this contribution, I will talk about the current status and their unique applications in environmental sciences [1-3], addressing the advantages and limitations of the XRF and XAS techniques at the Beijing Synchrotron Radiation Facilities (BSRF).

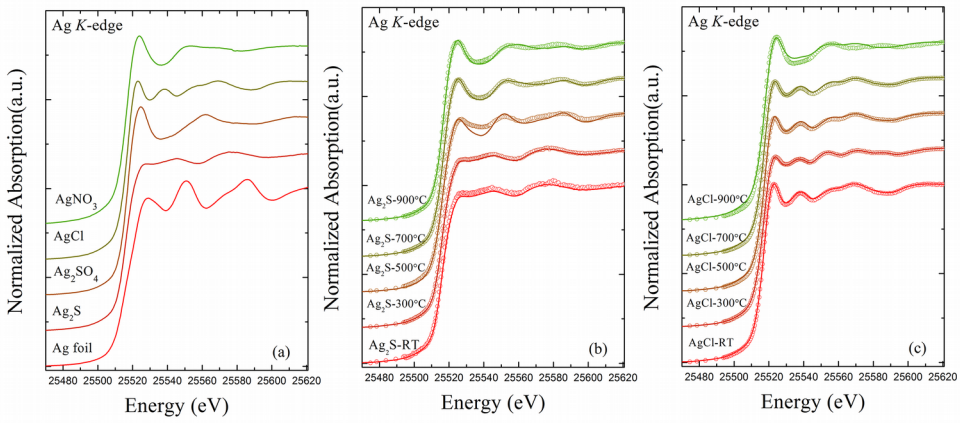

Figure 2: Experimental and fitted silver K-edge XANES spectra of (a) reference standards, (b) Ag_2S spiked sludge, and (c) AgCl spiked SMSW incinerated at various temperature. Data collected at Shanghai Synchrotron Radiation Facility. Courtesy of Prof. Yongguang Yin.

A new 6-GeV, low emittance, storage ring based photon source, dubbed temporarily as Beijing Advanced Photon Source (BAPS), will be built in Beijing in 2018-2024.[4] Thanks to much higher brilliance of the new source in comparison with the current synchrotron radiation sources, the detection limit and sensitivity of the related techniques (e.g. XRF, XAS, HERFD XAS, etc.) would be expected to get improved to an unprecedented level. Establishing effective collaborations and brain-storming among international environmental scientists and beamline scientists are essential for, by exploring the entire merits of the new ring, guaranteeing the crucial contributions of the related beamlines to the advancement of the environmental sciences, so as to help solve the global environmental issues.

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Eolian dust in Antarctica: a proxy for atmospheric circulation and climate in the Southern Hemisphere during the late Quaternary.

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Keywords: dust, ice cores, Antarctica, Quaternary

Ice cores from polar ice sheets provide direct records of climate and aerosol load of the atmosphere over different timescales [1]. They record forcing factors of global significance such as greenhouse gases as well as atmospheric parameters of hemispheric significance such as mineral dust aerosol. The eolian dust record from EPICA-Dome C [2] along with the paleo-temperature record inferred from stable isotopes of water [3] allowed assessing climate and atmospheric circulation changes in the Southern Hemisphere over the past ~800 kyrs. By showing a significant correlation between dust flux and temperature during cold glacial periods, which is absent during interglacial periods, the dust record from central East Antarctica provided robust evidence for a progressive coupling of Antarctic and southern Hemisphere climate as temperature became colder [4].
Mineral dust aerosol concentration in polar ice cores depends on a number of factors such as snow accumulation rate, source strength including soil properties and vegetation cover as well as other factors influencing the quantity of particles available for deflation, processes occurring en route and transport. The size distribution of eolian dust reaching the inner Antarctic plateau, conversely, can be used as proxy for atmospheric transport and atmospheric circulation variability in the past, as recently demonstrated in a multi-proxy study on the Dome B ice core [5].
Dust provenance can be identified by using different kind of tracers, which have varying degrees of applicability. Tracers must be distinctive of the source area and conservative from the source to the sink. Studies based on Sr and Nd radiogenic isotopes on several East Antarctic ice cores concluded that southern South America was the major dust supplier for central East Antarctica during glacial periods of the late Quaternary [2], as supported by Pb isotope data [6] and Rare Earth Elements patterns [7]. In addition, by coupling Sr and Nd radiogenic isotopes to single-grain Raman spectroscopy analyses and microscopic observations it was possible [5] to highlight the key role of the Patagonian emerged continental shelf as dust source at the time when sea level reached its minimum during the last glacial period.

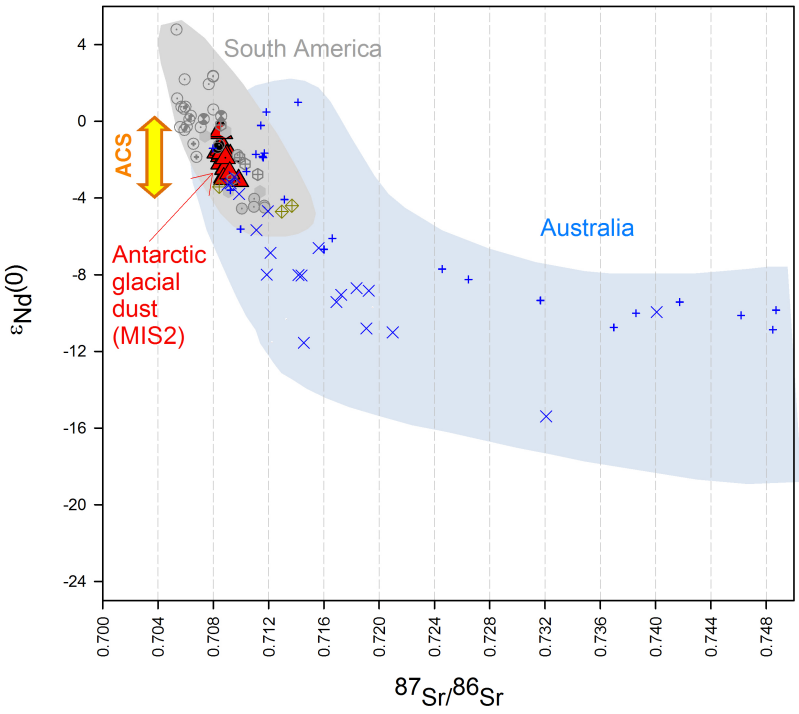

Figure 1: *Eolian dust provenance in central East Antarctica* (Dome B, EPICA-Dome C, old Dome C, Komsomolskaia) during the last glacial period (19-30 kyrs B.P.) detected through Sr and Nd radiogenic isotopes. ACS: Argentinean continental shelf, exposed at that time. Picture redrawn from Ref. [5].

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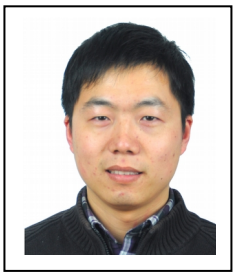
High-resolution mass spectrometric characterization of dissolved organic matter from warm and cold periods in the NEEM ice core.



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Keywords: NEEM, DOM, FTICR-MS

Dissolved organic matter (DOM) is an important component of ice cores but is currently poorly characterized [1]. DOM from one Holocene sample (HS: warm period aged at 1600–4500 BP) and one Last Glacial Maximum sample (LS: cold period aged at 21000–25000 BP) from the NEEM ice core (Greenland) were analysed by ultrahigh-resolution Fourier-transform ion-cyclotron-resonance mass spectrometry (FT-ICR-MS). CHO compounds contributed 50% of the compounds identified in negative-ionization mode in these two samples with significant contributions from organic N, S, and P compounds, likely suggesting that marine DOM was an important source in these samples. Overall, the chemical compositions are similar between these two samples suggesting their consistent DOM sources. However, subtle differences in the DOM between these two samples are apparent, and could indicate differences in source strength or chemistry occurring through both pre- and post-depositional processes.

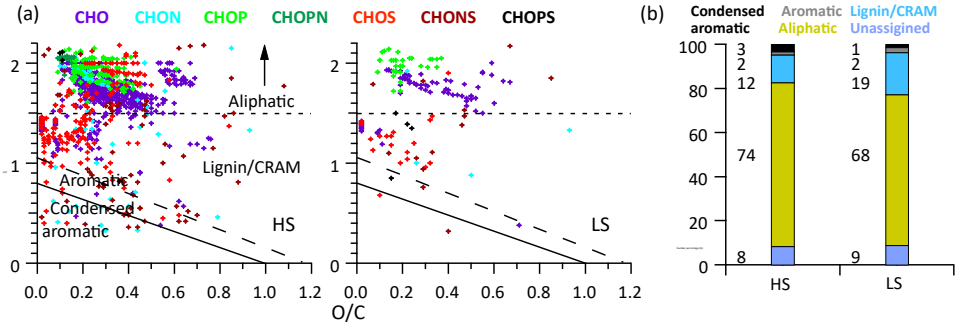

Figure 1: (a) van Krevelen plots for Holocene sample (HS) and LGM sample (LS) and (b) a bar chart showing the contributions of each structural class (determined using AI_{mod} and H/C ratio) to the total DOM.

For example, higher relative amounts of condensed carbon compounds in the HS DOM (5%) compared to the LS DOM (2%) suggest potentially important contributions from terrestrial sources. Greater incorporation of P in the observed DOM in the LS DOM (22%) compared to the HS DOM (13%) indicate more active microbiological processes that likely contribute to phosphorus incorporation into the DOM pool. While these two samples only present a preliminary analysis of DOM in glacial/interglacial periods, the data indicate a need to expand the analysis into a broader range of ice core samples, geographical locations, and glacial/interglacial periods.

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The bioavailable Fe associated with natural and anthropogenic emissions recorded in Arctic and central Asia ice cores

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Keywords: Greenland, Tienshan, Fe concentrations, natural and anthropogenic emissions.

Mineral dust can directly affects climate by supplying iron (Fe) and other essential bioavailable elements to the ocean. In this study, we present the dissolved Fe (DFe) and total Fe (TDFe), and the other elements concentrations in the NEEM ice core over the past 110 kyr B.P. The DFe and TDFe concentrations were positively correlated with the other elements, dust and Ca^{2+} concentrations and significantly negatively correlated with the $\delta^{18}O$ and CO_2 concentrations. The DFe/TDFe ratios were higher during warm periods (Holocene and the last interglacial period) than during cold periods (the last glacial maximum), indicating that the iron fertilization effect is not simply line relationship over the past 110 kyr B.P. In addition, our study shows that the changes in Fe flux between the NEEM ice core and Asian loess records are consistent with summer insolation in the Northern Hemisphere.
These results demonstrate that the variability of bioavailable reactive elements is most likely driven by solar radiation and dust in the Northern Hemisphere. The trace elements in Alpine ice can provide historical information about natural mineral dust and anthropogenic pollutant emissions. We studied bioavailable element records from 1955-2004 A.D. that were obtained from a shallow ice core from Miaoergou Glacier in East Tienshan, central Asia, to determine how Fe and the other element concentrations increased when anthropogenic pollutant emissions in the past 50 years. Toxic heavy elements (Pb, Cs, As and Cr) were also present, and their concentrations increased from 1955 to the early 1990s with increasing European industrial activities. Additionally, a second peak in emissions that potentially resulted from the rapid coal-driven growth of Asian economies was observed after 2000 A.D. Furthermore, the fraction of soluble Fe increased during this period, which was associated with nuclear tests and other anthropogenic toxic heavy-element variations. These results provide an ideal opportunity to investigate the effects of natural and anthropogenic sources of bioavailable metals on iron solubility in arid regions.

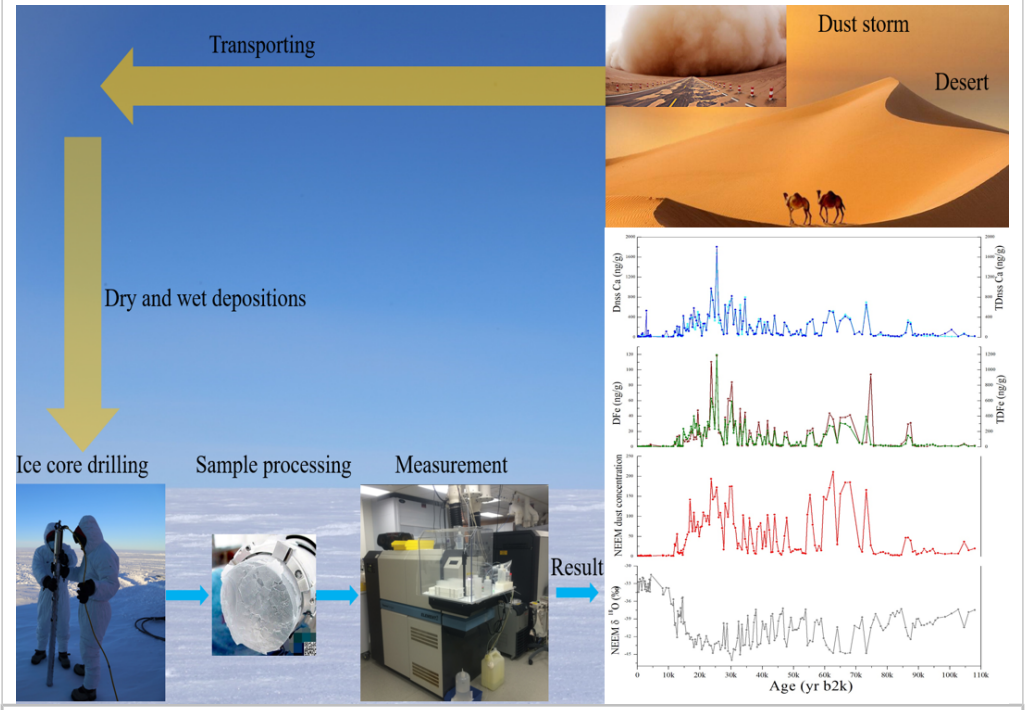

Figure 1: The process of ice core samples collecting, measure and result.

The mineralogical characterization of aerosols in snow and ice: technical challenges and synchrotron radiation methods.

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Keywords: Synchrotron Radiation, Aerosol analysis

Aerosols represent an excellent example of complex materials that pose significant technical challenges for their characterization. The starting materials, the mechanisms of aerosol formation, alteration, transport, deposition and preservation – all those components contribute on making aerosol a 'sample' for the researcher that is far from being ideal – not homogenous, of poor crystallinity, available often in minuscule amounts, prone to alteration and contamination from manipulation, of not well-defined provenance and conservation conditions. Aerosols deposited in ice and snow, of potentially extreme importance as those carry unique geological, social (as in pollution analysis) and climatic information are even more challenging, as must be recovered from almost pure ice in remote locations. State of the art analytical methods are necessary to gather significant information on the elemental and mineralogical composition of areosols form these sources. We will discuss our experience in this field, presenting the challenges, results and the developments achieved over the last years, with several synchrotron radiation techniques applied to the study of aerosol materials extracted from deep ice core perforations in Alpine an Artic environments.

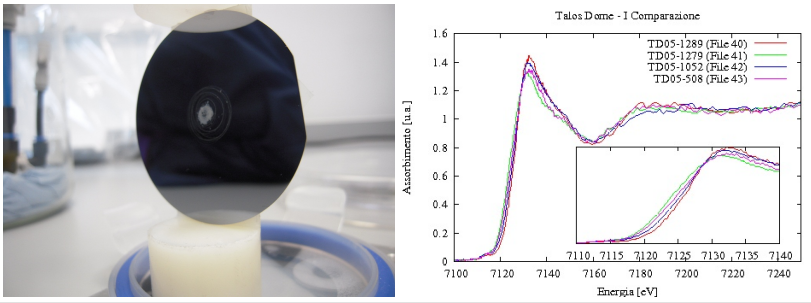

Figure 1: (left) An Antarctic Aerosol Sample deposited on a Silicon Wafer for TXRF measurements; (right) results of XANES investigations at the Fe K X-ray absorption edge across the last glacial transition.

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Spatial and temporal variations of total mercury in Antarctic snow along the transect from Zhongshan Station to Dome A.

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Keywords: mercury, Antarctica, anthropogenic activities.

In this study, the concentrations of total mercury (THg) and ions deposited in the surface snow and snow pits in the eastern Antarctic along the 29th inland route of the Chinese National Antarctic Research Expedition were analysed. The THg concentrations in the surface snow ranged from 0.22 to 8.29 ng/L and elevated concentrations were detected in the inland regions of higher altitudes (3000_4000 m). The spatial distribution of the THg in the snow pits showed greater inland concentrations with mean concentrations of B0.2_1.33 ng/L.

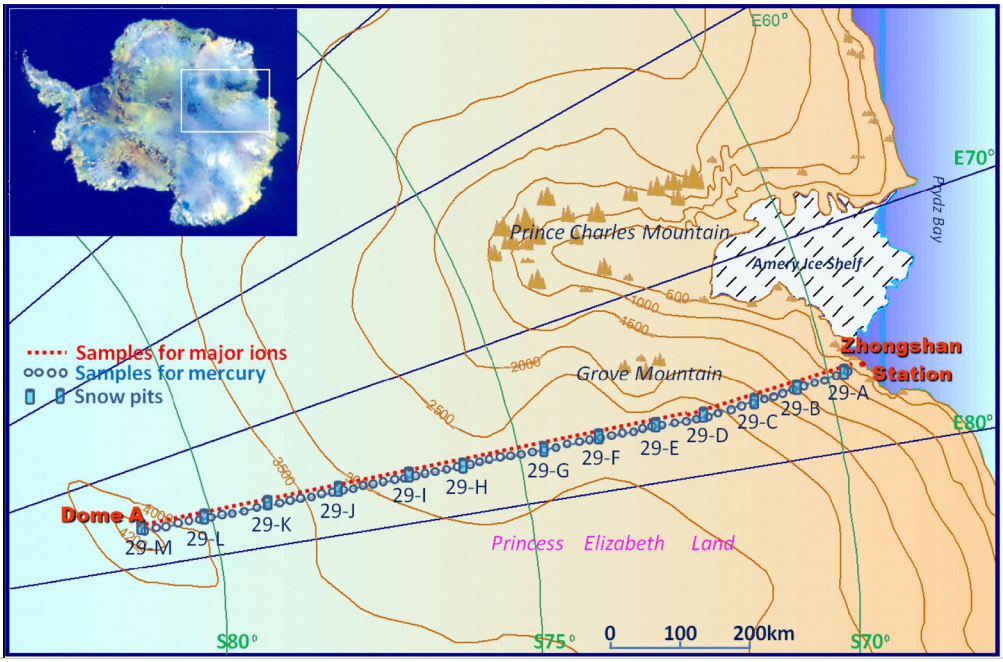

Figure 1: Sampling sites along the transect from Zhongshan Station to Dome A. Thirteen snow pit samples were collected during the inland journey.

The THg concentrations in the coastal snow pit (29-A) showed higher concentrations in the summer snow layers than in the winter snow layers. The THg records from the two inland snow pits (29-K and 29-L) spanned decades and indicated elevated THg concentrations between the late 1970s and early 1980s and during the mid-1990s. The temporal variations of THg in the Antarctic snow layers were consistent with anthropogenic emissions around the world. In addition, the Pinatubo volcanic eruption was the primary contributor to the 1992 THg peak that was observed in the inland snow pits.

Integrated multi-instrumental measurements to characterize chemical, morphological and optical properties of atmospheric aerosol.

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Keywords: atmospheric aerosols, multi-instrumental approach, aerosol properties

Atmospheric aerosols have been found to have a strong impact on human health, ecosystems and atmospheric issues including the Earth's radiative budget and the cloud formation [1,2]. Aerosols are characterized by high variability in terms of sources, chemical, physical and optical properties, spatial and temporal distribution and their transport over long distances strongly modifies their structure [3]. Many efforts have been made towards a deep characterization of atmospheric aerosol properties and an integrated approach of different instruments could be a useful tool not only to this aim, but also to investigate their mixing and aging as in [4].
The integrated approach was used to identify and study volcanic particles during the 2010 eruptions of Eyjafjallajökull volcano. Combining concentrations, chemical analyses and FESEM (Field Emission Scanning Electron Microscopy) observations performed on PM2.5 samples, not only highlighted the contribution of volcanic plume to the PM2.5 levels, but also helped to detect in the fine fraction secondary aerosols as such as sulphates and nitrates, likely related to the Eyjafjallajökull volcanic emissions [5]. Columnar radiometric measurements of direct solar irradiance, instead, allowed to discriminate between the two eruption phases (April and May 2010), highlighting the contribution of Saharan dust particles during the May eruption phase [4].
In another study, the comparison of PM2.5 and PM1 concentrations, chemical composition, and mineralogical, petrographycal and morphological features of atmospheric aerosols allowed to identify natural and anthropogenic contributions, both local and long range transport related [6,7].
Finally, useful information have been obtained by comparing the fine fractions of both surface gravimetric mass size distributions and columnar radiometric size distributions to EBC (Equivalent Black Carbon) content in a semirural site in South Italy [8]. In fact these parameters were in a good agreement under the circulation of northeast European polluted air masses, highlighting the predominance of surface aerosol optical properties over the entire atmospheric column.
A step ahead toward the integration of data was obtained during the short-term intensive multi-instrumental measurement campaign IMAA (Integrated Measurements

of Aerosol in Agri valley) performed in an area of a strong environmental interest in Southern Italy. These measurements were supported by gaseous pollutants ancillary data, measured by the Basilicata Regional Agency for the Environment. In particular, chain-like Black Carbon (BC) particles were observed (Fig. 1 up-left) and the good correlation between measured EBC and the finest channel of an Optical Particle Sizer (OPS) (Fig. 1 up-right) suggests "fresh" BC particles as one of the main component of fine aerosol.

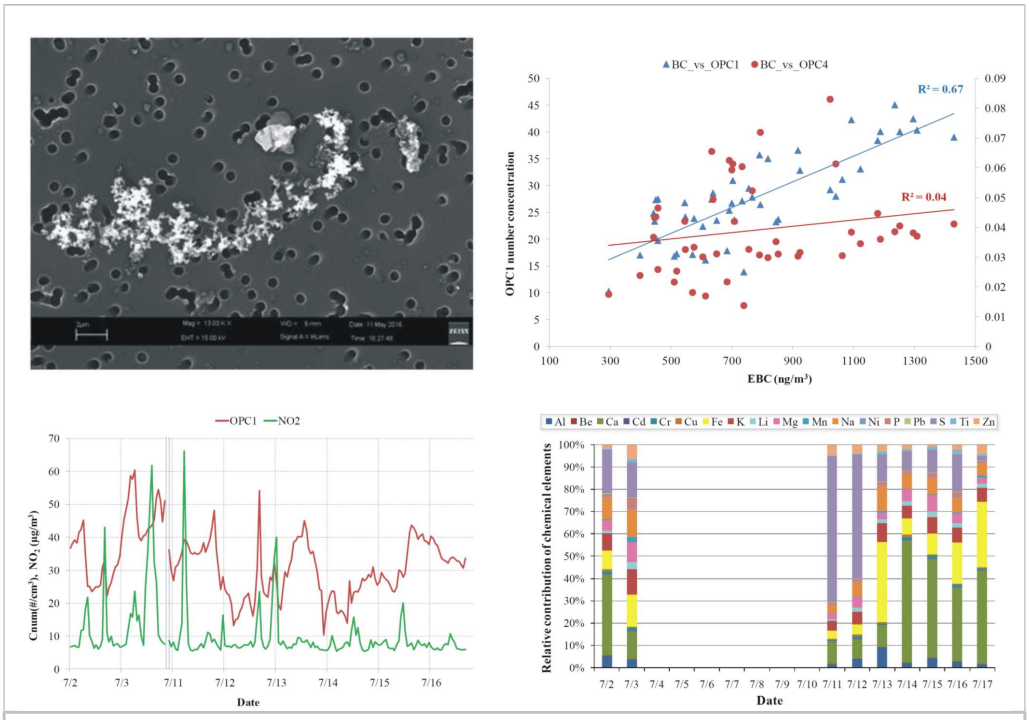

Figure 1: IMAA campaign, typical chain like BC particle (up-left); correlations plot of measured EBC with OPS channel 1 (blue triangles) and with OPS channel 4 (red circles) (up-right); common peaks structure of OPS channel 1 and NO2 concentrations (down-left); trace-elements PM2.5 chemical composition (down-right).

Depending on the industrial processes realized in that area, coincident peaks of both gaseous pollutant and the finest channel of the OPS were observed (Fig 1 down-left) whereas S, Ca, Fe, Na, K and Mg were the most abundant trace elements.
These results support the multi-instrumental approach to efficiently face environmental issues, regardless the area and sources under study.

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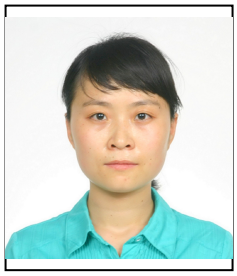
Black carbon and other light-absorbing impurities in snow enhance albedo reduction over the Third Pole region.



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Keywords: BC, light-absorbing impurities, Third pole region

The Tibetan Plateau (TP), often referred to as the "Third Pole", supplies a region where >2 billion persons live with freshwater – anthropogenic light-absorbing aerosols from nearby China, India and other regions are now causing accelerated glacier melting of the TP threatening to undermine and change the freshwater delivery. It is a major challenge for climate science to understand the types, sources and climatic effects of different components of the aerosol burden in the glacial snow/ice to this inaccessible region. Light-absorbing impurities deposited on snow and glacier can reduce the surface albedo, accelerate snow and ice melt, and trigger albedo feedback. Intend to link LAIs depositions to snow and glacier melt, this study performed an integrated investigation in snow cover and benchmark glaciers across the TP. BC concentrations cover generally showed lower values in the Himalayan region to southern TP, mainly affected by the different BC deposition and snow types. In the Himalayan and southeastern TP, we found contributions of the biomass-sourced BC was larger than 60%, whereas the biomass-sourced BC in the north TP and Tienshan contributed less than 30%. The simulation indicated that black carbon and dust accounted for about 20%–30% of the albedo reduction relative to clean snow. BC played a larger role on albedo reduction and radiative forcing than dust in the study area. Assessment of LAIs to the glacier melt can contribute approximately 30% of the total glacier melt. LAIs on the snow and glaciers can enhance glacier melt during summer, further enrich black carbon and other light absorbing impurities, and subsequently influence the water resources for people and social development at downstream.

The MIAMI Project: design and testing of an IoT low-cost device for mobile monitoring of PM and gaseous pollutants

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Keywords: PM particulate matter, mobile monitoring, low-cost sensors, PM sampling, mineralogical analysis

Particulate matter (PM) is a complex mixture of solid and liquid particles suspended in a gas phase that can be emitted by natural and anthropogenic sources. PM pollution has a considerable socio-economic impact, affecting public health, environment and climate. The finest the particles, the greater is the health risk. In particular, it has been demonstrated that ultrafine particles (UFP), i.e., particles with nanoscale size (<100 nm in diameter), are more effective in inducing respiratory diseases than larger particles with similar composition [1].
In this scenario, PM monitoring and characterization are fundamental aspects of this problem and, in the future, a great advancement is expected with the development of modern mobile instruments that integrate several and different quantitative and qualitative measurements [2]. Nowadays, air quality is typically monitored by national environmental agencies through measurement of pollutants concentration at fixed stations and large and accurate databanks are available for statistical analysis. The position of the fixed sampling stations is chosen on the basis of well-assessed criteria: type of area, representativeness, exposure to atmospheric agents, etc., although limitations regarding the reliability of fixed PM stations exist.
We present here the preliminary data from novel device for PM and additional gaseous pollutants (VOCs, CO_2 etc.) mobile monitoring that we recently assembled and tested in the frame of the MIAMI (*Monitoraggio dell'Inquinamento Atmosferico della Montagna Italiana*) project. The device, named SPARCO was conceived to integrate low-cost sensors in a compact system, suitable to be installed in mobile media such as car, cycle/motorcycles, drones, flying balloons, or even in a back-pack, to allow on-line, continuous PM monitoring, augmented by environmental parameters such as temperature, humidity and geographical positioning via a GPS. Sensors are integrated on IoT microcontrollers (such as Arduino, Raspberry, Wasp or similar) handling the data flux and their networking via WiFi, radio, or GPRS connections [3]. The device in addition may communicate in real-time with a smartphone through Bluetooth. The particulate is measured as total suspended particulate (TSP) and into its three main dimensional classes (PM_1, $PM_{2.5}$ and PM_{10}). Differently form similar systems already

existing, SPARCO is equipped with a micro-pumping system allowing to collect the atmospheric particulate on a polycarbonate filter that that can be used for further morphological and chemical (*off line*) analysis of the sampled materials with SEM, optical microscopies or spectrometry (FTIR, Raman, SERS etc.). The reliability of the sensors were tested against professional instruments for both PM and CO_2, and very promising results were obtained (Fig. 1).

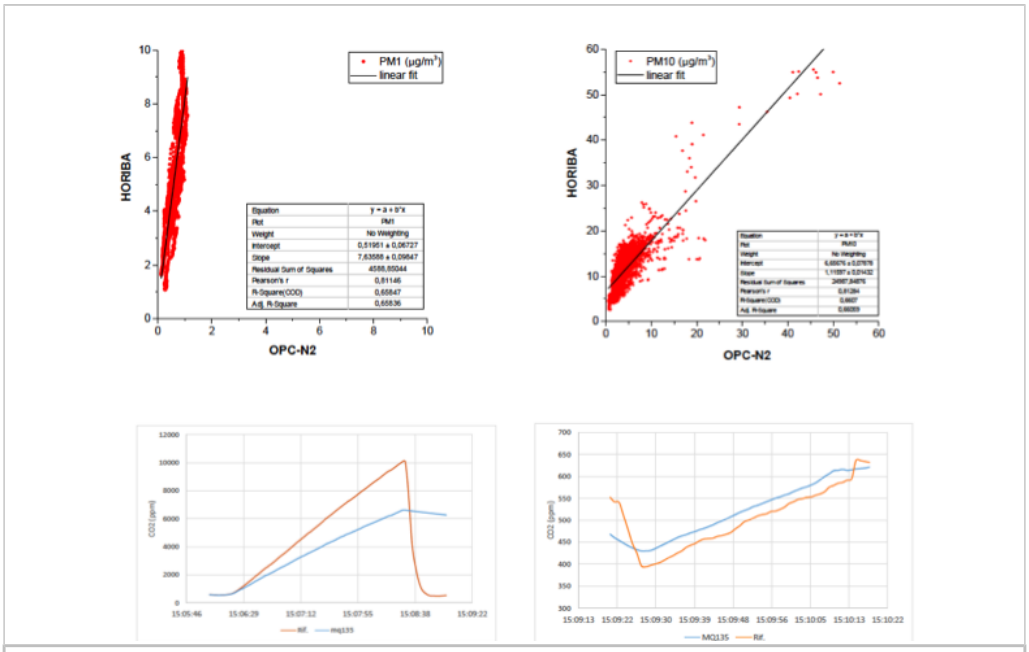

Figure 1: Relationship between (above) PM_1 and PM_{10} and (below) CO_2 concentrations measured with low-cost (blue) vs. professional sensors (orange).

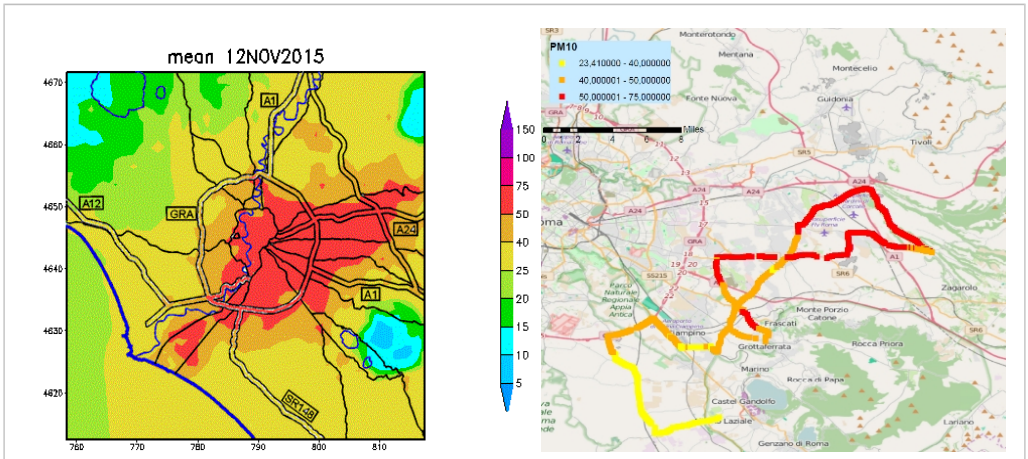

Figure 2: TSP variation along the route of the test conducted in the city of Rome. Right: map obtained from the data provided by ARPA Environmental Agency, while in the left panel is shown the route sampled in the same time interval by SPARCO.

Preliminary tests of the system were conducted in the metropolitan area of Roma, Italy under various meteorological and vehicular traffic conditions. The concentration of TSP and VOCs, and environmental data were sampled with a temporal resolution of 1 s. Figure 2 shows an example of the TSP concentrations measured along the route and the variation of the environmental data vs. time.
The sampled TSP were analysed manually by means of an electron-microscope coupled with energy dispersive X-ray analysis. Selected examples of SEM results are reported in Fig. 3.

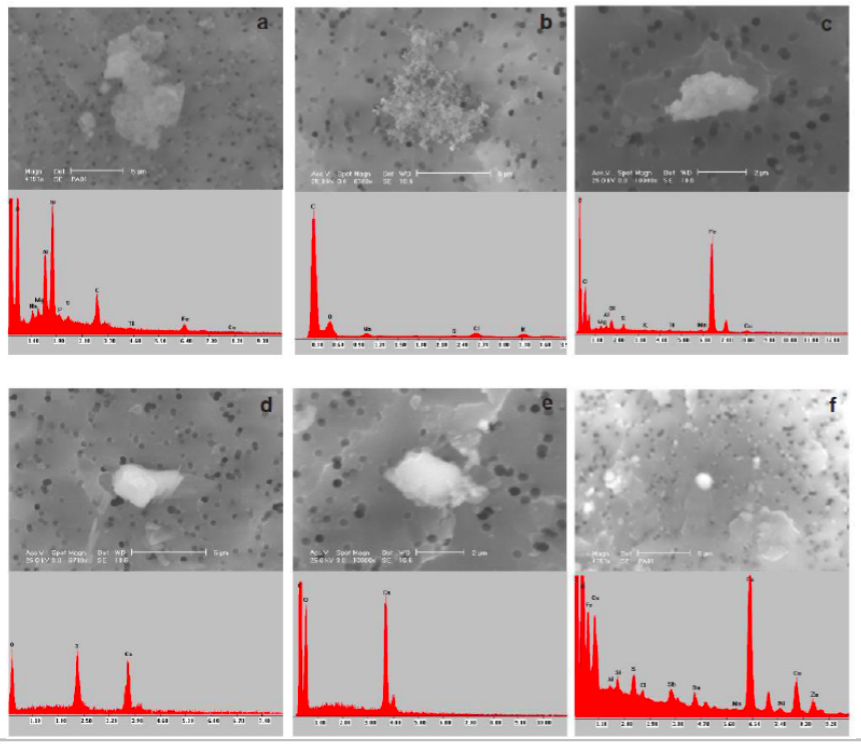

Figure 3: Typical SEM photomicrograph and EDX spectra of different airborne particles sampled in the urban area of Rome during the test shown in Fig. 2: a) terrigenous particle; b) soot aggregate; c) iron-oxide particle; d) gypsum crystal; e) carbonate particle; f) automotive brake wear particle.

Part of this research was carried out in the framework of the MIAMI project financially supported by DARA Department of the *Italian Presidenza del Consiglio dei Ministri* and by the BRIC-INAIL project ID12.

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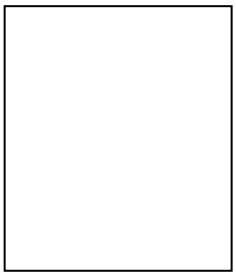
Levels and Spatial Distributions of Levoglucosan and Dissolved Organic Carbon in Snowpits Over the Tibetan Plateau Glacier



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Keywords: Tibetan Plateau, levoglucosan, dissolved organic carbon

In this study, we collected 60 snowpit samples on nine glaciers from the northern to the southern of the Tibetan Plateau (TP), to study levoglucosan and dissolved organic carbon (DOC). The lowest concentration of levoglucosan was found in the Yuzhufeng (YZF) glacier with the mean value of 0.24 ± 0.08 ng L^{-1}, while the highest concentration of levoglucosan was in the Gurenhekou (GRHK) glacier with the mean value of 11.72 ± 15.61 ng L^{-1}. For the DOC, the lowest concentration was in the Dongkemadi (DKMD) glacier with the mean value of 0.36 ± 0.21 mg L^{-1}, whereas the highest concentration was in the Muztagh (MZTG) glacier with the mean value of 1.04 ± 0.15 mg L^{-1}. Levels of levoglucosan and DOC in snowpits of the TP glaciers exhibited regional variations, demonstrated by levoglucosan / DOC ratio that ranged from 0.02 to 6.03 ‰ in the Tibetan Plateau glacier. The levoglucosan / DOC ratio and the correlations between levoglucosan and DOC suggested that biomass burning products contributed only marginally to DOC in the TP glaciers. An analysis of air mass backward trajectories showed that levoglucosan and DOC in TP glaciers should be transported from the northwestern TP, internal TP, Central Asia, South and East Asia regions.

The new LISA beamline at the ESRF: an opportunity for environmental sciences.

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Keywords: synchrotron instrumentation, XAS, LISA

LISA (**L**inea **I**taliana per la **S**pettroscopia di **A**ssorbimento di raggi X) [1] is the new italian CRG beamline at the European Synchrotron Radiation Facility (ESRF). The beamline is dedicated to X-ray Absorption Spectroscopy (XAS), covering a wide energy range $4 < E < 70$ keV which allows to probe the K and L edges of the most of Metals and Rare Earth elements.
The beamline is equipped with a liquid He/N_2 cryostat and a compact furnace for measurements in a wide temperature range (10 - 1000 K) allowing in-situ chemical treatments and measurements under controlled atmosphere. The high photon flux provided and the X-ray fluorescence detectors available (HP-Ge, SDD) allow the study of liquid and highly diluted samples.
These features open the possibility to characterise natural/anthropogenic complex matrixes that are not suitable for standard chemical and structural analyses despite being of crucial importance in many geochemical and environmental issues. Trace elements in geological or environmental samples can be analysed at very low concentration, gaining information on oxidation states and host phases.

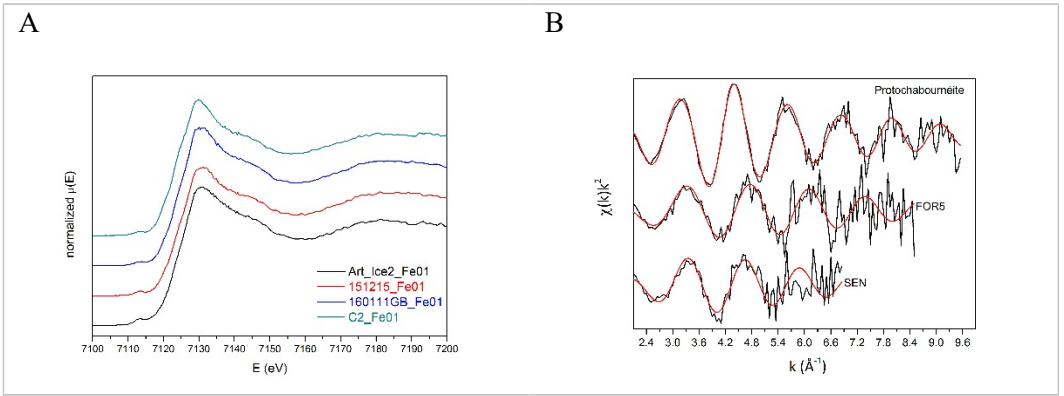

Figure 1: A) Fe K-edge XANES from a selection of aerosol and arctic snow filter samples. B) EXAFS spectra measured at Tl-L_3 edge on Tl-bearing pyrite; protochabournéite was used as a standard for Tl(I) sulphides. Both data sets were collected in the fluorescence mode.

Figure 1 (A) shows, as an example, the Fe K-edge spectra (XANES region) of aerosol and snow filter samples from glaciers located in the Tibetan plateau and Artic regions. The Fe concentration in the filters is estimated to vary around a few μg/cm^2. The analysis of Fe will increase the knowledge of its chemical speciation in snow and ice, improving the understanding of its effect on the climate.
Figure 1 (B) shows the absorption spectra (EXAFS region) of Tl in natural pyrite coming from the Apuan Alps area (Northern Tuscany, Italy), where Tl concentration is only a few hundreds of ppm. The study of Tl in this matrix became extremely important after the discovery of a heavy Tl contamination in drinking waters of the Valdicastello-Pietrasanta (Lucca, Italy) aqueduct. Experiments performed in LISA are currently underway in order to understand the speciation of Tl in these natural deposits and follow part of Tl cycle in the environment from the host rock to water pipes [2].
In this contribution a description of the project status will be provided and the main applications of the beamline are presented, ranging from structural analysis of materials to environmental science.

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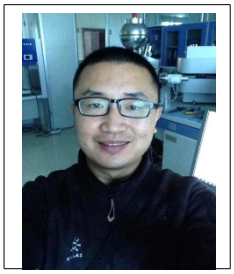
Provenance of cryoconite deposited on the glaciers of the Tibetan Plateau: New insights from Nd-Sr isotopic composition and size distribution.



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Keywords: Cryoconite, glacier, SEM-EDX, Nd-Sr isotopes, Tibetan Plateau

This study presents the Nd-Sr isotopic compositions and size distributions of cryoconite deposited on the glaciers at different locations on the Tibetan Plateau, in order to trace its source areas and the provenance of long-range transported (LRT) Asian dust on the Tibetan Plateau. The result of scanning electron microscope-energy dispersive X-ray spectrometer analysis indicated that mineral dust particles were dominant in the cryoconite. Most of the cryoconite samples from the Tibetan Plateau indicated different Sr and Nd isotopic composition compared with sand from large deserts, e.g., the Taklimakan and Qaidam deserts. Some cryoconite samples showed very similar Nd-Sr isotopic ratios compared with those of nearby glacier basins (e.g., at Laohugou Glacier No.12, Dongkemadi Glacier, and Shiyi Glacier), indicating the potential input of local crustal dust to cryoconite. The volume-size distribution for the cryoconite particles also indicated bimodal distribution graphs with volume median diameters ranging from 0.57 to 20 μm and from 20 to 100 μm, demonstrating the contribution of both LRT Asian dust and local dust inputs to cryoconite. Based on the particle size distribution, we calculated a mean number ratio of local dust contribution to cryoconite ranging from 0.7% (Baishui Glacier No.1) to 17.6% (Shiyi Glacier) on the Tibetan Plateau. In general, the marked difference in the Nd-Sr isotopic ratios of cryoconite compared with those of large deserts probably indicates that materials from the western deserts have not been easily transported to the hinterland of Tibetan Plateau by the Westerlies under the current climatic conditions, and the arid deserts on the Tibetan Plateau are the most likely sources for cryoconite deposition. The resistance of the Tibetan Plateau to the Westerlies may have caused such phenomena, especially for LRT eolian dust transported over the Tibetan Plateau. Thus, this work is of great importance in understanding the large-scale eolian dust transport and climate over the Tibetan Plateau.

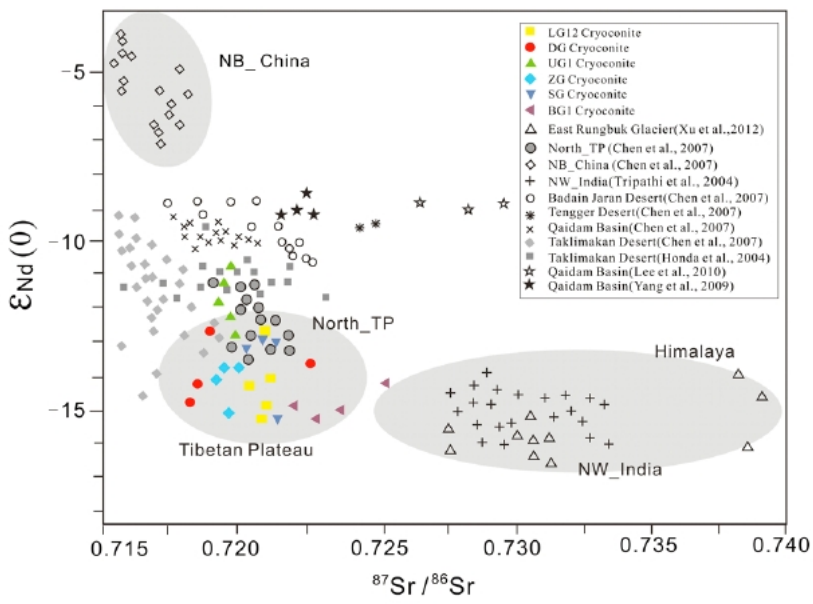

Figure 1: Comparison of the Nd-Sr isotopic composition of cryoconite with dust sources from arid regions in western China.

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Laboratory Based XRF-TXRF Experiments with Polycapillary Optics

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Keywords: TXRF, X-ray imaging, microXRF, polycapillary optics, low concentration

The identification of ice core insoluble mineral aerosol source areas is an important tool for the understanding of present day and past pathways of atmospheric transport toward the poles and the paleoclimatic information. To achieve this result it is very helpful to determine the geochemical composition of atmospheric dust particles deposited over the ice sheets and archived in ice core samples and to compare it with the composition of potential source areas sediments. The main experimental challenge is the very low concentration of mineral materials trapped in the snow, especially for Antarctic firn and ice samples, typically around 10-20 ppb (~ 5000 particles / cm^3) [1].

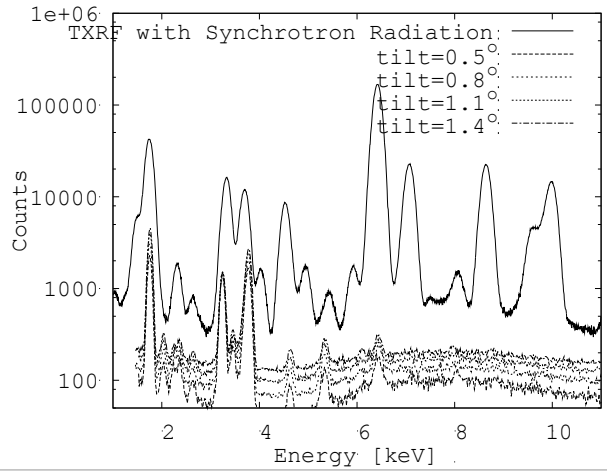

Figure 1: TXRF comparison of synchrotron radiation and our prototype with a X-ray conventional tube. For the latter, four different spectra are given, one for each tilt angle.

A complete studies of elemental concentrations in the ppb range (such as insoluble dust in deep ice core) require ultimate cleaning procedures to collect, prepare and perform non-destructive experiments, that require a very bright X-ray sources, such as synchrotron radiation, combined with a total external reflection regime.
In the last years, XLab-Frascati (Laboratori Nazionali di Frascati - INFN) has developed a series of prototypes based on polycapillary optics that allow performing a full X spectroscopy analysis [2,3]. Here, we demonstrate that a conventional source combined with a polycapillary semi-lens can provide a quasi-parallel beam intense enough for desktop TXRF analysis of low concentration samples and report preliminary results in comparison with Synchrotron Radiation.

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A new isolation method for biomass-burning tracers in snow: measurements of *p*-hydroxybenzoic, vanillic, and dehydroabietic acids

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Keywords: Glacier snow, p-hydroxybenzoic, vanillic, and dehydroabietic acids, solid-phase extraction, DOC, BC, biomass burning

Due to their climate effects, carbonaceous constituents (including black carbon and organic carbon) in snow and ice have recently become the subject of extensive research [1, 2]. They can strongly absorb the solar radiation, and alter the energy balance of snow, thereby resulting in the substantial snow melting [3, 4]. However, the sources, transport, and deposition process of carbonaceous constituents (black carbon and DOC) are very complicated. In particular, organic acids such as p-hydroxybenzoic, vanillic, and dehydroabietic acids have been exploited as unique biomass-burning tracers to differentiate the relative importance of fossil fuel combustion and biomass burning [5].

Nevertheless, the application of such organic acids as biomass-burning tracers in snow and ice is still scarce. The major reason is due to the limitation of the sample pretreatment and instrument analysis. For example, the method by Kawamura et al [6] is not practical in the field pretreatment and need complicated handling steps in the laboratory. Recently, Grieman et al [7] established a method for analysis of vanillic acid in Greenland ice core by HPLC-ESI-MS/MS. However, the requirement of the instrument is very expensive and is not available in most of the laboratories.

A method by solid-phase extraction (SPE) coupled with gas chromatography/ion trap mass spectrometry was developed for the determination of those organic acids in snow. The limit of detection (LOD) is 0.002, 0.001, 0.004 ng mL^{-1} for p-hydroxybenzoic, vanillic, and dehydroabietic acids, respectively. For p-hydroxybenzoic and vanillic acids, all the four SPE cartridges used produce good recoveries (>75%). However, for dehydroabietic acid, HLB cartridge has much better performance than DPA, FEP-2 and PAX cartridges (Fig. 1). The method was applied to the snow samples collected from Zhadang Glacier in the Tibetan Plateau (TP), and demonstrated its feasibility in pretreating and detecting of these target compounds.

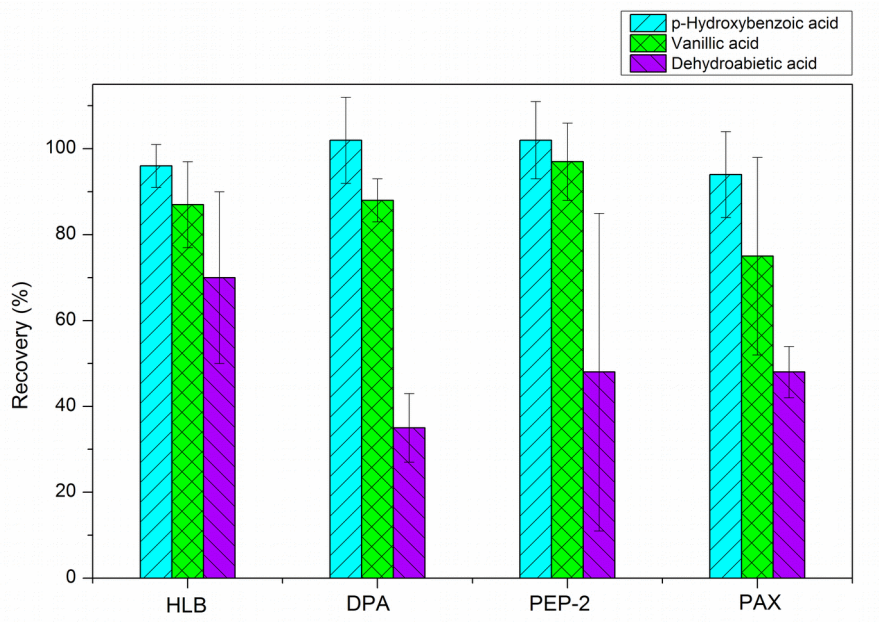

Figure 1: Recoveries of p-hydroxybenzoic, vanillic and dehydroabietic acids in snow samples using four types of SPE cartridges for their isolations and determination.

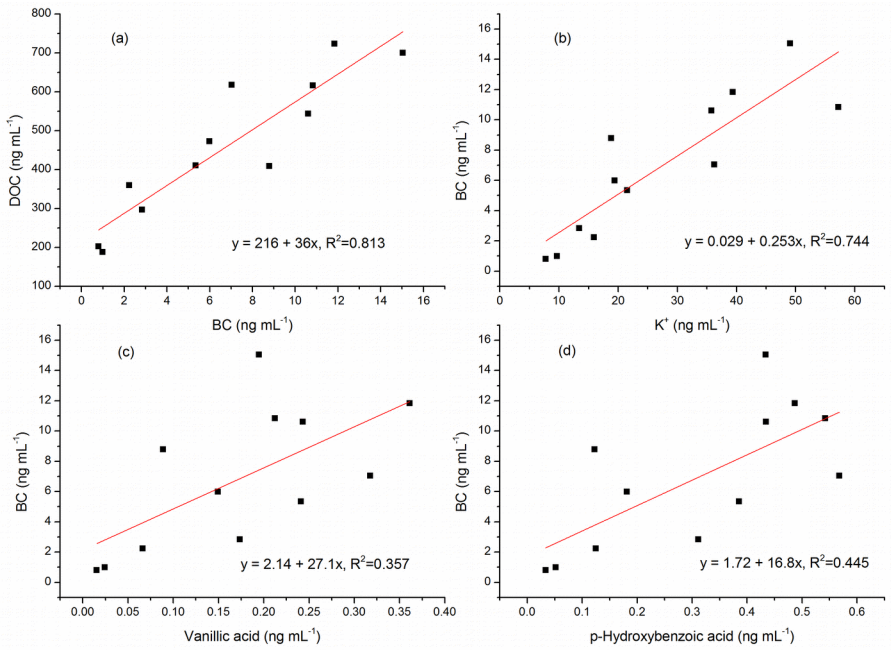

Figure 2: Correlations of BC with (a) DOC, (b) K^+, (c) vanillic acid, and (d) *p*-hydroxybenzoic acid in snow samples.

In this study, K^+ displayed good relations with DOC and p-hydroxybenzoic and vanillic acids, providing evidence to support that biomass burning dominantly contributed to the DOC in TP glaciers rather than fossil fuel combustion or biological process (e.g. microbe). Similar good correlations were also observed between black carbon and biomass-burning tracers (Fig. 2). Therefore, these results clearly demonstrate that both DOC and BC in the snow of the Zhadang Glacier are emitted from biomass burning. This finding is in agreement with the atmospheric aerosol observations over the TP. Our recent works have demonstrated that in the pre-monsoon season, emissions from agricultural and forest fires in South Asia could penetrate through the Himalayas and reach the TP [8, 9]. The time period of intensive air-pollution dispersion from South Asia to the TP (pre-monsoon) generally corresponds to the snow accumulation period covered by the snow pit samples (winter and spring).

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Design and characterization of a mapping device optimized to collect XRD patterns from highly inhomogeneous and low-density powder samples

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Obtaining information about the mineralogical composition of samples characterised by very small amounts of material is a real analytical challenge. A microscopic approach involving electron microscope techniques, such as high-resolution Transmission Electron Microscopy is often successful. It allows identifying individual particles' composition and structure [1]. However, this relies on the ability to extract, deposit and identify individual microscopic particles. In addition, the need to expose micron-sized minerals to vacuum conditions, does not guarantee they remain in their pristine state. On the other side, application of averaging analytical methods, such as X-ray Powder Diffraction (XRPD), potentially faster and with a higher statistical significance is restricted by detection limit conditions. A high sample dilution lowers the signal/background figure as the substrate contribution to the measurement becomes dominant.
We report in this contribution on the development of a device designed to improve X-ray Powder Diffraction data acquisition through mapping coupled to a rotational motion of the sample.
The device aims at overcome the experimental issues that accompany the analysis of inhomogeneous samples, such as powders or dust deposited on a flat substrate. Introducing the mapping of the substrate, and at the same time the rotation, we may overcome drawbacks associated to inhomogeneous distributions, e.g. ring-like patterns

due to the coffee stain effect generated by the evaporation of a solution. In order to perform both mineralogical and elemental composition analyses of mineral samples coupling XRPD, synchrotron-based X-ray Fluorescence and X-ray Absorption Spectroscopy analyses [2], we used a polycarbonate filter. Experimental data have been collected from powders of a NIST standard soil (11 µg) and from an airborne dust samples extracted from deep ice cores in Antarctica (9.6 µg).

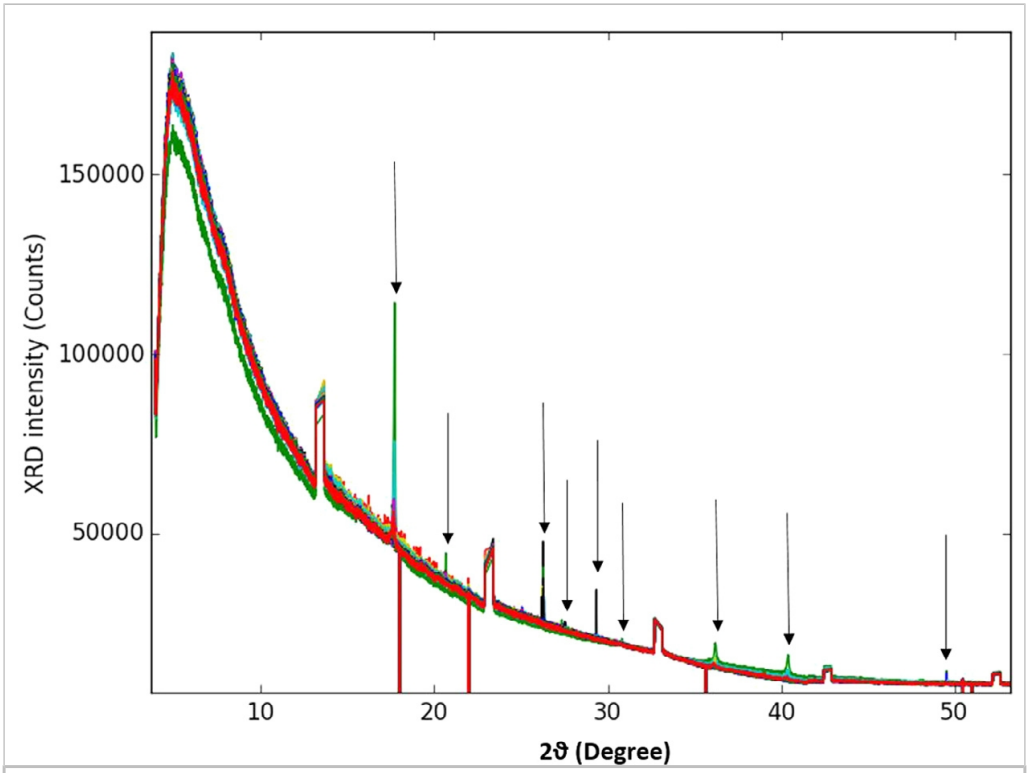

Figure 1: XRD patterns collected on a sample containing Antarctica dust (9.6 µg) using a square grid of 81 points. The patterns have been acquired at the photon energy of 7 keV.

Using this new device, we managed to improve the number of detected peaks for the NIST sample from 3 to 19 and we identified the presence of the quartz alpha phase setting an upper value to the mass detection limit of ~1-2 µg. In addition, thanks to the ability to map and rotate the sample, we managed to detect nine peaks in an airborne dust Antarctica sample respect to nothing using a standard non-rotating holder [3]. XRD patterns show that this approach makes possible to collect high quality data, certainly useful to identify mineral fractions present in these low density samples.

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Shipping emissions, air quality and short-lived climate forcers

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Shipping emissions have been to shown to affect air quality not only in port areas but in coastal areas where shipping lanes are relatively close to the coastline [1,2]. Ship emissions have an influence on NO_x, SO_x, Particulate Matter (PM), and Black Carbon (BC) atmospheric concentrations [3,4].
In regions with large coastal populations, and high levels of photochemical activity such as the Mediterranean, the west coast of California, the Bohai and Yellow Seas this is clearly of concern, particularly because these regions have significant terrestrial sources of pollution as well [5] .

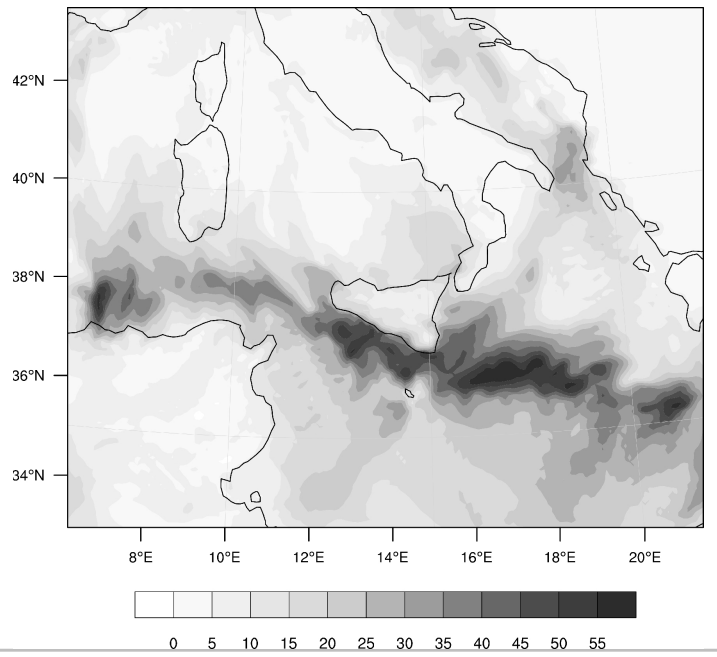

Figure 1: A map of the maximum difference in O_3 concentration (ppb) from modeling runs with and without shipping emissions (for the summer of 2009). The shipping lane from the Strait of Gibraltar toward the Suez Canal is clear as it passes between North Africa and Sicily.

Our experience of modelling the ship impact s in the Mediterranean indicate that ship emissions can be responsible for between 5 and 25% of the O_3 concentration over an 8 hour period and hourly as much as 35 - 40 ppb (reaching ≈ 50%). While the immediate effect of NO emission from ships is to titrate O_3 and reduce its concentration in the boundary layer the overall effect in the Mediterranean, in combination with industrial, urban and biogenic emissions, is to significantly enhance regional O_3 [1], see figure 1. However the impact of ships emissions is not only detrimental to air quality in terms of O_3, NO_x, enhanced primary and secondary aerosol concentrations. Ozone and BC are also short-lived climate forcers (SLCFs). Studies suggest that emissions from maritime traffic have a global influence on the radiation budget [5] and a recent study states that fishing vessels are already a major source of BC in the Arctic [6].

The role of shipping emissions play on the radiation are complex, sulphate and nitrate aerosols have a negative forcing effect while ozone production resulting from NO_x yields a positive forcing. Radiative forcing by BC is positive and it has the added effect of changing the albedo of ice and snow so that less radiation is reflected back into space has onshore emissions could have a detrimental effect on the regional radiation budget increasing the negative effects of climate change [7].

Given the expected increase in shipping [8] throughout the Arctic as the extent of sea-ice declines and the climate sensitivity of the Arctic region as a whole, the impact of shipping on the atmospheric aerosol budget requires further study and monitoring.

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From satellites to ice cores: investigating the impact of Light-absorbing impurities in the cryosphere of the European Alps

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Keywords: Light-absorbing impurities, remote sensing, cryoconite, mineral dust

The European Alps are located close to one of the most industrialized areas of the planet and they are 3.000 km from the largest desert of the Earth. Light-absorbing impurities (LAI) emitted from these sources can reach the Alpine chain and deposit on snow covered areas and mountain glaciers. Although several studies show that LAI have important impacts on the optical properties of snow and ice, reducing the albedo and promoting the melt, this impact has been poorly characterized in the Alps. In this contribution, we present the results of a multisource remote sensing approach aimed to study the LAI impact on snow and ice properties in the Alpine area. This process has been observed by means of remote and proximal sensing methods, using satellite (Landsat 8, Hyperion and MODIS data), field spectroscopy (ASD measurements), Automatic Weather Stations (AWS), aerial surveys with Unmanned Aerial Vehicle (UAV), radiative transfer modeling (SNICAR and TARTES) and laboratory analysis (hyperspectral imaging system). Furthermore, particle size (Coulter Counter), geochemical (Instrumental Neutron Activation Analysis, INAA) and optical (Multi-Wavelength Absorbance Analyzer, MWAA) analyses have been applied to determine the nature and radiative properties of particulate material deposited on snow and ice or aggregated into cryoconite holes. Our results demonstrate that LAI can be monitored from remote sensing at different scale. LAI showed to have a strong impact on the Alpine cryosphere, paving the way for the assessment of their role in melting processes.

The gas sensors array approach to monitoring and control of air quality

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Keywords: air quality, chemical sensors, sensor arrays

Indoor environments are composed by exogenous and endogenous compounds. In absence of proper filtering and conditioning of air, the quality of indoor air is necessarily worse than the external one.
In addition to outdoor sources, a number of volatile compounds have an indoor origin. They are exhaled from furniture, wall tapestries, masonry materials, eventual animals, moulds and fungi. Last but not least, the presence of humans is a further source of volatile compounds contributing to the overall composition of the air. Some of these volatiles are known to be harmful, for instance nitric acid (HNO_3), ozone (O_3), nitrogen oxides (NOx), hydrogen chloride (HC_l), sulphur dioxide (SO_2), ammonia (NH_3), formaldehyde (H_2CO), acetic acid ($C_2H_4O_2$).
Working places are characterized by additional compounds, often harmful, related to the specific chemical and physical processes. In this context, it is important to control these compounds indoor, to protect the workers, and outdoor, to protect the nearby citizens. It is also important to consider that many compounds, which may be present as traces, may be dangerous either as consequence of acute or long-time exposures.
The standard approach to the measure and monitoring of air quality consists in the application of a number of analytical techniques aimed at decomposing the air in its basic components and to determine quantitatively the amount of each (analysis in Greek means decomposition).
Rapid and distributed detection methods should be based on low-cost, highly integrated devices such as electronic sensors. However, the selective detection of known harmful compounds should require the development of specific devices. Specificity requires the development of dedicated chemical receptors. Such a development requires vast efforts for each compound, and given the large kinds of molecules of interest it can hardly result in distributed and low-cost devices. Furthermore, selectivity is hardly combined with other fundamental requirements for instance the reversibility. Being most of the interactions based on thermodynamics equilibrium, specificity automatically means strong, and then not reversible, bindings.

In the last two decades an alternative methodology to approach the analysis of chemically characterised samples was introduced. This method is based on the non-selective character of many solid-state chemical sensors. Surprisingly, this feature, detrimental from the analytical point view, defines an analogy between a set of non-selective sensors and the receptors of the animal olfaction [1]. This analogy is based on the fact that both artificial sensors and natural receptors are non-selective in the sense that each receptor is sensitive to more odorant compounds and each compound is sensed by more receptors [2]. Thus, the identification of an odour is not determined by the signals of a single receptor, but from the combination of signals of all the receptors. This is called combinatorial selectivity.
Once the link was established a growing number of researchers worked to develop this concept towards artificial systems able to mimic some functions of the human olfaction [3].

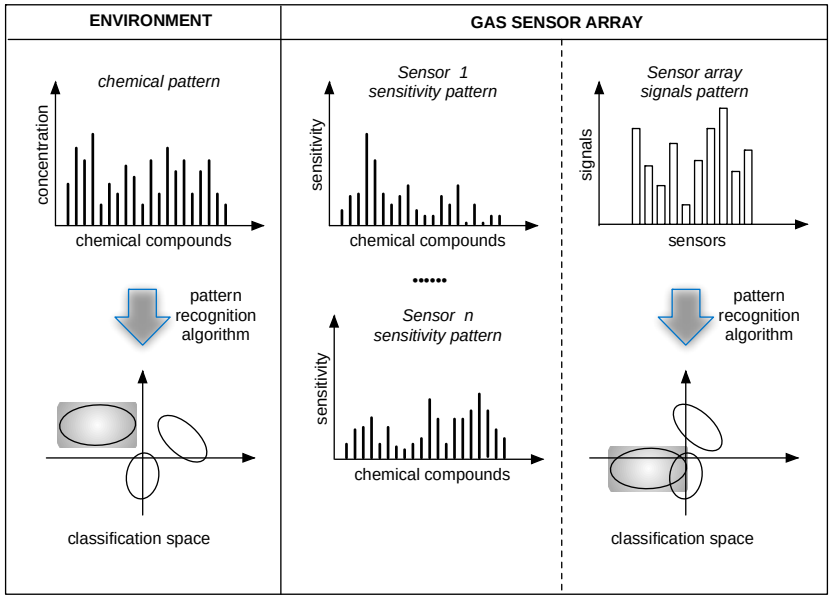

Figure 1: The figure shows the basic principle of gas sensor arrays. Environments are characterized by patterns of chemical compounds. It the concentrations are known, the patterns could be classified with some pattern recognition algorithm to distinguish between similar and different environments. A sensor array is formed by a limited number of sensors each characterized by a proper sensitivity pattern. When the gas sensor array is exposed to an environment, each sensor produces a different signal. Eventually, the sensor array compresses the unknown environmental pattern into a pattern of sensors signals. The application of some pattern recognition algorithm to these patterns allows for the classification of environments.

Efficient gas sensor arrays are made of broadly selective sensors but with different sensitivity parameters. It is important to remind that modern sensors are electronic devices that create signals (analogue or digital) that carry information about the sensed

compounds. Such devices are logically made up of two main components: the sensing material (or receptor) and the transducer. Gas sensor arrays are typically based on the same transducers but carrying different receptors. In this paper a different approach is presented. It is based on the integration of different sensors technologies gathered together in order to expand the gas sensor array performance. Examples of these technologies and their application to environmental control will be illustrated and discussed.

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Roles of supraglacial sediments in attenuating the contamination of pesticides deposited on glaciers

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Keywords: chlorpyrifos, biodegradation, microcosm, cryoconite

High mountains, acting as cold condensers, interfere with the atmospheric transport and global cycling of semi volatile organic compounds (SVOCs) [1]. These organic pollutants can be efficiently scavenged from the atmosphere by snow, along with aerosols, microorganisms and nutrients.

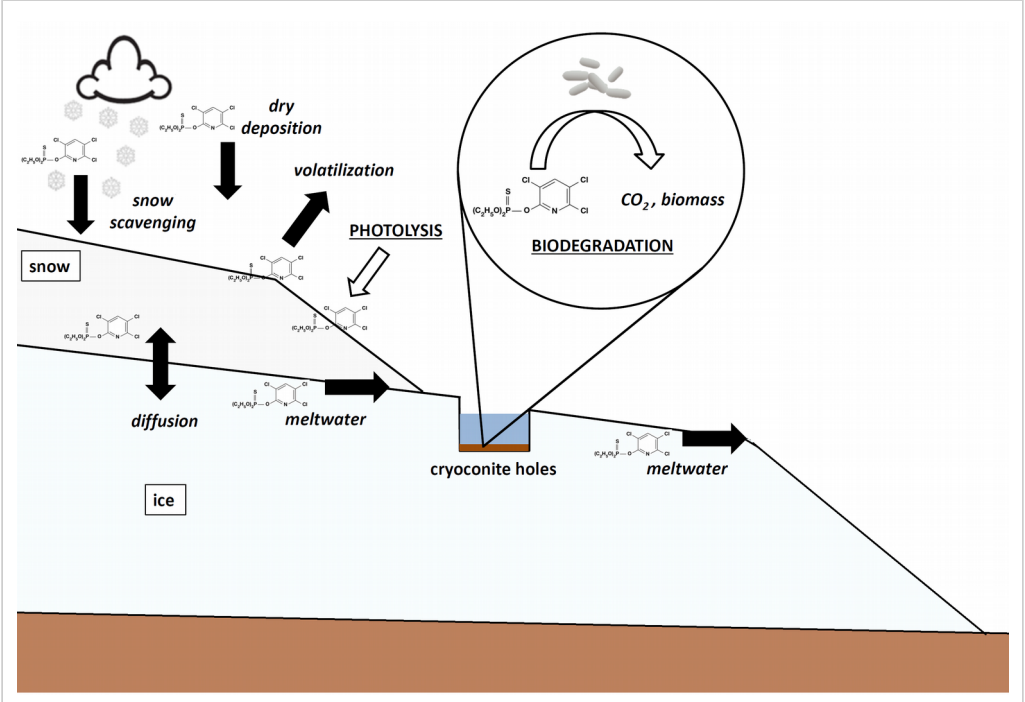

Figure 1: Partition (black arrows) and degradative (white arrows) processes affecting the fate of chlorpyrifos on glaciers.

When deposited on glaciers, pollutants undergo partitioning among different environmental matrices (e.g. snow, ice, water, interstitial atmospheric gases and supraglacial sediment) and post-depositional alteration processes (Figure 1).
Among these matrices, cryoconite, a wind-borne fine debris deposited on glacier surfaces, represents a potential sink for organic pollutants because of its high content of organic matter (OM). Indeed, recent studies showed that cryoconite can accumulate organic aromatic pollutants like polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs) and organochlorine pesticides [2,3]. This occurs particularly in cryoconite holes, small depressions on glacier surfaces filled with water and with a layer of cryoconite at the bottom, which are considered the most biologically active habitats on glaciers [4].
In this work, we tested the hypothesis that cryoconite might act as a "biofilter" for organic pollutants on glaciers by both accumulating them and promoting their biodegradation, thus significantly contributing to their removal. To this end, we conducted in situ microcosm experiments on an Alpine glacier simulating cryoconite hole systems exposed to the organophosphorus insecticide chlorpyrifos (CPF), a xenobiotic tracer that accumulates on glaciers after atmospheric medium- and long-range transport. We found that biodegradation contributed to the removal of CPF from the glacier surface more than photo- and chemical degradation. The high concentration of CPF (2-3 μg g^{-1} w.w.) detected in cryoconite holes and the estimated half-life of this compound (35–69 days in glacier environment) indicated that biodegradation can significantly reduce CPF concentrations on glaciers and its runoff to downstream ecosystems by degrading up 10% of the absorbed CPF released to surrounding freshwaters. Despite the total amount of CPF released by Forni glacier is rather low, the relative extent of biodegradation we documented implies that environmental fate models of pesticides in glacierized areas should account for biodegradative processes.

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Recent altitudinal variations of the main nivo-meteorologic parameters in the eastern italian alps

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Keywords: climatic change, trend, snow, isotherms of 0° and -1°C, LAN

In the last century, the temperatures recorded in the alpine domain were increased on average twice that calculated for the northern hemisphere and is estimated at about 2° C [1]. This signal, almost homogeneous throughout the Alpine region, has been particularly marked since 1980, with average annual rates of about 0.35° C per decade [2]. However, there are very few studies on the real thermal data in the high mountain environment on both sides of the Alpine chain [3]. Evident effects in the central - eastern Italian Alps are found in the very quick melting of glaciers, in temporal and spatial uneven snowmaking, in the modified thermodynamic genesis of precipitation and on a evident change in meteoric regimes, with corresponding impact and growing uncertainties on sustainable development of mountain areas..

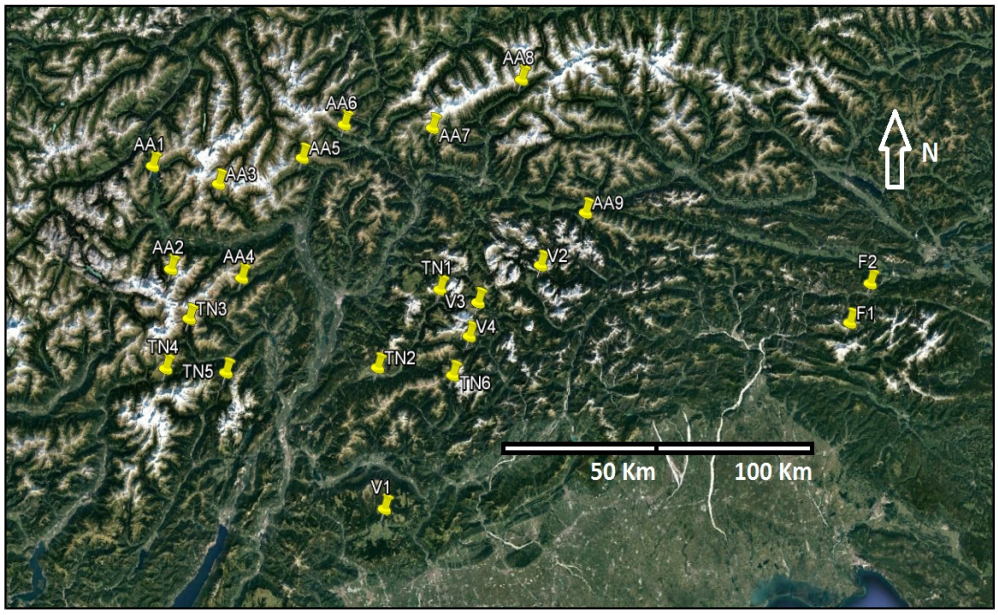

Figure 1: Spatial distribution of the clusters of stations where the climatic study was carried out.

The Italian alpine sectors have been particularly affected by global warming at high altitudes, so much so that the percentage of glacier retreat has increased to 89.5% and it is likely that most of the glaciers of the Southern Alps will disappear during the twenty-first century [4].
Based on these evidences, this study aims to provide a quantification of the increase in temperature in the Tridentine Alps - which include the findings of Trentino - Alto Adige, Veneto and Friuli. Thanks to the remarkable improvement - occurred since the beginning of the new century - of meteo-climatic monitoring to medium - high elevation, it was possible groped a preliminary study of the thermal climate - currently temporal generally extended from January 2003 to December 2016 - so as to determine the variation of the elevation of annual isotherms of 0° C and -1° C.
Twenty-one clusters were thus identified - consist of a 3 - 6 meteo climatic station, and located, respectively, in the valley bottom, slope and peak - so as to calculate the number of frost and ice days, the average vertical thermal gradients and extrapolate the elevation of just mentioned temperature thresholds (Fig.1). The altitude of the analysed stations varies between 640 and 3328 *m.asl* for an average of 1702 m.; the average annual temperature is 4.4°C, the minimum of 0.2° C and the maximum of 8.7° C; the increase for the period of study is 0.24° C. The mean temperature gradient is about 0.53° C/100 m, while the number of days of frost and ice is respectively 165 and 59. Finally, the average elevation of annual isotherms 0° C and -1° C are 2577 and 2769 m. The trends show a strong increase of the elevation, estimated respectively at 30 and 32 meters / year and often up to about 94 m/y in Venetian Dolomites (tab.1).

		AVERAGE TEMPERATURE °C			AVERAGE DAYS		ELEVATION m		TREND		GRADIENT
Cluster	Elev m.	AVERAGE	MIN	MAX	FROST	ICE	0°C	-1°C	0°C	-1°C	°C/100m
AA1	1799	-0,7	8,1	3,7	180	65	2394	2552	**19,38**	**21,69**	0,65
AA2	2686	-5,1	2,4	-1,3	262	143	2468	2632	**19,85**	**20,87**	0,61
AA3	2228	-1,7	5,9	2,1	200	86	2555	2708	**18,88**	**17,24**	0,66
AA4	1408	2,0	11,5	6,8	138	34	2532	2699	**5,59**	**4,91**	0,60
AA5	1664	0,9	9,0	4,9	159	66	2526	2701	**-1,26**	**-3,33**	0,57
AA6	1419	1,5	10,4	6,0	150	49	2477	2654	**23,52**	**24,40**	0,57
AA7	2002	-0,6	6,7	3,0	186	89	2507	2678	**22,31**	**29,50**	0,61
AA8	1852	-1,6	7,0	2,7	197	90	2346	2524	**11,48**	**11,99**	0,55
AA9	2015	-1,7	6,2	2,3	205	101	2437	2620	**20,28**	**21,12**	0,55
TN1	1397	4,0	-0,9	8,9	190	57	2994	3290	**-3,61**	**-15,87**	0,30
TN2	1429	6,6	1,9	11,4	146	33	2966	3197	**21,56**	**22,22**	0,40
TN3	2207	3,1	-1,1	7,2	166	65	2692	2875	**18,16**	**18,89**	0,50
TN4	2361	0,9	-2,7	4,4	169	82	2643	2818	**30,33**	**36,74**	0,60
TN5	1689	5,0	0,8	9,3	150	49	2630	2818	**38,17**	**42,72**	0,50
TN6	1371	5,3	0,8	9,9	133	29	2762	2969	**14,73**	**18,09**	0,50
V1	819	9,0	4,1	14,3	105	12	1816	1927	**40,17**	**41,54**	0,90
V2	1729	4,4	0,7	9,4	157	50	2742	2969	**88,36**	**93,59**	0,40
V3	1812	3,9	-0,4	9,0	175	56	2677	2892	**82,81**	**93,90**	0,40
V4	1311	6,2	2,3	11,4	135	32	2696	2916	**83,93**	**88,86**	0,40
F1	1273	7,4	4,5	10,9	---	---	2783	3003	**65,77**	**72,12**	0,40
F2	1277	5,5	1,5	10,2	---	---	2483	2701	**14,49**	**13,69**	0,40
Average	**1702**	**2,6**	**3,8**	**7,0**	**169**	**63**	**2577**	**2769**	**30,23**	**32,14**	**0,53**

Table 1: Climatological features of climatic clusters.

A slight countertrend signal is observed only in the high Fassa valley (north - eastern Trentino). At the same time, for the 1992-2016 time span, the trends of seasonal fresh

snow sum, the persistence of snow on the ground and snowy days and the LAN skiable natural snow reliability threshold - were calculated. The observation of the trends obtained from the manual weather stations for these nivometric parameters shows a situation with no significant variations. In particular, a slight decrease of 2.8 cm is found - for the fresh snow sum, 6 for the number of days with snow on the ground and 2 days for the number of days when the snow depth exceeds 30 cm.
For the snow cover, the signal is contrasting, although on average there is a negative tendency - estimated in 14 days for the duration of the snow on the ground and even about 22 days as regards the days when the snow thickness is more than 30 cm. Moreover, choosing the stations located in the most important South Tyrol ski resorts, share was determined, the elevation at which the duration of the snow on the ground greater than 30 cm - being at least 100 days in a winter season. The calculus was finalized to the altitudinal quantification of the LAN. The analysis of the recent period 2005/2006 - 2015/2016 places this elevation at about 1745 m, with a trend increasing by 29 meters per year. Finally, to confirm these preliminary results, would be advisable to extend this simple methodology to other sectors of the mountain chain, to understand even if it is a signal at the regional scale rather than whole Alpine domain.

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