

UC Irvine

UC Irvine Previously Published Works

Title

Characterization of atmospheric total gaseous mercury at a remote high-elevation site (Col Margherita Observatory, 2543 m a.s.l.) in the Italian Alps

Permalink

<https://escholarship.org/uc/item/9pf4d0wg>

Authors

Vardè, Massimiliano

Barbante, Carlo

Barbaro, Elena

et al.

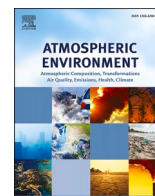
Publication Date

2022-02-01

DOI

10.1016/j.atmosenv.2021.118917

Peer reviewed



Characterization of atmospheric total gaseous mercury at a remote high-elevation site (Col Margherita Observatory, 2543 m a.s.l.) in the Italian Alps

Massimiliano Vardè^{a,b,c,*}, Carlo Barbante^{a,c}, Elena Barbaro^{a,c}, Francesca Becherini^{a,c}, Paolo Bonasoni^d, Maurizio Busetto^d, Francescopiero Calzolari^d, Giulio Cozzi^{a,c}, Paolo Cristofanelli^d, Federico Dallo^{c,f}, Fabrizio De Blasi^{a,c}, Matteo Feltracco^{c,a}, Jacopo Gabrieli^{a,c}, Andrea Gambaro^{c,a}, Niccolò Maffezzoli^{c,a}, Elisa Morabito^c, Davide Putero^e, Andrea Spolaor^{a,c}, Warren R.L. Cairns^{a,c}

^a Institute of Polar Sciences, National Research Council of Italy, (CNR – ISP), Via Torino 155, I-30172, Venice, Italy

^b Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, (UniFE – DipSCFA), Via L. Borsari 46, I-44121, Ferrara, Italy

^c Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, (UniVE – DAIS), Via Torino 155, I-30172, Venice, Italy

^d Institute of Atmospheric Sciences and Climate, National Research Council of Italy, (CNR – ISAC), Via P. Gobetti 101, I-40129, Bologna, Italy

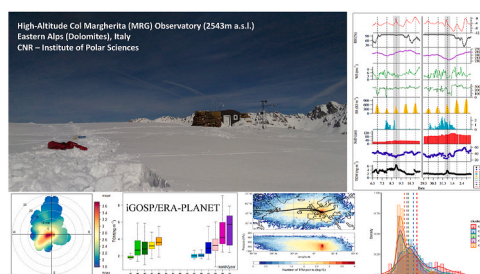
^e Institute of Atmospheric Sciences and Climate, National Research Council of Italy, (CNR – ISAC), Corso Fiume 4, I-10133, Turin, Italy

^f Center for the Built Environment, University of California, (UC Berkeley-CBE), 390 Wurster Hall, CA-94720, Berkeley, United States

HIGHLIGHTS

- A one-year record mean TGM concentration at the MRG was higher than other long-term values observed in remote mountain sites.
- TGM was characterized by high values in spring and summer and lower values in winter.
- A diel trend of TGM was observed, with low concentrations in the daytime and higher concentrations in the late evening.
- TGM levels were influenced by local meteorology, as well as regional and long-range transport of air masses.
- Analysis of specific atmospheric mercury elevated events (AMEEs) was performed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Mercury
Ozone
High-altitude station
Air masses trajectories

ABSTRACT

The Col Margherita (MRG) Observatory is a high-altitude background station located in the Eastern Italian Alps. Its elevation and distance from major anthropogenic and natural sources make it ideal for monitoring baseline mercury levels and investigating its geochemical cycles. In this work, total gaseous mercury (TGM), ozone (O₃) and meteorological variables were studied to investigate seasonal and diurnal variability of TGM measurements from March 2018 to May 2019. We found that the year-round mean TGM concentration was 1.8 times higher

* Corresponding author. Institute of Polar Sciences, National Research Council of Italy, (CNR – ISP), I-30172, Venice, Italy.

E-mail address: massimiliano.varde@cnr.it (M. Vardè).

Eastern Dolomites
Europe

than the annual atmospheric mercury measurements previously reported during the GMOS project at the same measurement site. The seasonal variation of TGM was characterized by high values in spring and summer and lower values in winter. A systematic diel pattern of TGM was obtained, with low concentrations during the daytime and higher concentrations in the late evening. Spatial patterns and temporal changes in TGM, back-trajectories (BTs) and planetary boundary layer (PBL) analysis showed that total gaseous mercury levels were influenced by local meteorology, as well as regional and long-range transport of air masses. The lowest TGM concentrations in winter are associated with high wind speeds, low boundary layer height and cleaner air masses originating from the Western sector. Conversely, the highest TGM concentrations in spring and summer were attributed to polluted air masses passing over North-eastern and Continental Europe and were probably favoured by the higher PBL height. During the snow cover season, investigation of TGM peak events also demonstrated the potential influence of re-emission processes of previously reactive mercury deposition over snow surfaces.

1. Introduction

High-elevation monitoring sites are crucial for studying environmental pollution and the impact of climate change on mountain glaciers and the ecosystems of remote and pristine mountainous areas (Beniston et al., 1997). The presence and variability of Hg and O₃, two harmful pollutants for both humans and ecosystems, have been widely investigated in both remote mountain sites and polar regions (Berg et al., 2013; Cole and Steffen, 2010; Ebinghaus et al., 2002; Fäin et al., 2009; Fu et al., 2010, 2016; Kang et al., 2019; Lu and Schroeder, 2004; Sprovieri et al., 2016; Steffen et al., 2015; Yin et al., 2017, 2018). Long-term monitoring of atmospheric mercury (Hg) at high mountain sites is one key to understanding the global cycling and fate of Hg, by decoupling global trends from local sources, since most anthropogenic Hg emissions occur at lower altitudes (Sprovieri et al., 2016). Most atmospheric Hg observations are of either gaseous elemental mercury (GEM) or total gaseous mercury (TGM). These are effectively operationally defined fractions depending on the instrumentation used. GEM which is Hg in its gaseous elemental state Hg⁰ makes up over 95% of the mercury in the atmosphere while the remaining fraction consists of a mixture of reactive/oxidized gaseous mercury (RGM or GOM) and particulate bound mercury (PBM) species (Lin et al., 2019; Munthe et al., 2001; Prete et al., 2018; Wängberg et al., 2007). In this paper we use TGM to denote GEM plus RGM or GOM as defined by previous authors (Ambrose et al., 2015; Gustin and Jaffe, 2010; Gustin et al., 2015; Lu et al., 2003).

The global atmospheric residence time of GEM is thought to be in the order of 0.5–2 years, whilst the latter two (GOM and PBM) remain for days or weeks, limiting their transport to a local or regional scale. A recent study by Horowitz et al. (2017) suggests that under certain conditions, the tropospheric lifetime of GEM can be as short as 2.7 months. Mercury observations at high altitude sites also help to reduce the gap between field measurements and model simulations, especially when combined with Hg studies over oceans (Mao et al., 2016) and aircraft-based measurements (Ebinghaus et al., 2007; Slemr et al., 2009, 2016). Regional and global networks of in-situ monitoring stations have been developed for the study of Hg (e.g., Canadian Atmospheric Mercury Network-CAMNet, American Atmospheric Mercury Network-AMNET, Global Mercury Observation System-GMOS, Asia Pacific Mercury Monitoring Network-APMMN), aimed at establishing long-term air quality and meteorological datasets (Blanchard et al., 2002; Gay et al., 2013; Kaiser et al., 2007; Kellerhals et al., 2003; Schultz et al., 2015; Sheu et al., 2019; Sprovieri et al., 2016; Temme et al., 2007; Tørseth et al., 2012). Limited accessibility to remote areas and logistical complexities however result in elevated maintenance and management costs for mountain sites, resulting in a lack of long-term data for analytes such as Hg (Mao et al., 2016) and persistent organic pollutants (POPs) (Loewen et al., 2005).

A coordinated Global Mercury Observation System (GMOS) (www.gmos.eu) was established during a five-year project (2010–2015) funded by the European Commission to create a global dataset of Hg background concentrations in ambient air and wet deposition, in the lower/upper troposphere and lower stratosphere, as well as in the marine environment (Sprovieri et al., 2016, 2017). It also aimed to provide

background levels for monitoring the progress in the implementation of the Minamata Convention (www.mercuryconvention.org). The text of the Minamata Convention was approved in 2013 and entered into force on August 16th 2017. The GMOS project coordinated Hg data collection and quality control using a real-time web-based QA/QC system. The system called GMOS-Data Quality Management (G-DQM), plugged into a cyber-infrastructure and deployed as a service, has been finalised to provide a high-quality dataset for Hg in air and precipitation. A Spatial Data Infrastructure was finally developed assuring a timely up to date sharing of information on Hg (D'Amore et al., 2015). The same kind of effort should be envisaged to establish a common procedure and instrumental method for the monitoring of other environmental parameters, i.e. for non-continuous measurements, in order to share robust and reliable datasets, to reduce uncertainties and increase measurement traceability. Col Margherita Observatory (MRG) was one of the 40 ground-based stations of the GMOS project and is now part of the Integrated Global Observing Systems for Persistent Pollutants (iGOSP) project, of the ERA-Planet Horizon 2020 Program. The MRG Observatory has also been recently included in the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) Programme as a regional station.

In Europe, major contributors to atmospheric Hg emissions are anthropogenic sources with 239.3 Mg y⁻¹ (Pacyna et al., 2006). Emissions of Hg from primary natural sources and re-emission processes (mainly Hg emissions from surface waters and volcanoes) were estimated as between 110 and 177 Mg y⁻¹ for the Mediterranean region and Continental Europe (referring to the EMEP domain), respectively (Pacyna et al., 2006; Pirrone et al., 2001; Travníkov and Iluyin, 2005). The Italian atmospheric emissions of Hg generated from major industrial/man-made sources, were published in the National Emission Inventory Report, that showed a reduction between 1990 and 2017 from 15.2 to 9.2 Mg y⁻¹. This trend is in accordance with what was previously reported for atmospheric Hg emissions in Europe (Pacyna et al., 2006). This slight decrease was obtained using the best available technologies to introduce control and abatement systems for several activities such as coal and oil combustion, processes in inorganic chemical industries (i.e., chlorine production), iron and steel production, coal industry, non-ferrous metal and non-metallic mineral sector, waste incineration, cement production, and geothermal production. For instance, part of the reduction in Hg emissions was due to the conversion of chlor-alkali production plants from the Hg cells to the membrane technology (Taurino et al., 2019) and through the use of abatement systems for Hg and hydrogen sulphide (H₂S) in geothermal power plants (Parisi et al., 2019).

In Italy natural sources of Hg include the mining districts of Mt. Amiata (Breder and Flucht, 1984; Cabassi et al., 2017; Ferrara et al., 1998; Vaselli et al., 2013), active volcanoes (e.g., Etna, Stromboli and Vulcano) (Bagnato et al., 2007; Ferrara and Maserti, 1990; Ferrara et al., 2000) and geothermal areas (e.g., Campi Flegrei) (Bagnato et al., 2009, 2014; Bagnoli and Gartner, 2018; Cabassi et al., 2017; Ferrara et al., 1994) that were not considered in the above-mentioned report. Although the estimated budget from these sources represents a small fraction of the annual global volcanic output, it is estimated that

emissions from Mt. Etna are the equivalent of about 5% of the Hg emitted in the Mediterranean basin from anthropogenic activities (Bagnato et al., 2007; Ferrara et al., 2000). Since Hg emission data are still incomplete, more effort should be taken to consolidate Hg emission assessments. In this respect, Hg measurements in the atmosphere, as well as in other environmental media, are crucial to improve our knowledge of the impact of Hg on contaminated and remote/rural sites. There is lack of long-term measurements of Hg in Italy, with only a few datasets at remote and/or rural sites available (Sprovieri et al., 2016), so it is particularly important to present and analyse our results of atmospheric monitoring of TGM at MRG from March 2018 to May 2019. To help explain the variability of TGM, other data recorded at MRG are considered and analysed in this work: near-surface ozone (O_3), snow depth and meteorological parameters. Tropospheric O_3 is recognised as a powerful greenhouse gas (UNEP and WMO, 2011) and acts as a powerful oxidizing agent and is able to determine the overall oxidative capacity of the troposphere, affecting the fate of other atmospheric compounds including TGM (Schultz et al., 2015). Measurements at high altitude sites of O_3 and its temporal variability can help in attributing the origin of air masses, especially in conjunction with other atmospheric tracers and transport models (e.g., Cristofanelli et al., 2016).

The main objectives of this study are to investigate (i) the seasonal and diurnal variations of TGM; (ii) the relationship between TGM and other variables (ozone and the main meteorological parameters); (iii) back-trajectories (BTs) and the atmospheric planetary boundary layer (PBL) changes; and (iv) the identification of potential sources of TGM in terms of local, regional and long-range transport.

2. Measurements and methods

2.1. Site description

The Col Margherita Observatory (46.36° N, 11.79° E, 2543 m a.s.l.) a GAW-WMO Regional Station (GAW ID: MRG) is located in the mountainous area of the Belluno Dolomites (UNESCO World Heritage site), between the Veneto and Trentino-Alto Adige regions, in North-eastern Italy. It is included in the ski area of the Passo San Pellegrino, in the municipality of Falcade. MRG is about 5 km from Falcade (Belluno) and 10 km from Moena (Trento), respectively (Fig. 1). These two towns, with a total of 4500 inhabitants contribute to a density population of less than 35 inhabitants km⁻² over the area, which can increase significantly in the summer and winter due to tourism.

MRG Observatory was established in October 2012 as a GMOS secondary site for background monitoring of TGM in air and Hg in precipitation (Cairns et al., 2019; Sprovieri et al., 2016, 2017; Vardè et al., 2019a; Vardè, 2021). It is located on the South-eastern side of the Alps, between the emission sources of the Po Valley basin, one of the most populated regions with the highest air pollution levels in Southern Europe (Bigi and Ghermandi, 2016; Diémoz et al., 2019), and the industrial areas of North-eastern Europe (Kaiser et al., 2007).

Several anthropogenic pollutants such as trace elements, ionic species, organic compounds (FASs, PBDEs and PAHs) and microplastics (MPs) have been found in the snow at the site. All of which were associated with emissions from the Po Valley basin (Barbante et al., 2004; Gabrieli et al., 2010, 2011; Kirchgörg et al., 2016; Parolini et al., 2021). At high-altitude environments, snow and rain act as scavengers of atmospheric pollutants and during the snowmelt season both snowmelt and rain are sources for the recharge of Alpine springwaters with different seasonal contributions depending on the altitude of the recharge areas (Lucianetti et al., 2020). The “altitude effect”, i.e. the isotopic signature of precipitation and natural waters (Clark and Fritz, 2013; Coplen, 1993), was recently observed for Hg concentrations in groundwaters, that showed a relationship with elevation of water sources (Vardè et al., 2019b).

There are no known significant local Hg sources such as cement plants, incinerators, industrial activity, or mining activities near the

summit or in the surrounding areas of MRG. The effects of tourism and artificial snow making in the winter are to date completely unknown and should be investigated. The nearest commercial and industrial areas are about 60 km from the site, where the main urban districts of the Adige Valley (North-east) and Belluno area (South-west) are located. At a distance of about 20 km from MRG there is the ex-mining district of Valle Imperina (pyrite) and in the surrounding area there are other mines (Vallalta and Transacqua), where mining activities closed permanently in the 1960s. In particular, Vallalta was well known for the extraction of cinnabar and native Hg (Wahsha et al., 2014).

According to the updated Köppen-Geiger classification map (Kottek et al., 2006), climate at MRG can be included in the “Polar” class, but it also shows continental features, due to the large seasonal temperature excursions (i.e., from −18 °C in January to 18 °C in July during the analysed period). It is characterized by temperate summers and cold winters, with abundant rainfall in summer, and snow during winter/early spring. In winter, Westerly winds are prevalent, while in other seasons the ESE direction becomes more frequent. The highest wind speed values, up to 20 m s⁻¹, are measured in winter and are associated with Northerly directions. Snow deposition usually begins in November/December and can occur throughout April/May with a lasting snow cover on the ground that generally disappears by late May. In winter, wind speeds are high enough for freshly fallen snow to become quickly remobilized, and accumulate in drifts even against the station.

Measurements of TGM were performed at MRG within the GMOS project (Sprovieri et al., 2016), where the site is quoted with the code CMA and a mean TGM concentration of 1.69 ± 0.29 ng m⁻³ was reported for 2014. Monitoring re-started again in March 2018 within the EU ERA-PANET iGOSP project (2017–2020).

2.2. Sampling methods and analysis

2.2.1. Atmospheric mercury measurements

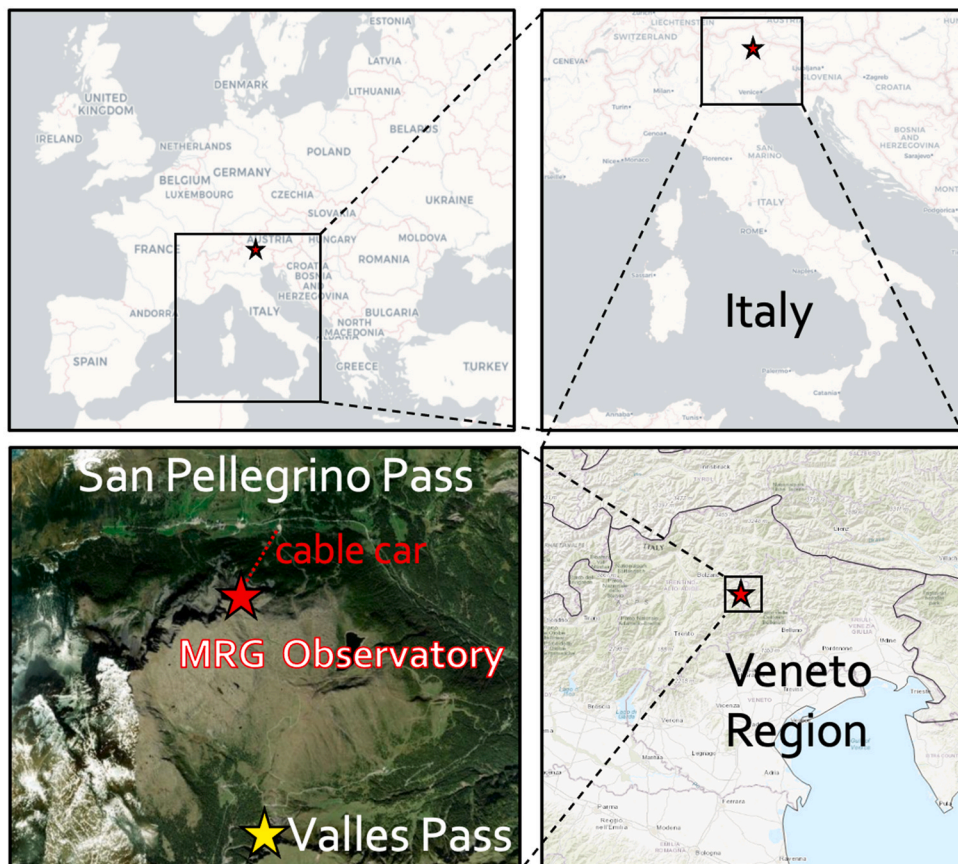
TGM was measured using a Tekran model 2537B instrument (Tekran Instruments Corp., Toronto, Ontario, Canada) following the GMOS project protocols (GMOS, 2011). The Hg analyser was installed with the sample inlet probe on top of the shelter, 4 m above the ground. A cylindrical frame in Teflon was mounted to protect the inlet from rain and snow. Due to the high elevation of the site and the consequently low atmospheric pressure, an open-phase filter holder with 47 mm Teflon filters (pore size 0.45 µm) instead of the 0.2 µm filter as recommended by the GMOS SOP, was used to remove particulate matter. Another 0.2 µm filter mounted on the instrument before the sample in port, prevented PBM from reaching the gold preconcentration cartridges, ensuring that we sampled only TGM as defined in the introduction. It is also possible that a small fraction of GOM might be lost in the sampling line. The cabin, where the analyser was housed, is heated in the winter and ventilated with outside air during summer. The median temperature inside the MRG Observatory was 17.8 °C.

TGM (where [TGM] = [GEM] + [GOM]) measurements were performed by the Hg analyser using dual gold Hg traps placed in series, with thermal desorption of the Hg and its detection atomic fluorescence spectrometry at 253.7 nm (Munthe et al., 2001; Tekran, 2012). Ultra-high purity (grade 5.0) argon (Società Italiana Acetilene e Derivati, SIAD, Italy) was used as carrier gas. A sampling flow rate of 0.5 L min⁻¹ (at standard temperature and pressure) and a 10-min sampling interval were selected, to ensure a stable sampling volume and to avoid straining the sampling pump due to the low atmospheric pressure (MRG is at an altitude higher than that recommended by Tekran specifications (Tekran, 2012)). The time reference system for the dataset is UTC (Coordinated Universal Time), the same as used in all GMOS reports and publications.

2.2.2. Quality Assurance/Quality Control (QA/QC)

Automated calibration of the 2537B analyser, using the internal permeation source, has been set every 72 h, performing separately two-

(a)



(b)



Fig. 1. Geographical location (a) and picture (b) of the Col Margherita Observatory in the Eastern Alps, Italy.

point calibrations (zero and span) for each gold cartridge. To check the automated calibrations, manual injections as standard additions of known amounts of Hg into the sample stream have been performed twice a year on site using the Tekran Model 2505 external calibration unit, during yearly routine maintenance cycles.

Automated calibrations and manual injections showed a relative percent difference less than 8%. The difference in TGM concentrations between the two gold cartridges was kept < 10% by changing the sampling cartridges with new or cleaned ones when the difference became too high. The response factor values of the Tekran 2537B were on average about 6×10^6 (units). The 2537B analyser performance was evaluated by comparing the two gold cartridges response factors from the internal calibrations with previous responses. The detector gain and lamp current were adjusted to maintain the response factor variation below 5%.

All GMOS technical recommendations regarding TGM/GEM measurements were followed by site operators during periodic MRG site visits. Results for TGM were reported as the average mass of TGM per volume of air at 273.15 K and 101.325 kPa (0 °C and 1 atm), measured over a specified time interval (10 min). TGM concentrations are reported as nanograms per cubic meter (ng m^{-3}). The detection limit (LOD) of the 2537B is reported as < 0.1 ng m^{-3} based on 7.5 L samples (Tekran, 2012).

The Hg dataset of MRG has been stored in the Data Storage Layer of the Cyber Infrastructure created for GMOS to provide all users with a common QA/QC procedure. Data management through the Spatial Data Infrastructure (SDI) using the GMOS-Data Quality Management (G-DQM) system, generated automated flags so the operator knew when specific maintenance was scheduled or required together with an automated process for data set treatment.

2.2.3. Near-surface ozone measurements

An O₃ analyser was installed at MRG on June 17th 2017. Surface O₃ measurements were carried out using a Thermo 49c UV-absorption photometric analyser (Thermo Environmental Instruments Inc., USA), following the EC reference method (EN 14625:2012). The limit of detection (LOD) was 1.0 ± 1.0 ppbv (Thermo Environmental Instruments Inc, 2000). The metrological traceability of O₃ measurements to the WMO reference scale is assured by comparison to a laboratory calibrator (Thermo Tei 49i-PS, Thermo Scientific Inc., USA) at the Institute of Atmospheric Science and Climate-National Research Council of Italy (CNR-ISAC) which, in turn, is routinely certified against the Standard Reference Photometer SRP#15 maintained at the WMO/GAW “World Calibration Centre for surface O₃, CO₂, CH₄ and CO” (WCC-Empa Standard Reference Photometer SRP#15). Comparison against the CNR-ISAC laboratory standard is performed roughly every 2 years or after the occurrence of major instrumental failures. These comparison exercises allow us to estimate that the total combined instrumental uncertainty of the O₃ analyser is less than 1.5 ppb within the 1–100 ppb range, according to the uncertainty methodology calculation provided by Klausen et al. (2003). This temporal frequency is not optimal (a calibration every 2–3 months is recommended by WMO World Meteorological Organization (2013)), but represents the best compromise between metrological requirements and difficulty in accessing the measurement site. Zero and span checks were executed on a daily basis. The zero air was generated using an activated charcoal cartridge, while an internal UV source was used to generate a span level of approximately 100 ppb. These checks regularly test the calibration and can help identify possible instrumental problems.

The execution of quality control/quality check (QA/QC) actions (including the inspection of daily data products, the analysis of instrumental internal parameters or data outliers) are supported by the use of a system based on a suite of automatic processing routines which also produce data files following the WMO/GAW common data model (Naitza et al., 2020). Public access to the MRG O₃ data is available at <https://nextdata.bo.isac.cnr.it>.

2.2.4. Meteorological parameters

Meteorological sensors are installed on a compact aluminium tower at 3 m above the ground (ATW3, Campbell Scientific), close to the observatory. The measured parameters were: air temperature (T) and relative humidity (RH), accuracy ± 0.1 °C and $\pm 2\%$, respectively (CS215, Campbell Scientific); atmospheric pressure (P), accuracy ± 0.3 hPa at +20 °C (PTB110 barometer, Vaisala); snow depth (SnD), accuracy ± 1 cm (Sonic Ranging Sensor SR50A, Campbell Scientific). The sampling time was every 5 min, but hourly averages were used for data analysis. Data of other meteorological parameters have been extracted from two weather stations of the Regional Agency for the Protection and Prevention of the Environment of the Veneto Region (ARPAV) located about 3 km away from MRG: wind direction (WD), accuracy $\pm 1^\circ$ (t033 TDV, SIAP + MICROS), wind speed (WS), accuracy 0.15 m s^{-1} (t031 TVV, SIAP + MICROS), and global solar radiation (SR), accuracy $\pm 10 \text{ W m}^{-2}$ (t055 TPiR, SIAP + MICROS) from Cima Pradazzo (46.35° N, 11.81° E, 2195 m a.s.l.), while precipitation (R), accuracy 0.1 mm (FAK015AA, MTX s.r.l.) from Passo Valles (46.33° N, 11.80° E, 2032 m a.s.l.).

2.2.5. Backward trajectory analysis and boundary layer height

To determine the synoptic origin of the air masses reaching the measurement site, 120-h 3D back-trajectories (BTs) were calculated every 6 h (00, 06, 12, and 18 UTC) with the Lagrangian Analysis Tool LAGRANTO (Sprenger and Wernli, 2015; Wernli and Davies, 1997). The model calculations were based on the ERA5 reanalysis dataset of the European Centre for Medium-Range Weather Forecasts (ECMWF, see Hersbach et al., 2020). For each set, 7 BTs were computed, with starting points shifted by $\pm 1^\circ$ in latitude/longitude and in a vertical range of ± 50 hPa with respect to the station location, to partially compensate for the absence of subgrid scale processes in LAGRANTO. The temporal resolution for the back-trajectories is one point every hour.

To identify the main flows on a synoptic-scale occurring at the measurement site, a cluster analysis was performed (see Dorling et al., 1992). The standard Euclidean distance between each pair of trajectories was chosen to compute the different clusters. Only those trajectories with endpoints of 750 hPa were selected as being representative of the exact location of the station (results including trajectories at 700 and 800 hPa showed similar patterns).

The PBL height for MRG was estimated by using the ERA5 reanalysis dataset (Hersbach et al., 2020). ERA5 provides data with a spatial resolution of $0.25^\circ \times 0.25^\circ$, and with a temporal resolution of 1 h. The calculations for estimating the PBL height are based on the bulk Richardson number (a measure of atmospheric conditions). It is well known that derived PBL heights can suffer from uncertainties in mountainous regions; nevertheless, the closest ERA5 PBL height value to MRG was used, in the absence of any other direct or indirect measurements.

3. Results and discussion

3.1. Temporal trends of TGM

3.1.1. Annual and seasonal patterns of TGM

TGM measurements were carried out with data coverage from March 2018 to May 2019, with a gap in autumn 2018, when the Hg analyser was not operational. Overall, measurements at MRG in the period 2018–2019 had some programmed interruptions due to routine equipment maintenance, but there are other gaps, particularly in the summer-autumn rainy season, due to unstable power supply issues caused by thunderstorms that frequently occur in the summer. Despite these missing measurements, a total of n. 29050 data points was collected (Fig. 2a).

From March 2018 to May 2019 the mean concentration of TGM was $3.14 \pm 1.29 \text{ ng m}^{-3}$ (mean $\pm$ standard deviation (SD)), which is 1.8 times higher than the previous long-term averaged value (1.73 ± 0.34

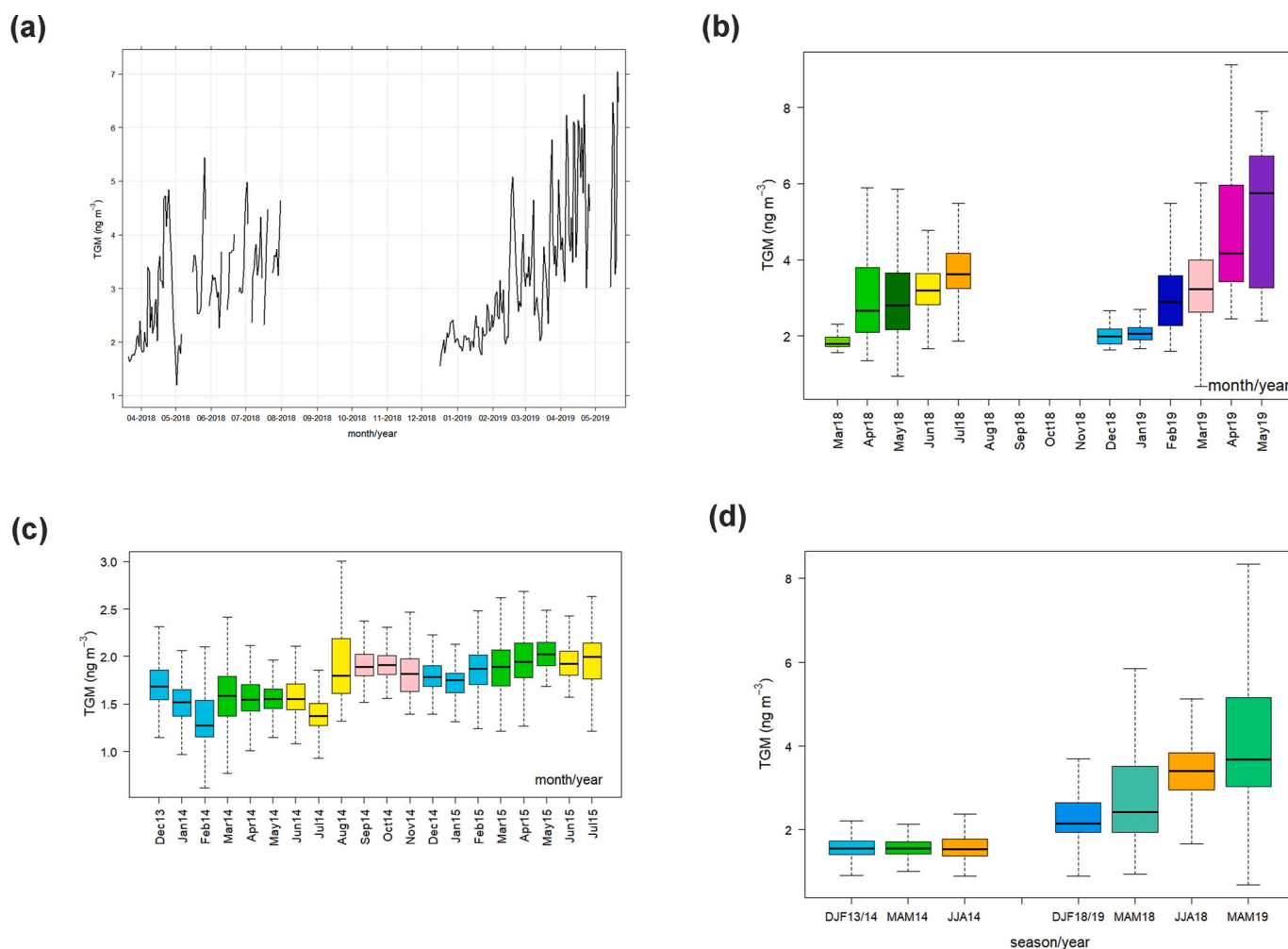


Fig. 2. Temporal trend of daily total gaseous mercury (TGM) concentration (ng m^{-3}) at MRG (a) from March 2018 to May 2019; (b) monthly (2018–2019) box and whisker plots; (c) monthly box and whisker plots from December 2013 to June 2015; (d) seasonal TGM means for 2013–2014 and 2018–2019 (seasons available for comparison). Seasons are defined as 3-month periods: winter (DJF: December, January, February), spring (MAM: March, April, May), summer (JJA: June, July, August) and autumn (SON: September, October, November).

ng m^{-3}) calculated from measurements performed between December 2013 to July 2015 (Table ESM1) (ESM, [Electronic Supplementary Material](#)). This value, regardless of the year reported, is the highest amongst all the TGM values measured in other mountainous, continental and coastal sites at remote and rural locations in Europe (Denzler et al., 2017; Kentisbeer et al., 2015; Kock et al., 2005; Lee et al., 1998; Slemr and Scheel, 1998; Wängberg et al., 2016), with a few exceptions related to high TGM levels up to 8.2 ng m^{-3} that were observed during short field campaigns (Halle/Leipzig/Bitterfeld and Langenbrügge) at low altitudes in North-western and Central Europe (Ebinghaus et al., 1995). In addition, only a few measurements carried out at elevated remote and rural sites in China showed higher TGM concentrations than those at MRG (Fu et al., 2008, 2009; Chen et al., 2013, 2016; Yu et al., 2015; Wan et al., 2009). The mean concentrations of atmospheric gaseous mercury (TGM and GEM) observed in elevated or mountainous sites around the world are reported in Table ESM1. Levels similar to and/or higher to those found at MRG have been reported by the Regional Agency for Environmental Protection (ARPA) of the Piedmont Region, who report an annual mean GEM value of 3 ng m^{-3} for the city of Turin in 2018 and 2019 with values up to 4 ng m^{-3} (ARPA Piemonte, 2018, 2019). The median value of TGM at MRG in the 2018–2019 period was 2.91 ng m^{-3} , 1.22 ng m^{-3} higher than the 2014 median value at MRG (Sprovieri et al., 2016) and 1.61 ng m^{-3} higher than the 2011–2012 median value recorded in the Swiss Alps at Jungfraujoch (3580 m) (Denzler et al.,

2017).

We acknowledge that the TGM concentrations reported in this work are well above those reported in previous studies. Our instrument has been recalibrated autonomously every 72 h (via an internal permeation source that releases a constant amount of Hg) and manually every 6 months. The difference between the automated and manual calibrations were less than 5% (Sect. 2.2.2). The lamp brilliance and detector gain were also adjusted both automatically and manually to maintain instrumental sensitivity. No systematic sources of uncertainty have been found in our measurement routine and we therefore consider the reported data robust (see details in Sect. 2.2.2). We have attempted to identify a combination of different climatic and meteorological conditions as the source of discrepancy between the TGM concentrations reported here and in previous studies and we will continue to investigate possible causes for our results.

The descriptive statistics for TGM and the main ancillary variables measured at MRG are summarized respectively in Table ESM2 and Table ESM3. Monthly average TGM concentrations ranged from a minimum of 1.89 ng m^{-3} (in March and December 2018) to a maximum of 5.19 ng m^{-3} (May 2019) (Table ESM2). A clear increasing tendency was registered from March to July 2018, while a larger increase was observed in 2019 from January to May (Table ESM2 and Fig. 2a and b). Fig. 2c shows the monthly means during the previous, longer TGM measurement period from December 2013 to July 2015. In this dataset, the lowest

monthly TGM mean value was registered in February 2014, and the highest in May 2015. Overall, at MRG, the annual TGM cycle is characterized by a seasonal increase from winter to spring/summer.

Our dataset also has a very high inter-annual variability in the spring, the differences between the 2019 and 2018 mean TGM concentrations in March, April and May were 1.52 ng m^{-3} , 1.70 ng m^{-3} and 2.17 ng m^{-3} respectively. April and May of both years were also characterized by a large variability, as clearly indicated by the high SD values (Table ESM2). Slemr (1996) and Slemr and Scheel (1998) reported that high SDs of monthly mean TGM values at the Wank mountain site in Southern Germany were related to the arrival of polluted air masses during these months. In 2018, when 3 out of 4 seasons are available, TGM concentrations at MRG show a pronounced seasonality (Fig. 2d), with the highest concentration measured in summer ($3.45 \pm 0.74 \text{ ng m}^{-3}$) and the lowest in winter between 2018 and 2019 ($2.41 \pm 0.81 \text{ ng m}^{-3}$) (Table ESM2). Unfortunately, autumn 2018 is missing, so a whole yearly trend cannot be completed. A surprisingly high increase in mean TGM levels was registered between spring 2018 and spring 2019, with an increase from $2.79 \pm 1.06 \text{ ng m}^{-3}$ to $4.13 \pm 1.54 \text{ ng m}^{-3}$ (Table ESM2). During the GMOS monitoring period, the seasonal variation of TGM over 2014 was much lower, and increased in the order of: winter 2013–2014 ($1.54 \pm 0.37 \text{ ng m}^{-3}$), spring ($1.58 \pm 0.26 \text{ ng m}^{-3}$), summer ($1.65 \pm 0.42 \text{ ng m}^{-3}$) and autumn ($1.91 \pm 0.19 \text{ ng m}^{-3}$). This trend was confirmed during the following year, with the mean TGM concentration in winter 2014–2015 resulting slightly lower ($1.83 \pm 0.32 \text{ ng m}^{-3}$) than spring ($1.93 \pm 0.26 \text{ ng m}^{-3}$) and summer ($1.95 \pm 0.26 \text{ ng m}^{-3}$) (Fig. 2d).

This seasonal trend has already been discussed in several papers. Maxima in summer and minima in winter have been observed in remote locations in both the Northern and Southern Hemispheres, including at high-elevation sites (Karthik et al., 2017; Karuppasamy et al., 2020; Yin et al., 2018) and baseline monitoring stations (Slemr et al., 2008). Summer peaks in atmospheric Hg level have also been observed in the Arctic (Fisher et al., 2012; Schroeder et al., 1998; Steffen et al., 2015) with minima occurring in the spring during atmospheric Hg depletion events (AMDEs) that occur sometimes concurrently with ozone depletion events (ODEs) (Angot et al., 2016; Dommergue et al., 2010; Lindberg et al., 2001; Skov et al., 2004). Maxima in atmospheric Hg concentrations in the upper troposphere were associated with enhanced convective activity in the warm seasons during measurements onboard the CARIBIC (Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrumented Container) flights. These measurements were taken on passenger aircraft during flights over Europe. As described by Slemr et al. (2009) a noticeable seasonal minimum in TGM concentrations was observed between December–April.

Ozone seasonality at MRG is similar to that of TGM during 2018. O_3 showed a clear seasonal variability with lowest monthly mean values in December ($35.5 \text{ nmol mol}^{-1}$) and the highest in July ($49.6 \text{ nmol mol}^{-1}$) (Fig. 3). This seasonal cycle nicely fits with the typical seasonal variability affecting near-surface O_3 at other high-altitude sites in alpine regions, where a winter minima and broad spring-summer maxima are reported (Cristofanelli et al., 2015). This summer peak is related to an increase in the photochemical production of O_3 in the lower troposphere, coupled with more efficient vertical transport of polluted air masses rich in reactive photochemical precursors (e.g. CO, NO_x, VOCs) (Crutzen, 1970; Kaiser et al., 2007; Reiter, 1990). Enhanced photochemical and oxidative atmospheric processes have been documented at MRG during the summer (Barbaro et al., 2020). The occurrence of dicarboxylic acids and two photo-oxidation products of α -pinene was probably due to the presence of oxidants such as hydroxyl radicals (OH) and ozone, both of which are considered in modeling studies of Hg as key oxidation pathways in the free troposphere (Travnikov et al., 2017).

Since our TGM dataset does not satisfy one-way ANOVA assumptions, a non-parametric Kruskal-Wallis (KW) test was applied to the hourly data to calculate the 95% confidence limits. It confirmed the robustness of the differences between the available seasonal data (p-value < 0.001). As the KW test indicated seasonal differences do exist,

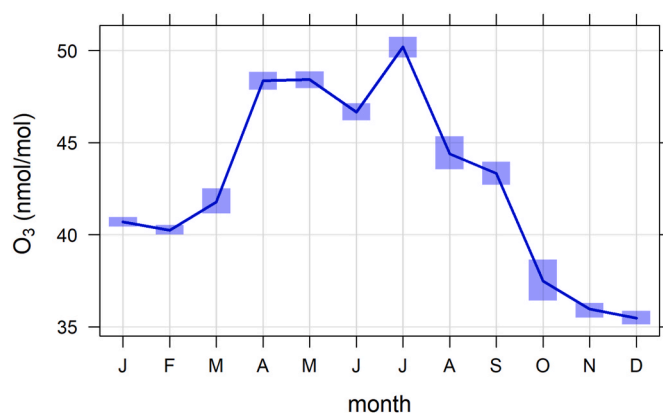


Fig. 3. Average monthly variations of O_3 at MRG: the vertical bars represent the 95% confidence interval.

but could not be more specific, several post-hoc tests (Dunn, Conover, Nemenyi, and pairwise comparison) were performed and differences were found between all seasons (p-value < 0.001).

The hourly averaged TGM concentrations ranged between 0.69 and 9.12 ng m^{-3} over the whole measurement period. They showed a bimodal distribution, with mode 1 around 2.0 ng m^{-3} and mode 2 between 3.0 and 4.0 ng m^{-3} (Fig. ESM1a). From a seasonal perspective, mode 1 is associated with the values from spring 2018 and winter 2018–2019, while mode 2 is related to the TGM concentrations in summer 2018 and spring 2019 (Fig. ESM1b). Differences in TGM seasonal frequency distributions have also been observed at other sites (Slemr and Scheel, 1998; Wan et al., 2009). In contrast with TGM levels at MRG, other authors (Sheu et al., 2010) found higher GEM levels in winter/autumn with winter/spring enhancements in Hg concentrations registered at several locations (Kim et al., 2005). This seasonal pattern of atmospheric Hg was explained by lower PBL heights, low oxidation rates and increased anthropogenic Hg emissions during winter. These effects were also related to local meteorological differences between the cold and warm seasons.

A potential single local source for Hg emissions at MRG could have been the intense local forest fire on the 24th of October 2018 followed by the Mediterranean storm “Vaia”. This storm with heavy precipitation and extremely intense wind gusts knocked down trees over a large area (650 – 900 ha) of the Agordina valley. The fire was only 10 km away from the MRG site (ARPAV, 2018; Davolio et al., 2020) and the storm probably remobilized the ashes into the local atmosphere. From the Sentinel 2 satellite images (Fig. ESM2a) and associated Normalised Difference Vegetation Index (NDVI), we estimate that the burned area was about 4.9 km^2 (Fig. ESM2b,c). Hg stored in forest vegetation and soil can be released during biomass burning in the smoke and/or ash as both gaseous and particulate species (Gustin et al., 2008; Witt et al., 2009). The Hg that was liberated into the atmosphere could have precipitated to the Earth’s surface via dry and wet deposition processes, preserved in the soil, and then covered by snowfall (ARPAV, 2018; Witt et al., 2009). Aerosol from biomass burning has been detected at MRG through the quantification of organic tracers (anhydrosugars and phenolic compounds) in PM₁₀ samples from the spring/summer sampling campaign (Barbaro et al., 2020). Therefore, Hg chemical analyses on both bulk deposition and surface snow samples could provide important supporting information on the effects of these fires at MRG.

3.1.2. Diel trends of TGM

Daily variations of TGM systematically show a daily maximum in the early evening followed by a decrease to the daily minimum in the morning. Values then increase again to the maximum in the second half of the day (Fig. 4). The timing of the maximum and minimum values depends on the season, during summer the min occurs at 12:00 and the

max at 22:00 UTC. During winter the min occurs at 7:00 and the max at 14:00 UTC. Overall, the TGM hourly average concentrations are lowest in winter and highest in the summer. The amplitude of the TGM daily changes is larger in summer (0.70 ng m^{-3}) than in winter (0.19 ng m^{-3}) (Fig. 4a). A similar diurnal pattern was observed during 2014 despite lower amplitude and concentration levels (Fig. 4b).

A previous study at a lower altitude site (1509 m a.s.l.) (Stamenkovic et al., 2007), found higher TGM concentrations during the night due to increased PBL stability that trapped atmospheric Hg. This should be the case for MRG, which is located on a mountain top. However, night-time air masses may contain residual Hg remaining from daytime upward transport of air-masses from the regional boundary layer (Weiss-Penzias et al., 2006). Summer maxima have been observed by other authors (Kellerhals et al., 2003; Stamenkovic et al., 2007). Spring 2019 was an exception to this, as TGM daily variations displayed a trimodal trend (Fig. ESM3).

At MRG in summer and spring, temperature and solar radiation show opposite daily trends to TGM (Fig. ESM4a,b), while in winter the TGM maximum is more in line with T and SR (Fig. ESM4c). As mentioned previously, Hg atmospheric dynamics can be influenced by several seasonal and daily factors (Kellerhals et al., 2003; Lan et al., 2012; Stamenkovic et al., 2007). Daytime atmospheric Hg concentrations (TGM or GEM) are generally lower than night-time values, and winter values are lower than summer values (Lan et al., 2012; Lee et al., 1998).

At MRG, the snow depth was almost constant throughout the day when snow cover was present. In spring, before melting of the seasonal snow cover, atmospheric Hg accumulates in the snowpack as Hg^{II} as it is scavenged from the air during the snow making process (Lalonde et al., 2002). This Hg is then released as elemental Hg into the interstitial air and from the snow surface (Faïn et al., 2007). Hg re-emission is well correlated with solar irradiation indicating photochemical processes at work (Spolaor et al., 2019), and our results support this observation. Faïn et al. (2013) found that the presence of liquid water enhanced GEM production, and melt waters were found to contain up to 72 ng L^{-1} of Hg. Photochemical production of GEM in the snowpack can lead to levels in the surface interstitial air of up to 8 ng m^{-3} . Under low wind conditions, GEM levels can remain high even during the night, suggesting a weak production mechanism even in the absence of sunlight. This diurnal GEM production is strongest after fresh snowfall, which replenishes the surface with reducible Hg. Lalonde et al. (2002) found that this can occur even under cloudy conditions, so is probably induced by UV radiation. This suggests that photochemical GEM production is not limited by visible radiation.

In summer, the TGM lowest concentrations were reached when solar radiation and air temperature were at their maxima, while the highest values were measured during the dark hours before sunrise. This behaviour has been observed in different locations in mountainous areas (Lin et al., 2019) as well as urban sites (Prete et al., 2018). Other studies have described a greater diurnal variability with results that contrast with our own, that are characterized by daily minima before sunrise and maxima near solar noon. This again occurred especially in the summer, and may have been possible due to other factors such as greater insolation and/or higher temperatures (Kellerhals et al., 2003). Carpi and Lindberg (1997) and Scholtz et al. (2003) investigated the effects of solar radiation and temperature on atmospheric Hg concentration, and its diurnal variability. Light, soil temperature and ozone all resulted as key factors in Hg evasion from the Earth's surface (Engle et al., 2005; Moore and Carpi, 2005; Poissant and Casimir, 1998; Xin and Gustin, 2007), and we intend to follow up this finding in future studies to help explain our results.

3.1.3. Influence of daily valley wind system on TGM measurements

To investigate the effect of thermal mountain winds on the TGM measurements, we analysed the diurnal variability of specific humidity (SH) and wind speed (Fig. 5c). Specific humidity is a tracer widely used to diagnose vertical transport of air masses from the PBL to mountain

sites (e.g., Cooper et al., 2020; McClure et al., 2016), while wind speed can show the occurrence of upslope and downslope mountain winds (e.g., Weiss-Penzias et al., 2015). No clear diurnal variations of wind speed have been observed, while SH shows a diurnal variability with higher values during the daytime especially in summer and autumn (Fig. 5c), which is virtually absent during the winter. This pattern is similar to what was observed at Mt. Bachelor (43.98° N , 121.69° E , 2763 m a.s.l. , Oregon, US; McClure et al., 2016), suggesting a possible (but limited) impact of vertical thermal air mass transport during daytime (maximized in summer and minimized in winter).

This, together with meteorological variables, and the inspection of O_3 results can be used to understand which processes are able to affect TGM since their values follow the same general trends (Fig. 5a). Both TGM and O_3 registered lower values in the winter with small variations over 24 h. Instead, in spring and summer the amplitude of their daily cycle is much higher, with the lowest values during the daytime when solar radiation (Fig. 5b) and temperature reached their maxima. For O_3 , this “reversed” diurnal variation is typically caused by valley winds (e.g., Weiss-Penzias et al., 2015) and is further indicative of the vertical transport of air-masses still poor in O_3 from the PBL. O_3 depletion can also be caused by dry deposition processes or uptake of ozone by vegetation growing on the mountain slopes during the central part of the day. Other possible removal processes that should be considered are removal via aqueous-phase chemistry in fog droplets (Ou Yang et al., 2012) or reaction with locally produced nitrogen oxides (i.e., emitted by soil) (see Crowley et al., 2010; Wang et al., 2006; Warneck, 1999). During the night-time, higher O_3 values indicate the impact of the arrival of air masses from the free troposphere and/or with regional baseline conditions (see e.g., Cooper et al., 2020), which is consistent with the converse behaviour of SH (Fig. 5c). It is thus quite conceivable that the TGM daily variability at MRG is affected by the same transport processes.

3.1.4. Planet boundary layer analysis

We analysed the PBL height derived from ERA5 to specifically evaluate the effect of diurnal and seasonal variability of the regional PBL height on atmospheric observations at MRG. Differences in TGM concentration levels on a seasonal and diurnal basis could be partially driven by the evolution of the PBL height. The height of the PBL reached its highest levels in summer 2018, followed by spring 2018 and 2019 (Fig. 6) which were both very similar. The lowest PBL height was observed in winter. As no marked difference in PBL height between spring 2018 and 2019 was found, this variable cannot explain the difference in the mean concentrations of TGM (Fig. 6) observed in the spring of those two years. However, the low PBL height in winter easily explains why the lowest TGM concentrations occur then.

As expected, the atmospheric mixing height showed a diurnal profile in every season, reaching its maximum at around midday (ranging from $> 500 \text{ m a.g.l.}$ during the winter up to 1500 m a.g.l. during summer) and the minimum levels at night-time, resulting in the transition from boundary layer to free tropospheric air at MRG. So, we may argue that during spring and summer, there is a potential contribution from anthropogenic and natural sources caused by transport of air masses from the PBL to MRG as observed by Obrist et al. (2008). This is supported by data from the ARPA of Piedmont that show mean GEM levels of 3 ng m^{-3} in spring 2018 in the city of Turin (at the Western side of the Po Valley), and levels up to 4 ng m^{-3} in spring 2019 (ARPA Piemonte, 2018, 2019). Changes in PBL height and contributions from regional point sources, together with local meteorological, are considered the main factors affecting the diurnal Hg patterns.

These patterns could be augmented by legacy mercury emissions by volatilization of previously deposited Hg (Faïn et al., 2009; Prete et al., 2018) from locally contaminated sources. Emissions from vegetation and water bodies as well as photochemical reactions are possible reasons for strong diurnal variations in TGM (Kellerhals et al., 2003). Col Margherita is almost devoid of vegetation and has sparse soil cover. It is

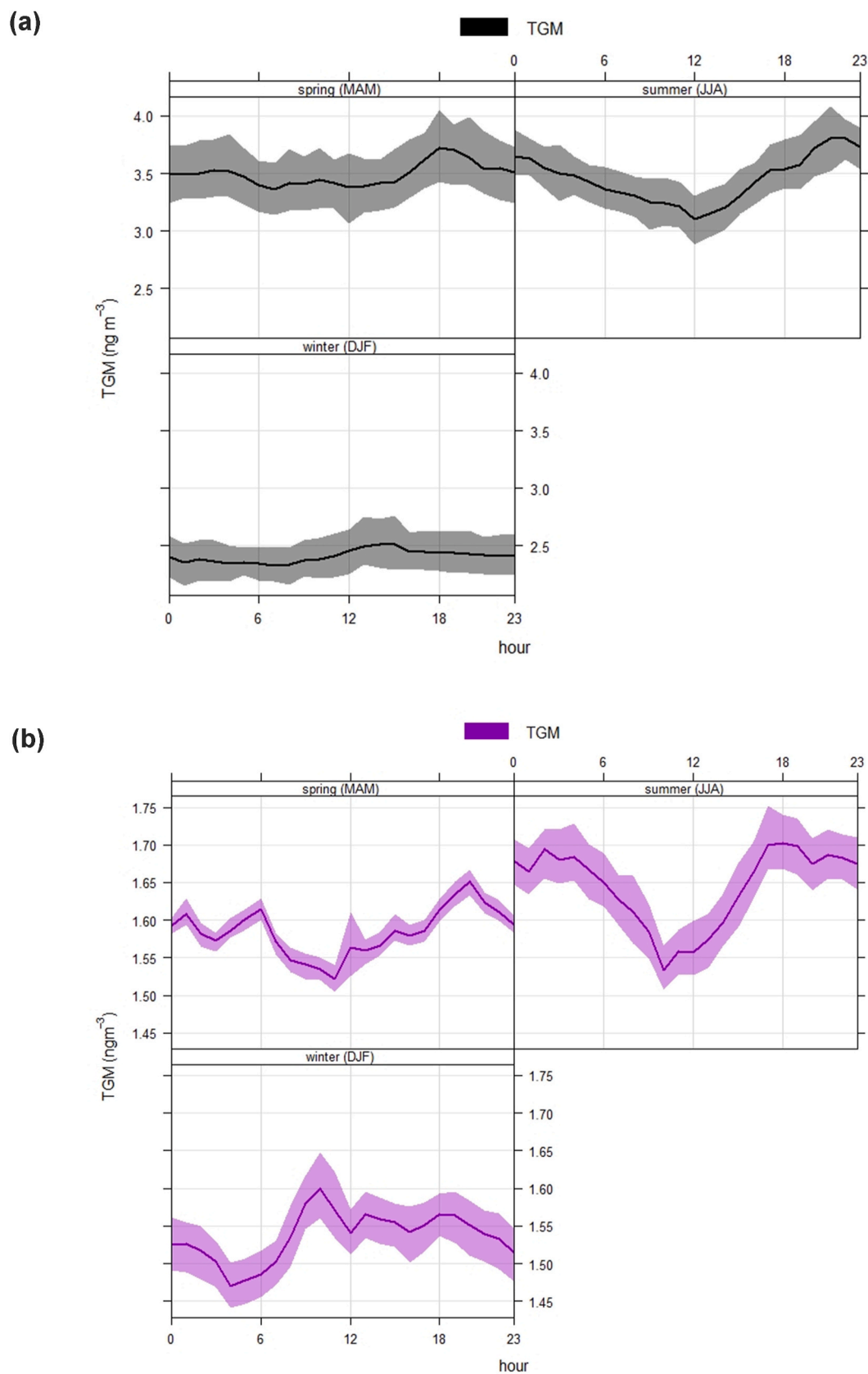


Fig. 4. Time variation of average hourly TGM concentrations in the different seasons (a) in 2018 and (b) in 2014 at MRG. The 95% confidence level is shown by grey and purple shading, respectively.

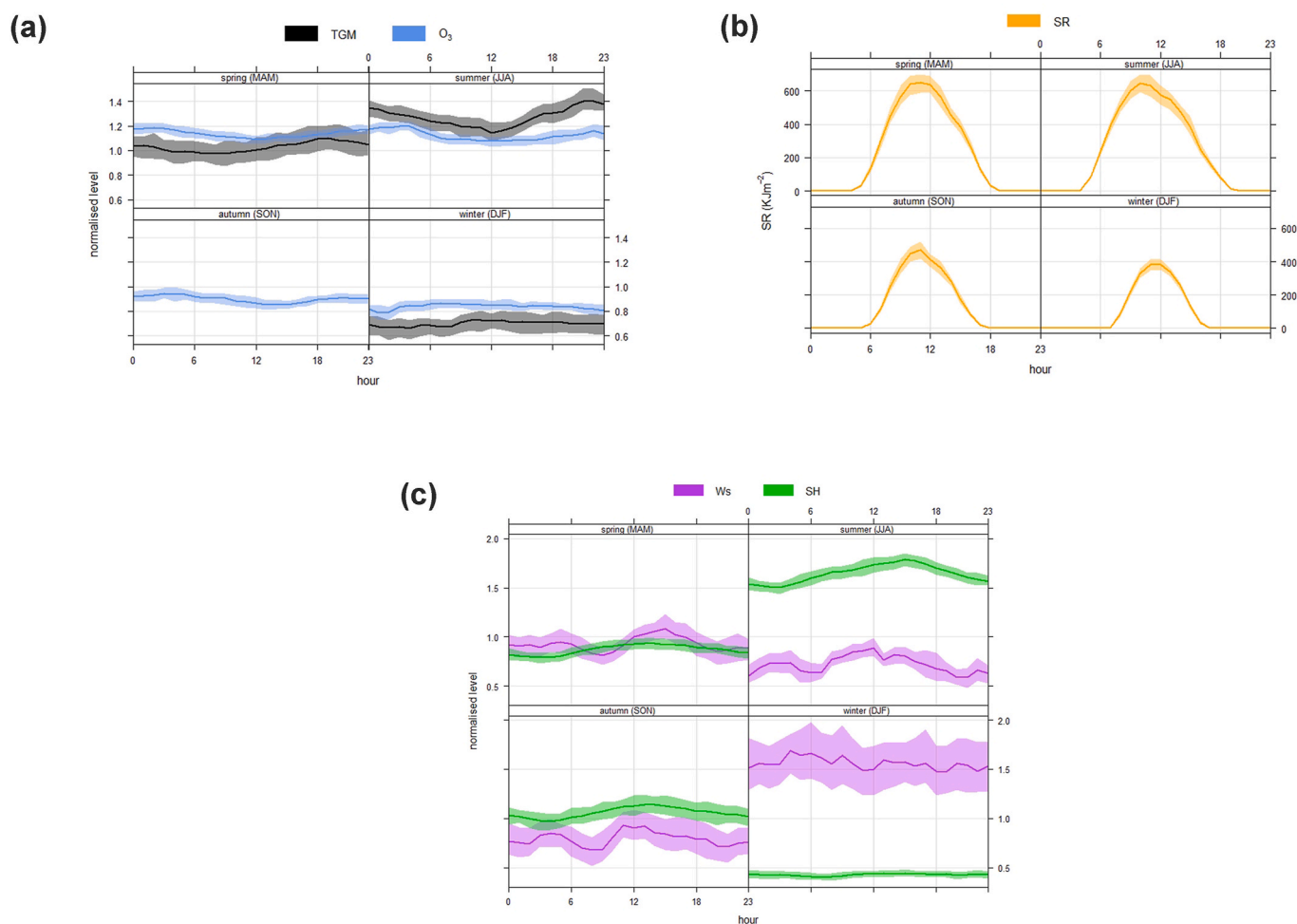


Fig. 5. (a) Diurnal variation of TGM (black line) and O₃ (blue line). The variables are normalised, i.e. they are divided by their mean values, to ease comparison of the shape of the diurnal trends for variables that are on different scales; for the different seasons in 2018 (b) solar radiation (orange line) together with (c) normalised wind speed and specific humidity (purple and green line, respectively). Note that the TGM values for autumn 2018 are missing (due to instrumental problems). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

however close to several artificial and natural lakes that require further investigation.

3.1.5. Influence of synoptic-scale air mass transport

The different seasonal levels of TGM can possibly be explained by analysing the path of the atmospheric back-trajectories as well as the relationship between TGM and other ancillary parameters along with potential re-emission of gaseous Hg from Earth's surfaces (i.e., snow and soil) (Faïn et al., 2007; Gustin et al., 2006). The following sections will investigate these possibilities.

Fig. 7a shows the density map for the back-trajectories originating at MRG over the whole study period, with the mean trajectories for each cluster superimposed (see Sect. 2.2.5) as black line. Cluster 1 accounted for 15.5% of the BTs and is characterized by air masses originating in Eastern Europe, to the East of the measurement site. Cluster 2 was the most dominant (35.7%) with trajectories mainly from continental Europe. These air masses were also at relatively low travel altitudes, compared to the others. Clusters 3, 4, and 5, all represented different types of transport from the West. While cluster 3 showed the second highest occurrence (24.4%) and still had some "continental" characteristics, clusters 4 and 5 occurred less frequently (17.7% and 6.7%, respectively), and were indicative of long-range transport from North America across the Atlantic Ocean. The detailed density maps for the different clusters can be found in the Supplementary Material (Fig. ESM5).

The TGM concentrations were then analysed based on the different air mass transport regimes. Fig. 7b shows the histograms and probability density functions of the TGM measurements as a function of the clusters reported in Fig. 7a. Since 5 cluster attributions were possible for each set of BTs (i.e., 5 BTs at 00, 06, 12, and 18 UTC each day), the mode of cluster values was chosen as representative of each set of BTs. The TGM concentrations for those specific times were then selected to calculate the histograms. A sensitivity check was made by averaging the hourly concentrations around each set of BTs. For example, the 00 UTC set was checked against the average of the TGM values between 21 and 3 UTC, and no significant difference was found. Cluster 1 had the highest TGM values on average (see dashed lines, Fig. 7b), possibly indicating pollution from the largely industrialized areas of Eastern Europe. Values for this cluster were quite uniformly distributed, with a maximum density between 3 and 4 ng m⁻³, and a secondary smaller density peak between 6 and 7 ng m⁻³. Cluster 2 had a value of 3.4 ng m⁻³ which is slightly lower than that of cluster 1, the mean value was also close to the frequency distribution peak. In this case, air masses from continental Europe or from the nearby Po Valley seem likely contributors to the high TGM values. Clusters 3, 4, and 5 had the lowest averages (< 2.8 ng m⁻³), and all the cluster's distribution densities peaked at ~ 2 ng m⁻³, which corresponded with the arrival of cleaner air masses from the West.

To further analyse the TGM variability as a function of the different air masses, we also used the potential source contribution function (PSCF) approach, in the "openair" R package (Carslaw and Ropkins,

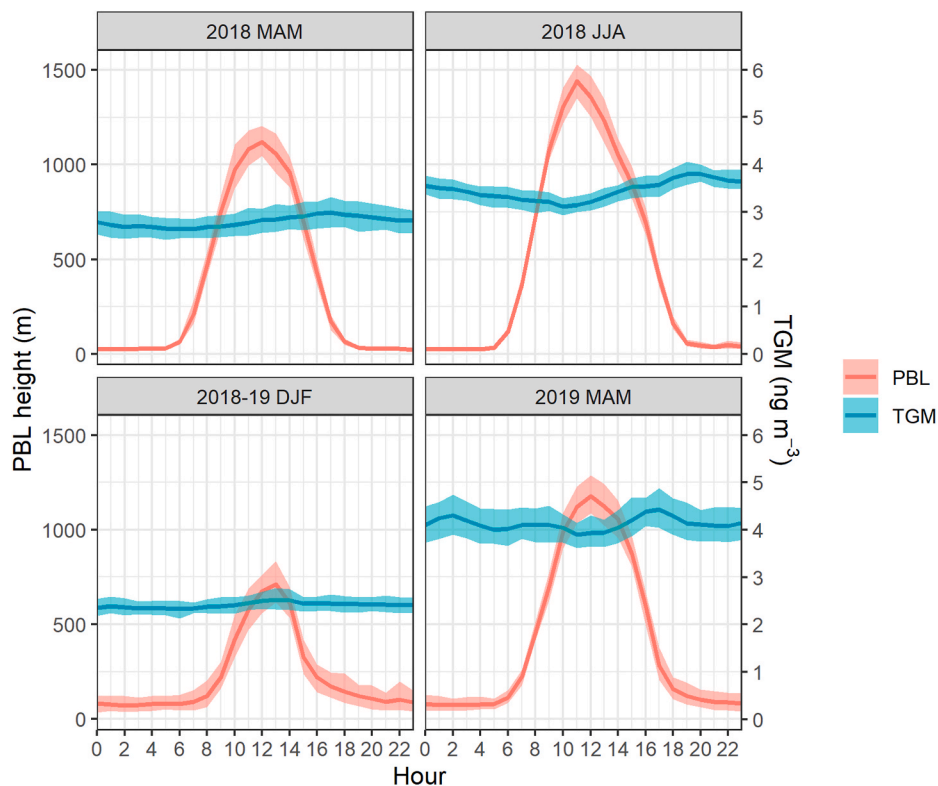


Fig. 6. Diurnal variation of PBL and TGM in the different seasons.

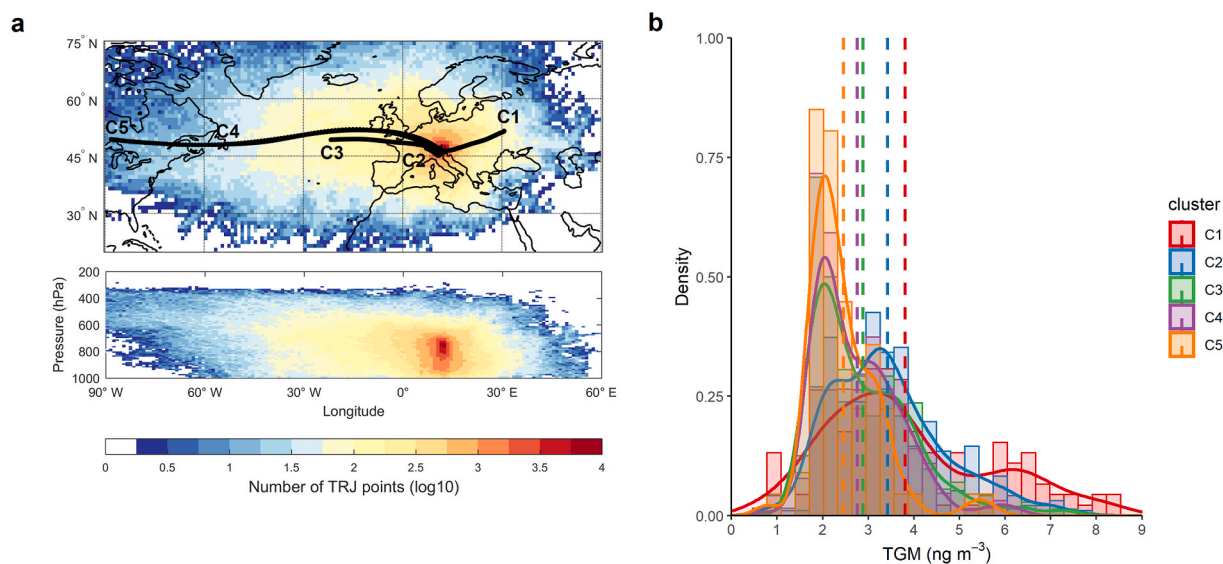


Fig. 7. (a) Concentration field (vertical cross section included) for back-trajectories starting at MRG, together with the mean trajectories for each cluster; (b) probability density function of TGM measurements for each cluster, together with the average values of each cluster (dashed lines).

2012). This is a widely used technique for locating the sources of a pollutant, depending on the back-trajectory positions (see e.g., Hopke et al., 1995). For each grid cell ij , if n_{ij} is the total number of back-trajectory points falling in that cell during the whole observation period, and m_{ij} is the number of back-trajectory points that fall in the ij -th cell during a certain event (e.g., TGM concentrations higher than a certain threshold), the PSCF is computed as $PSCF_{ij} = \frac{m_{ij}}{n_{ij}}$. The PSCF values can then be interpreted as the conditional probability that the TGM concentration at the measurement site exceeds the threshold value if the air masses passed through the ij -th cell before reaching the station.

To account for uncertainties due to cells with low n_{ij} occurrence, which can lead to unexpectedly high PSCF values, the PSCF values in this work were scaled with a weighting function $W(n_{ij})$ (Equation (1)) (implemented into the “openair” function):

$$W(n_{ij}) = \begin{cases} 1.00, & n_{ij} > 2\bar{n} \\ 0.75, & \bar{n} < n_{ij} \leq 2\bar{n} \\ 0.50, & \bar{n}/2 < n_{ij} \leq \bar{n} \\ 0.15, & n_{ij} \leq \bar{n}/2 \end{cases} \quad (1)$$

where $\bar{n}$ is the average number of endpoints per cell, computed on every

cell with at least one endpoint.

To retain only “acute pollution events”, the threshold was set as the 90th percentile of TGM concentrations. Fig. ESM6 shows the PSCF maps divided into different seasons, to investigate potential source regions. Since no data for autumn are present, the corresponding map is not shown. To help explain the differences already shown in Sect. 3.1.1, the maps for both spring seasons are shown separately. By considering the two years together, spring contained almost half of the episodes (49.8%) where the threshold was exceeded. The episodes were almost equally distributed (23.4% for 2018 and 26.4% for 2019). But because of the different threshold values, the PSCF patterns are quite different. While 2018 showed only some high PSCF values for air masses originating from South of Greenland, 2019 showed the highest contributions from Eastern Europe, as was already identified by the density functions shown in Fig. 7b. Another important contribution for 2019 was from the Northern Africa/Mediterranean Sea basin. The elevated contribution from Eastern Europe appeared constant in winter and summer, with a lower occurrence of events (31.5% and 18.7%, respectively). Nevertheless, some limitations of the PSCF approach have to be taken into account: firstly, all trajectories converge at MRG, it is difficult to identify possible local sources, secondly, the PSCF field indicates the geographic origin of the air-masses, but does not necessarily indicate a source location (which could effectively be upwind or downwind of the high PSCF region). This is especially true when dealing with secondary pollutants or with regions crossed by a low number of BTs. The third limitation is that regions with high PSCF values and a low frequency of back-trajectory occurrences provide only limited integral contributions to the overall observed TGM variability. The last limitation is that these

results can only be considered valid for MRG, and cannot be extended to other measurement sites.

3.1.6. Spatial patterns of TGM

To study the potential local sources of TGM measured at MRG, wind speed and direction were investigated (Fig. 8). Polar plots of TGM and the wind polar frequency plots have been produced for the whole measurement period.

TGM concentrations are found to be inversely proportional to wind speed (Fig. 8a), as high concentrations were recorded at wind speeds $< 5 \text{ m s}^{-1}$ for 83% of the total values in our study period. This suggests that local influences are significant for this site. The prevalent wind directions at MRG are West and East-southeast (Fig. 8b) with the highest wind speeds coming from the North. The lowest TGM concentrations were measured in air from the North at wind speeds of up to 20 m s^{-1} , even though these events were quite rare (Fig. 8a). The overall wind speed and direction frequencies between the two campaigns, iGOSP (2018–2019) and GMOS (2013–2014) projects, are very similar, despite the differences in mercury results (Fig. 8c and d). The same analysis performed at a seasonal level confirms the previously described differences in seasonal trends (see section 3.1.1). In winter, low TGM concentrations are associated with high wind speeds and a Northerly wind direction (Fig. ESM4c; Fig. ESM7a). In summer, high TGM values were related to wind speeds $\leq 15 \text{ m s}^{-1}$ blowing from the Western sector in air masses that originally passed over Eastern Europe, as detected by the back-trajectory analysis. Comparison between spring 2018 and 2019 show a similar pattern, with the same prevailing directions, the main difference being the higher contribution in 2019 from the North-west

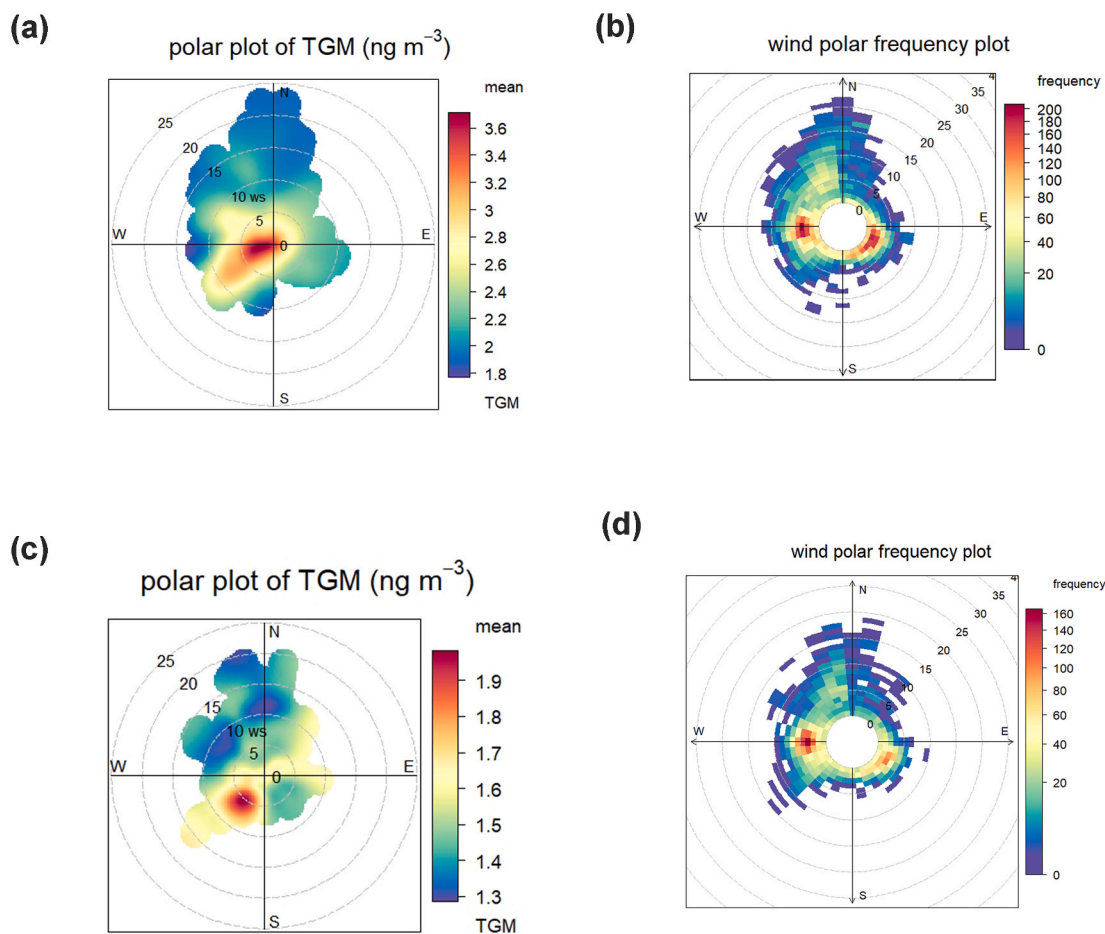


Fig. 8. Polar plot (a) of mean TGM (ng m^{-3}), showing the variation in concentration by wind speed (m s^{-1}) and direction ($^{\circ}\text{N}$), and polar frequency plot (b) of wind speed and direction, referring to the whole investigated time period (iGOSP, 2018–2019); Polar plot (c) of mean TGM (ng m^{-3}), and polar frequency plot (d) of wind speed and direction, referring to the GMOS project (2013–2014). Plots are generated using OpenAir in R.

sector (Fig. ESM4a,d; Fig. ESM7b). As already reported in Section 3.1.1, the TGM values in 2018 were lower than in 2019, when the highest TGM values were associated with wind speeds $\leq 5 \text{ m s}^{-1}$ (Fig. ESM4a,d; Fig. ESM7b). In the following section, we will further elaborate on the differences observed in TGM between spring of 2018 and 2019.

3.2. The difference between spring 2018 and 2019: investigation of the relationship between TGM and meteorological factors on different scales

The relationship between atmospheric Hg species and meteorological variables has already been explored in a number of studies, but few data are available for mountain sites (Berg et al., 2013; Diéguez et al., 2019; Faïn et al., 2009; Fu et al., 2012a, 2012b; Wan et al., 2009). Wind speed and direction are found to play a particularly important role in the identification of TGM sources and transport patterns (Zhang et al., 2015, 2016), whilst temperature, solar radiation and wind speed were often related to the TGM diurnal cycle (Yin et al., 2018). Since Hg has a low melting point and a high evaporation rate compared to other metals, increased air temperatures can contribute to the evaporation of Hg^0 from shallow layers of surface soil. As a consequence, typically during the warmer seasons, high soil temperatures are generated by increased solar radiation which favours the emission of GEM produced by the abiotic reduction of Hg^{2+} previously deposited onto the soil surface (Carpi and Lindberg, 1997; Karthik et al., 2017; Scholtz et al., 2003).

The seasonal analysis at MRG showed quite different TGM concentrations in spring 2018 and 2019, so the possibility of a relationship between TGM and the meteorological variables was investigated in more detail, to try to identify the processes driving this difference.

Firstly, a correlation chart of the daily averages of all the variables was produced for each spring period (Fig. ESM8a,b). Daily averages were used to remove any bias from diurnal variability. The most remarkable differences are the positive correlations between TGM and atmospheric pressure (P) in 2018 (Fig. ESM8a), and between TGM and snow depth (SnD) in 2019 (Fig. ESM8b). For the other meteorological parameters, in 2019 significant correlations appeared between: (i) atmospheric pressure (P) and solar radiation (SR), precipitation (R) and relative humidity (RH); (ii) and between wind speed (WS) and direction (WD). Analysis of the daily and monthly trends indicates that the meteorological conditions in the two spring periods were quite different. Some events were identified in April 2019 that may explain the high TGM level. The beginning of April 2019 was characterized by high snow accumulation, low atmospheric pressure and reduced solar radiation due to increase in cloud cover. Notably, April 2019 had a very high precipitation amount (326 mm) with a sudden increase of SnD from the beginning of the month until May, when it reached the highest value of the whole monitoring period, of about 160 cm (Table ESM3). In 2018, SnD showed a gradual decreasing trend from March to May as the snow cover melted, with the snow cover almost completely gone by the end of May. In April 2018 the temperature increased to $5\text{--}10^\circ\text{C}$ favouring snow melt, in 2019 it remained between -5°C and 0°C , contributing to a lasting snow cover. At the end of March 2019, the wind speed suddenly decreased, and the direction changed from the NW sector to E. So, the higher TGM values measured in Spring 2019 can be associated with the different meteorological conditions that favoured the arrival of polluted air-masses from Eastern Europe and the North Africa/Mediterranean Sea basin with the re-emission processes from the snow cover.

The LAGRANTO back-trajectories analysis also suggested significant differences in synoptic-scale air mass circulation between spring 2018 and spring 2019 (Fig. ESM6). While a dominant Westerly contribution was evident for spring 2018, important contributions from Eastern Europe and the North African/Mediterranean Sea basin were evident for spring 2019. Eastern Europe, and especially Poland is a well-known source of anthropogenic Hg and the primary contributor of Hg emissions in the EU, mainly from coal power plants (Pacyna et al., 2006; Pyta et al., 2020; Zyśk et al., 2011). While the Mediterranean Sea plays a key role as a natural sink and source of several pollutants. Open seawater is

an important source of Hg due to re-emission processes, geothermal activity and bacterial action (Kotnik et al., 2014; Žagar et al., 2014). Furthermore, Hg adsorbed on desert dust from North Africa may be an additional carrier for the transport and deposition of atmospheric Hg (Huang et al., 2020). According to the LAGRANTO analyses of the atmospheric transport regimes, air masses coming mainly from Eastern Europe were likely transported by atmospheric circulation to MRG in spring 2019. This possibly contributed to the high TGM concentrations, whilst low TGM levels in spring 2018 were associated with air masses from the Atlantic passing over Western Europe (Fig. ESM6).

In conclusion, the differences in TGM concentrations between spring 2018 and 2019 can be attributed to a combination of different factors: (i) synoptic-scale atmospheric circulation more favourable to the transport of polluted air-masses from Eastern Europe and North Africa/Mediterranean Sea in spring 2019; (ii) different meteorological conditions; (iii) a very high amount of snow precipitation in winter and spring 2019 that resulted in (iv) more remarkable snowpack re-emission of Hg in spring 2019.

These preliminary findings show that further data are required to improve knowledge of the sources of Hg and the effects of transport processes both on local and large scales on the observed TGM concentrations at MRG.

4. Analysis of specific atmospheric mercury elevated events (AMEEs)

At MRG, unusual short TGM concentration profiles, lasting only a few hours have been observed. During these so-called “atmospheric mercury elevated events – AMEEs” (Cole and Steffen, 2010), the TGM concentration rises rapidly above the average. This TGM behaviour has been examined in a time slot around two specific events together with additional variables such as ozone and meteorological parameters. These two events were identified by an hourly average TGM concentration at least 5% above or below the average concentrations of the previous or following 24 h as described by other authors (Ci et al., 2011; Han et al., 2014; Mao et al., 2016).

Event #1 occurred on March 31st 2018 (Fig. 9) and shows an increase in TGM between 06:00 UTC (08:00 LST, local standard time) and 18:00 UTC, with a maximum TGM concentration of 3.81 ng m^{-3} at 11:00 UTC, while the ozone concentration reached its lowest value at 12:00 UTC on the same day ($24.5 \text{ nmol mol}^{-1}$), which was also the lowest value recorded for the entire spring and summer of 2018. The values of other parameters during the event were: air $T = -5.2^\circ\text{C}$, $P = 732 \text{ hPa}$, $RH = 98\%$, with wind blowing from the South-east at a speed of $< 2.0 \text{ m s}^{-1}$. In addition, during event #1 a change in the wind direction from West to East may have promoted the mixing of two air masses from different origins together with low wind speeds that favoured high TGM concentrations. During event #1 the snow depth (SnD) increased by 14 cm, and was measured as 32 mm of wet deposition (snow precipitation) by the rain gauge.

A similar event (event #2) occurred on March 8th 2019 (Fig. 9), where a rapid rise in TGM concentrations (maximum of 6.65 ng m^{-3} at 11:00 UTC) was recorded, a few hours after 24 h of continuous snowfall (SnD increase $> 4.5 \text{ cm}$). At the same time the registered meteorological parameters were air $T = -0.9^\circ\text{C}$, a low wind speed of 2.4 m s^{-1} , and RH up to 95%. Similar to event #1, the ozone concentrations were low (29 nmol mol^{-1}) compared to those before and after the events (around 40 nmol mol^{-1}).

Both sudden increases in hourly TGM were registered after significant snow deposition. We hypothesise that the snow surface probably accumulated Hg during the snowfall events, and then released it within 24 h, contributing to a TGM peak that recycled Hg between the snow and the lower atmosphere (Spolaor et al., 2018, 2019).

Snowfall is indeed an atmospheric Hg scavenger as well as an active substrate for transferring Hg from the atmosphere to the surface and vice versa (Faïn et al., 2007, 2009; Spolaor et al., 2019). Additionally, the

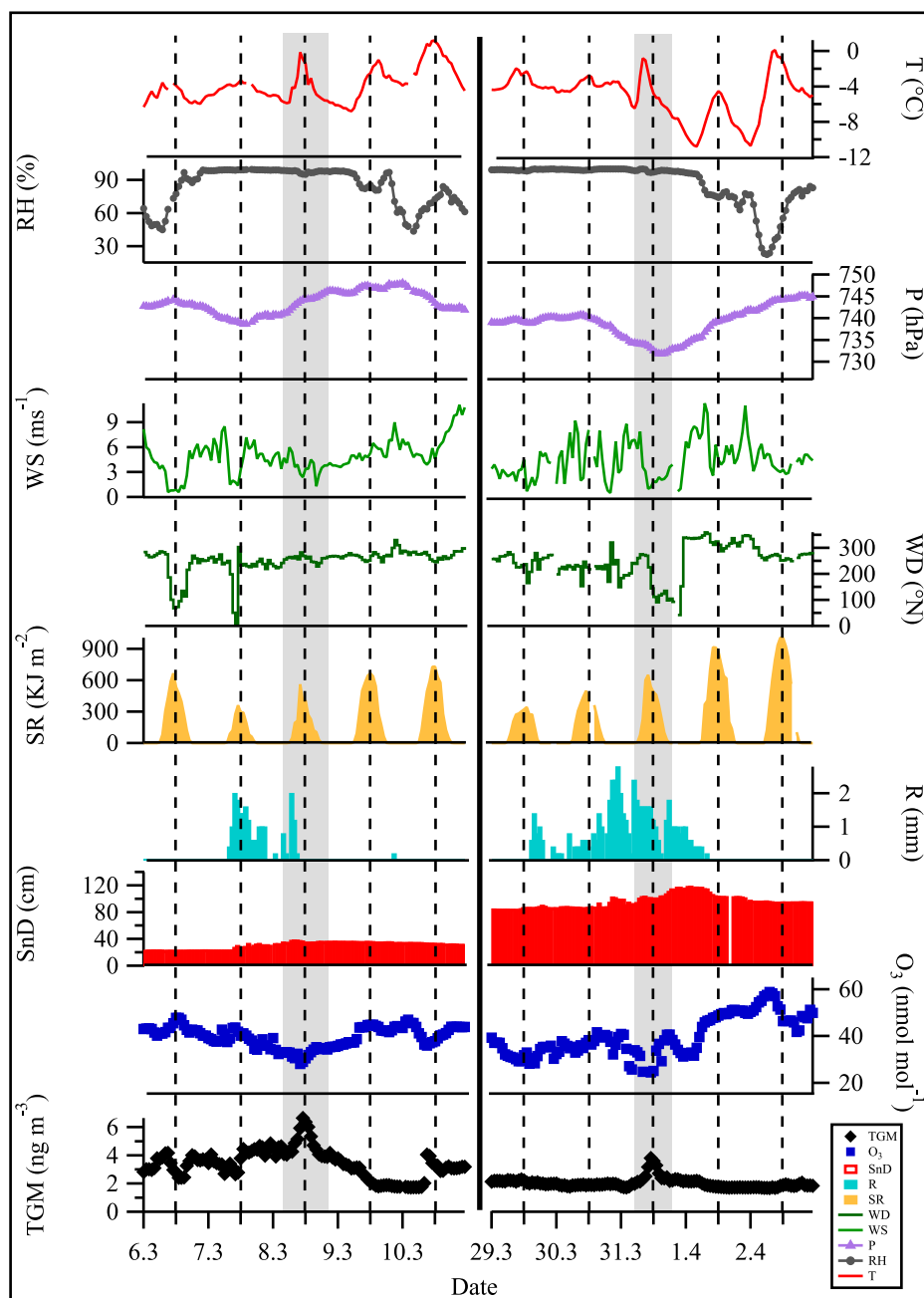


Fig. 9. Summary of the profile of hourly measured parameters during the event#1 (left panel), event#2 (right panel). From the bottom to the top: TGM concentrations (black diamond), O_3 (blue square), snow depth (SnD) (red-white bar), precipitation (rain equivalent) (R) (turquoise bar), solar radiation (SR) (yellow bar), wind direction (WD) ($^{\circ}$ N, dark green line), wind speed (WS) (light green line), atmospheric pressure (P) (purple triangle), relative humidity (RH) (grey dot), air temperature (T) (red line). Event#1 and event#2 time-ranges are highlighted by the grey shading, respectively. The dates (day.month) correspond to time 0:00 at the start of each day. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

sudden increase in TGM in both events occurred with (i) temperatures close to, or below zero ($\leq 0^{\circ}\text{C}$), (ii) high relative humidity, (iii) low wind speed and (iv) presence of sunlight. These AMEEs can be interpreted as the release into the ambient air of GEM after photoreduction of Hg^{2+} deposited by snowfall onto the snowpack via wet (and possibly some dry) deposition (Subir et al., 2012; Swartzendruber et al., 2006). We suppose that Hg^{2+} , as GOM and PBM, underwent a photoreduction process that usually takes place in aquatic media (either wet or frozen such as at the snow surface) (Weiss-Penzias et al., 2015). This, combined with the wind direction effect, suggests a switch between local and regional influences and sources (Fu et al., 2010, 2012a, 2012b; Kentisbeer et al., 2014, 2015; Swartzendruber et al., 2006). Finally, these two events support the active role of the snowpack in modulating TGM concentrations above the snow surface, as previously demonstrated in polar areas (Spolaor et al., 2018, 2019). Snow can act as an extremely efficient atmospheric Hg scavenger. However, due to the reactivity of Hg, the deposited mercury can be rapidly released at the end of

precipitation events causing a large, rapid and intense emission process driving the AMEEs that we observed. Considering that the snowpack at MRG is usually present from late November to May, AMEEs occurring in this period may have been modulated by processes occurring at the snow-atmosphere interface, or by high wind speeds reducing their amplitude.

5. Conclusions

In this work, TGM was monitored continuously at Col Margherita, the highest atmospheric observatory for studying Hg in Italy from March 2018 to May 2019. Atmospheric mercury and ozone measurements were carried out concurrently, together with acquisition of the main meteorological parameters. The mean TGM concentration over the investigated period was $3.14 \pm 1.29 \text{ ng m}^{-3}$. This value is considerably higher than other long-term averaged values observed in remote, rural or mountainous sites in continental or coastal locations in Europe and

North America, but are lower than those registered at some elevated remote and rural stations in China. TGM levels showed an increasing trend from cold to warm seasons similar to some other remote sites located in the Northern and Southern Hemispheres. The diurnal variability of TGM exhibited a similar pattern over different seasons with a diel minimum in the first half of the day, a maximum in the second half of the day, and with a higher amplitude in summer than winter. The spatial patterns of TGM showed seasonal differences, with low TGM concentrations associated with high wind speed. Low winter and high summer values were associated respectively with dominant West/South-west and North-east wind directions. Considering the whole measurement period, high TGM concentrations were associated with a low wind speed and prevailing from the West, indicating a significant contribution from regional and local sources, with possible re-emission mechanisms from snow and soil surfaces.

The higher TGM concentrations and different profiles measured during spring 2019 compared to spring 2018 are attributed to a combination of environmental factors and processes. Besides the meteorological differences between the two spring seasons, the higher 2019 TGM values can be associated with long-range transport of polluted air-masses from Eastern Europe and the North Africa/Mediterranean Sea basin leading to enhanced re-emission processes of Hg from the snow-pack due to higher snow precipitation.

Atmospheric mercury elevated events were observed in association with certain weather conditions, such as below zero temperature, presence of sunlight and abundant snow deposition. These quick increases in TGM may be attributed to photochemical reduction of reactive mercury previously deposited onto snow surfaces.

The levels and temporal trends of TGM detected at MRG demonstrate the importance of this remote site. To understand the effects of air pollution and the potential impacts of climate change, further investigations are needed in terms of continued TGM monitoring activity with more robust instrumentation (i.e., passive samplers), and some site improvements to protect the instrumentation better from electrical spikes. In addition, we expect to increase the collection and measurement of Hg in atmospheric deposition, snow and soil. Further studies are also needed to investigate the rapid oscillations that have been found outside of the snow season.

The future goal will be to improve knowledge of the behaviour of Hg and its deposition/re-emission processes to/from the Earth's surface, as these play an important role as sinks and sources of Hg in remote high-altitude alpine regions.

Data availability

All the data presented in this work are available for scientific purposes upon request to the corresponding authors.

Information on funding sources supporting the work described in the manuscript

The Hg measurements of this study were supported by ERA-PLANET (www.era-planet.eu), trans-national project iGOSP - Integrated Global Observing Systems for Persistent Pollutants (www.igosp.eu), funded under the EU Horizon 2020 H2020-SC5-15-2015 "Strengthening the European Research Area in the domain of Earth Observation", type of action: ERA-NET-Cofund Grant, (Grant Agreement N. 689443). The authors are grateful for financial support from the National Project of Interest Next-Data (www.nextdatapoint.it) by the Italian Ministry for University and Research (MUR), for ozone and meteorological measurements.

CRediT authorship contribution statement

Massimiliano Vardè: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing –

original draft, Writing – review & editing, Visualization, Supervision. **Carlo Barbante:** Project administration, Funding acquisition. **Elena Barbaro:** Writing – review & editing. **Francesca Becherini:** Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Paolo Bonasoni:** Writing – review & editing, Project administration, (Next-Data). **Maurizio Busetto:** Software, (ozone). **Francescopiero Calzolari:** Software, (ozone). **Giulio Cozzi:** Software. **Paolo Cristofanelli:** Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration, (NextData). **Federico Dallo:** Software, Data curation, (TGM, meteorological dataset), Writing – review & editing. **Fabrizio De Blasi:** Data curation, (meteorological dataset), Writing – review & editing. **Matteo Feltracco:** Writing – review & editing. **Jacopo Gabrieli:** Resources, Writing – review & editing. **Andrea Gambaro:** Resources. **Niccolò Maffezzoli:** Investigation, Writing – review & editing. **Elisa Morabito:** Writing – review & editing. **Davide Putero:** Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Andrea Spolaor:** Data curation, Writing – review & editing. **Warren R.L. Cairns:** Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition, All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank Dr. Federico Scoto (CNR-ISAC) and Dr. Ilaria Crotti (Ca' Foscari University of Venice) for providing the Col Margherita location maps and additional graphs using QGIS open-source software and MATLAB, respectively. The authors are grateful to Dr. Michael Sprenger at the atmospheric dynamics group at IAC-ETH, Zurich, for help in using the LAGRANTO.FTP tool for calculating the backward trajectories. This work includes modified Copernicus Atmosphere Monitoring Service information [2020]. The ERA5 PBL dataset has been downloaded from the Climate Data Store (<https://cds.climate.copernicus.eu/#/home>). We also thank Dr. Marco Dianin and Dr. Alberto Bonini Baraldi (ARPAV-U.O. Meteorologia e Climatologia, www.arpa.veneto.it) and Meteotrentino (www.meteotrentino.it) for providing the meteorological parameters dataset from the weather stations of Cima Pradazzo (Belluno, Italy) and Passo Valles (Trento, Italy), respectively. Finally, the authors would like to cordially thank Mr. Loris Scola and Mr. Renzo Minella, head of the cable car service and director of the Ski area San Pellegrino, respectively, and all technical staff for their greatly appreciated cooperation and support during field activities at the Col Margherita Observatory (www.skiareasanpellegrino.it). We thank the Editors (DR. DAVID A. GAY AND DR. JAMES J. SCHAUER) and the four ANONYMOUS Reviewers for their efforts and useful comments. Special thanks are due to Mr. Franco Cofone (CNR-Nanotec) for insightful suggestions during the final revision process. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the National Research Council of Italy.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2021.118917>.

References

- Ambrose, J.L., Gratz, L.E., Jaffe, D.A., Campos, T., Flocke, F.M., Knapp, D.J., Stechman, D.M., Stell, M., Weinheimer, A.J., Cantrell, C.A., Mauldin III, R.L., 2015. Mercury emission ratios from coal-fired power plants in the southeastern United States during NOMADSS. *Environ. Sci. Technol.* 49, 10389–10397. <https://doi.org/10.1021/acs.est.5b01755>.
- Angot, H., Dastoor, A., De Simone, F., Gårdfeldt, K., Gencarelli, C.N., Hedgecock, I.M., Langer, S., Magand, O., Nerentorp Mastromonaco, M., Nordström, C., Pfaffhuber, K. A., Pirrone, N., Ryjkov, A., Selin, N.E., Skov, H., Song, S., Sprovieri, F., Steffen, A., Toyota, K., Travníkov, O., Yang, X., Dommergue, A., 2016. Chemical cycling and deposition of atmospheric mercury in polar regions: review of recent measurements and comparison with models. *Atmos. Chem. Phys.* 16, 10735–10763. <https://doi.org/10.5194/acp-16-10735-2016>.
- ARPA Piemonte, 2018. Agenzia Regionale per la Protezione Ambientale del Piemonte, Dipartimento Territoriale Piemonte Nord Ovest - Anno 2018, cod. doc. F06_2019_00288_001 Rapporto di sintesi sui dati prodotti dalla stazione di monitoraggio della qualità dell'aria di proprietà di TRM S.p.A. ubicata nel Comune di Beinasco. ARPA Piemonte, pp. 1–67 (in Italian).
- ARPA Piemonte, 2019. Agenzia Regionale per la Protezione Ambientale del Piemonte, Dipartimento territoriale Piemonte Nord Ovest - Anno 2019, cod. doc. F06_2020_00198_001 Rapporto di sintesi sui dati prodotti dalla stazione di monitoraggio della qualità dell'aria di proprietà di TRM S.p.A. ubicata nel Comune di Beinasco. ARPA Piemonte, pp. 1–76 (in Italian).
- ARPAV, 2018. Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto (in Italian). <https://www.arpa.veneto.it/arpavinforma/comunicati-stampa/archivio/comunicati-2018/incendio-boschivo-in-data-24-ottobre-2018-nella-valle-agordina>.
- Bagnato, E., Aiuppa, A., Parello, F., Calabrese, S., D'Alessandro, W., Mather, T.A., McGonigle, A.J.S., Pyle, D.M., Wängberg, I., 2007. Degassing of gaseous (elemental and reactive) and particulate mercury from Mount Etna volcano (Southern Italy). *Atmos. Environ.* 41 (35), 7377–7388. <https://doi.org/10.1016/j.atmosenv.2007.05.060>.
- Bagnato, E., Parello, F., Valenza, M., Caliro, S., 2009. Mercury content and speciation in the Phlegrean Fields volcanic complex: evidence from hydrothermal system and fumaroles. *J. Volcanol. Geoth. Res.* 187 (3–4), 250–260. <https://doi.org/10.1016/j.jvolgeores.2009.09.010>.
- Bagnato, E., Barra, M., Cardellini, C., Chiodini, G., Parello, F., Sprovieri, M., 2014. First combined flux chamber survey of mercury and CO₂ emissions from soil diffuse degassing at Solfatara di Pozzuoli crater, Campi Flegrei (Italy): mapping and quantification of gas release. *J. Volcanol. Geoth. Res.* 289, 26–40. <https://doi.org/10.1016/j.jvolgeores.2014.10.017>.
- Bagnoli, A., Gartner, I., 2018. Monitoraggio delle aree geotermiche toscane: concentrazioni di H₂S e Hg nelle aree geotermiche toscane. Monitoraggi ARPAT e validazione dati Enel (Area Vasta Sud. Report anno 2017. Prot. n° 0046235 ARPA Toscana 1–41 (Technical Report), 2018, (in Italian).
- Barbante, C., Schwikowski, M., Döring, T., Gäggeler, H.W., Schotterer, U., Tobler, L., Van de Velde, K., Ferrari, C., Cozzi, G., Turetta, C., Rosman, K., Bolshov, M., Capodaglio, G., Cescon, P., Bouton, C., 2004. Historical record of European emissions of heavy metals to the atmosphere since 1650s from alpine snow/ice cores drilled near Monte Rosa. *Environ. Sci. Technol.* 38 (15), 4085–4090. <https://doi.org/10.1021/es049759r>.
- Barbaro, E., Morabito, E., Gregoris, E., Feltracco, M., Gabrieli, J., Vardè, M., Cairns, W.R. L., Dallo, F., De Blasi, F., Zangrando, R., Barbante, C., Gambaro, A., 2020. Col Margherita Observatory: a background site in the Eastern Italian Alps for investigating the chemical composition of atmospheric aerosols. *Atmos. Environ.* 221, 117071. <https://doi.org/10.1016/j.atmosenv.2019.117071>.
- Beniston, M., Diaz, H.F., Bradley, R.S., 1997. Climatic change at high elevation sites: an overview. *Clim. Change* 36 (3–4), 233–251. <https://doi.org/10.1023/A:1005380714349>.
- Berg, T., Pfaffhuber, K.A., Cole, A.S., Engelsen, O., Steffen, A., 2013. Ten-year trends in atmospheric mercury concentrations, meteorological effects and climate variables at Zeppelin, Ny-Ålesund. *Atmos. Chem. Phys.* 13, 6575–6586. <https://doi.org/10.5194/acp-13-6575-2013>.
- Bigi, A., Ghermandi, G., 2016. Trends and variability of atmospheric PM_{2.5} and PM_{10-2.5} concentration in the Po Valley, Italy. *Atmos. Chem. Phys.* 16, 15777–15788. <https://doi.org/10.5194/acp-16-15777-2016>.
- Blanchard, P., Froude, F.A., Martin, J.B., Dryfhout-Clark, H., Woods, J.T., 2002. Four years of continuous total gaseous mercury (TGM) measurements at sites in Ontario, Canada. *Atmos. Environ.* 36 (23), 3735–3743. [https://doi.org/10.1016/S1352-2310\(02\)00344-8](https://doi.org/10.1016/S1352-2310(02)00344-8).
- Breder, R., Flucht, R., 1984. Mercury levels in the atmosphere of various regions and locations in Italy. *Sci. Total Environ.* 40, 231–244. [https://doi.org/10.1016/0048-9697\(84\)90353-X](https://doi.org/10.1016/0048-9697(84)90353-X).
- Cabassi, J., Tassi, F., Venturi, S., Calabrese, S., Capecciacchi, F., D'Alessandro, W., Vaselli, O., 2017. A new approach for the measurement of gaseous elemental mercury (GEM) and H₂S in air from anthropogenic and natural sources: examples from Mt. Amiata (Siena, Central Italy) and Solfatara Crater (Campi Flegrei, Southern Italy). *J. Geochem. Explor.* 175, 48–58. <https://doi.org/10.1016/j.gexplo.2016.12.017>.
- Cairns, W.R.L., Vardè, M., Dallo, F., de Blasi, F., Maffezzoli, N., Gabrieli, J., Cozzi, G., Barbante, C., Cristofanelli, P., Naitza, L., Calzolari, F., Busetto, M., Davolio, S., Bonasoni, P., 2019. Total gaseous mercury (TGM) and ozone (O₃) over spring - summer 2018 and winter 2019 at the Col Margherita atmospheric observatory (2543 m a.s.l.). In: Proceedings of the ICMGP 2019, the 14th International Conference on Mercury as a Global Pollutant, September 7–13, 2019. Krakow, Poland, pp. 109–110. M.P.1.13. www.mercury2019krakow.com/public/files/ICMGP2019-abstract-volume.pdf.
- Carpi, A., Lindberg, S.E., 1997. Sunlight-mediated emission of elemental mercury from soil amended with municipal sewage sludge. *Environ. Sci. Technol.* 31, 2085–2091. <https://doi.org/10.1021/es960910+>.
- Carslaw, D., Ropkins, K., 2012. Openair – an R package for air quality data analysis. *Environ. Model. Software* 27–28, 52–61. <https://doi.org/10.1016/j.envsoft.2011.09.008>.
- Chen, L., Liu, M., Xu, Z., Fan, R., Tao, J., Chen, D., Sun, J., 2013. Variation trends and influencing factors of total gaseous mercury in the Pearl River Delta - a highly industrialized region in South China influenced by seasonal monsoons. *Atmos. Environ.* 77, 757–766. <https://doi.org/10.1016/j.atmosenv.2013.05.053>.
- Chen, W.K., Li, T.C., Sheu, G.-R., Lin, N.H., Chen, L.Y., Yuan, C.S., 2016. Correlation analysis, transportation mode of atmospheric mercury and criteria air pollutants, with meteorological parameters at two remote sites of mountain and offshore island in Asia. *Aerosol Air Qual. Res.* 16, 2692–2705. <https://doi.org/10.4209/aaqr.2015.07.0455>.
- Ci, Z., Zhang, X., Wang, Z., Niu, Z., 2011. Atmospheric gaseous elemental mercury (GEM) over a coastal/rural site downwind of East China: temporal variation and long-range transport. *Atmos. Environ.* 45 (15), 2480–2487. <https://doi.org/10.1016/j.atmosenv.2011.02.043>, 1352–2310.
- Clark, I.D., Fritz, P., 2013. Environmental Isotopes in Hydrogeology. Informa Limited, London, UK.
- Cole, A.S., Steffen, A., 2010. Trends in long-term gaseous mercury observations in the Arctic and effects of temperature and other atmospheric conditions. *Atmos. Chem. Phys.* 10, 4661–4672. <https://doi.org/10.5194/acp-10-4661-2010>.
- Cooper, O.R., Schultz, M.G., Schroeder, S., Chang, K.-L., Gaudel, A., Benítez, G.C., Cuevas, E., Fröhlich, M., Molloy, I.E., Molloy, S., Kubistin, D., Lu, X., McClure-Begley, A., Nédélec, P., O'Brien, J., Oltmans, S.J., Petropavlovskikh, I., Ries, L., Senik, I., Sjöberg, K., Solberg, S., Spain, G.T., Spangl, W., Steinbacher, M., Tarasick, D., Thouret, V., Xu, X., 2020. Multi-decadal surface ozone trends at globally distributed remote locations. *Elem. Sci. Anth.* 8 (1), 1–23. <https://doi.org/10.1525/elementa.420>.
- Coplen, T.B., 1993. Uses of environmental isotopes. In: Alley, W.B. (Ed.), *Regional Ground-Water Quality*. Van Nostrand Reinhold, New York, NY, USA, pp. 227–254.
- Cristofanelli, P., Scheel, H.-E., Steinbacher, M., Saliba, M., Azzopardi, F., Ellul, R., Fröhlich, M., Tositti, L., Brattich, E., Maione, M., Calzolari, F., Duchi, R., Landi, T.C., Marinoni, A., Bonasoni, P., 2015. Long-term surface ozone variability at Mt. Cimone WMO/GAW global station (2165 m a.s.l., Italy). *Atmos. Environ.* 101, 23–33. <https://doi.org/10.1016/j.atmosenv.2014.11.012>.
- Cristofanelli, P., Landi, T.C., Calzolari, F., Duchi, R., Marinoni, A., Rinaldi, M., Bonasoni, P., 2016. Summer atmospheric composition over the Mediterranean basin: investigation on transport processes and pollutant export to the free troposphere by observations at the WMO/GAW Mt. Cimone global station (Italy, 2165 m a.s.l.). *Atmos. Environ.* 141, 139–152. <https://doi.org/10.1016/j.atmosenv.2016.06.048>.
- Crowley, J.N., Schuster, G., Pouvesle, N., Parchatka, U., Fischer, H., Bonn, B., Bingemer, H., Lelieveld, J., 2010. Nocturnal nitrogen oxides at a rural mountain-site in south-western Germany. *Atmos. Chem. Phys.* 10, 2795–2812. <https://doi.org/10.5194/acp-10-2795-2010>.
- Crutzen, P.J., 1970. The influence of nitrogen oxides on the atmospheric ozone content. *Quart. J. Roy. Meteor. Soc.* 96, 320–325. <https://doi.org/10.1002/qj.49709640815>.
- Davolio, S., Della Fera, S., Laviola, S., Miglietta, M.M., Levizzani, V., 2020. Heavy precipitation over Italy from the mediterranean storm “Vaia” in October 2018: Assessing the role of an atmospheric river. *Mon. Weather Rev.* 148, 3571–3588. <https://doi.org/10.1175/MWR-D-20-0021.s1>.
- Denzler, B., Bogdal, C., Henne, S., Obrist, D., Steinbacher, M., Hungerbühler, K., 2017. Inversion approach to validate mercury, emissions based on background air monitoring at the high altitude research station Jungfraujoch (3580 m). *Environ. Sci. Technol.* 51, 2846–2853. <https://doi.org/10.1021/acs.est.6b05630>.
- Diéguez, M.C., Bencardino, M., García, P.E., D'Amore, F., Castagna, J., De Simone, F., Soto Cárdenas, C., Ribeiro Guevara, S., Pirrone, N., Sprovieri, F., 2019. A multi-year record of atmospheric mercury species at a background mountain station in Andean Patagonia (Argentina): temporal trends and meteorological influence. *Atmos. Environ.* 214, 116819. <https://doi.org/10.1016/j.atmosenv.2019.116819>.
- Diémioz, H., Barnaba, F., Magri, T., Pession, G., Dionisi, D., Pittavino, S., Tombolato, I.K. F., Campanelli, M., Della Ceca, L.S., Hervio, M., Di Liberto, L., Ferrero, L., Gobbi, G. P., 2019. Transport of Po valley aerosol pollution to the northwestern Alps – Part 1: Phenomenology. *Atmos. Chem. Phys.* 19, 3065–3095. <https://doi.org/10.5194/acp-19-3065-2019>.
- Dommergue, A., Sprovieri, F., Pirrone, N., Ebinghaus, R., Brooks, S., Courteaud, J., Ferrari, C.P., 2010. Overview of mercury measurements in the Antarctic troposphere. *Atmos. Chem. Phys.* 10, 3309–3319. <https://doi.org/10.5194/acp-10-3309-2010>.
- Dorling, S.R., Davies, T.D., Pierce, C.E., 1992. Cluster analysis: a technique for estimating the synoptic meteorological conditions on air and precipitation chemistry – method and applications. *Atmos. Environ.* 26 (14), 2575–2581. [https://doi.org/10.1016/0960-1686\(92\)90110-7](https://doi.org/10.1016/0960-1686(92)90110-7).
- D'Amore, F., Bencardino, M., Cinnirella, S., Sprovieri, F., Pirrone, N., 2015. Data quality through a web-based QA/QC system: implementation for atmospheric mercury data from the global mercury observation system. *Environ. Sci.: Process. Impacts* 17 (8), 1482–1491. <https://doi.org/10.1039/c5em00205b>.
- Ebinghaus, R., Kock, H.H., Jennings, S.G., McCartin, P., Orren, M.J., 1995. Measurements of atmospheric mercury concentrations in Northwestern and Central Europe - comparison of experimental data and model results. *Atmos. Environ.* 29 (22), 3333–3344. [https://doi.org/10.1016/1352-2310\(95\)00229-R](https://doi.org/10.1016/1352-2310(95)00229-R).

- Ebinghaus, R., Kock, H.H., Temme, C., Einax, J.W., Löwe, A.G., Richter, A., Burrows, J. P., Schroeder, W.H., 2002. Antarctic springtime depletion of atmospheric mercury. *Environ. Sci. Technol.* 36 (6), 1238–1244. <https://doi.org/10.1021/es015710z>.
- Ebinghaus, R., Slemr, F., Brenninkmeijer, C.A.M., van Velthoven, P., Zahn, A., Hermann, M., O'Sullivan, D.A., Oram, D.E., 2007. Emissions of gaseous mercury from biomass burning in South America in 2005 observed during CARIBIC flights. *Geophys. Res. Lett.* 34 (8), 1–5. <https://doi.org/10.1029/2006GL028866>. L08813.
- EN 14625, 2012. Ambient Air - Standard Method for the Measurement of the Concentration of O₃ by Ultraviolet Photometry. Comité Européen de Normalisation, 2012.
- Engle, M.A., Gustin, M.S., Lindberg, S.E., Gertler, A.W., Ariya, P.A., 2005. The influence of ozone on atmospheric emissions of gaseous elemental mercury and reactive gaseous mercury from substrates. *Atmos. Environ.* 39, 7506–7517. <https://doi.org/10.1016/j.atmosenv.2005.07.069>.
- Faïn, X., Grangeon, S., Bahlmann, E., Fritsche, J., Obrist, D., Dommergue, A., Ferrari, C. P., Cairns, W.R.L., Ebinghaus, R., Barbante, C., 2007. Diurnal production of gaseous mercury in the alpine snowpack before snowmelt. *J. Geophys. Res.* 112, 1–12. <https://doi.org/10.1029/2007JD008520>. D21311.
- Faïn, X., Obrist, D., Hallar, A.G., McCubbin, I., Rahn, T., 2009. High levels of reactive gaseous mercury observed at a high elevation research laboratory in the Rocky Mountains. *Atmos. Chem. Phys.* 9, 8049–8060. <https://doi.org/10.5194/acp-9-8049-2009>.
- Faïn, X., Helmig, D., Hueber, J., Obrist, D., Williams, M.W., 2013. Mercury dynamics in the Rocky mountain, Colorado, snowpack. *Biogeosciences* 10, 3793–3807. <https://doi.org/10.5194/bg-10-3793-2013>.
- Ferrara, R., Maserti, B.E., 1990. Atmospheric mercury levels in the Mount Etna volcanic area after an eruptive phase. *Environ. Technol.* 11 (1), 51–56. <https://doi.org/10.1080/09593339009384838>.
- Ferrara, R., Maserti, B.E., De Liso, A., Cioni, R., Raco, B., Taddeucci, G., Edner, H., Ragnarson, P., Svanberg, S., Wallinder, E., 1994. Atmospheric mercury emission at Solfatara volcano (Pozzuoli, Phlegraean fields-Italy). *Chemosphere* 29 (7), 1421–1428. [https://doi.org/10.1016/0045-6535\(94\)90275-5](https://doi.org/10.1016/0045-6535(94)90275-5).
- Ferrara, R., Mazzolai, B., Edner, H., Svanberg, S., Wallinder, E., 1998. Atmospheric mercury sources in the Mt. Amiata area. *Italy, Sci. Total Environ.* 213 (1–3), 13–23. [https://doi.org/10.1016/S0048-9697\(98\)00067-9](https://doi.org/10.1016/S0048-9697(98)00067-9).
- Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N., 2000. Volcanoes as emission sources of atmospheric mercury in the Mediterranean basin. *Sci. Total Environ.* 259 (1–3), 115–121. [https://doi.org/10.1016/S0048-9697\(00\)00558-1](https://doi.org/10.1016/S0048-9697(00)00558-1).
- Fisher, J.A., Jacob, D.J., Soerensen, A.L., Amos, H.M., Steffen, A., Sunderland, E.M., 2012. Riverine source of Arctic Ocean mercury inferred from atmospheric observations. *Nat. Geosci.* 5, 499–504. <https://doi.org/10.1038/ngeo1478>.
- Fu, X., Feng, X., Zhu, W., Wang, S., Lu, J., 2008. Total gaseous mercury concentrations in ambient air in the eastern slope of Mt. Gongga, South-Eastern fringe of the Tibetan plateau, China. *Atmos. Environ.* 42 (5), 970–979. <https://doi.org/10.1016/j.atmosenv.2007.10.018>.
- Fu, X., Feng, X., Wang, S., Rothenberg, S., Shang, L., Li, Z., Qiu, G., 2009. Temporal and spatial distributions of total gaseous mercury concentrations in ambient air in a mountainous area in southwestern China: implications for industrial and domestic mercury emissions in remote areas in China. *Sci. Total Environ.* 407, 2306–2314. <https://doi.org/10.1016/j.scitotenv.2008.11.053>.
- Fu, X.W., Feng, X., Dong, Z.Q., Yin, R.S., Wang, J.X., Yang, Z.R., Zhang, H., 2010. Atmospheric gaseous elemental mercury (GEM) concentrations and mercury depositions at a high-altitude mountain peak in south China. *Atmos. Chem. Phys.* 10, 2425–2437. <https://doi.org/10.5194/acp-10-2425-2010>.
- Fu, X.W., Feng, X., Liang, P., Deli-Geer, Zhang, H., Ji, J., Liu, P., 2012a. Temporal trend and sources of speciated atmospheric mercury at Waliguan GAW station, Northwestern China. *Atmos. Chem. Phys.* 12 (4), 1951–1964. <https://doi.org/10.5194/acp-12-1951-2012>.
- Fu, X.W., Feng, X., Shang, L.H., Wang, S.F., Zhang, H., 2012b. Two years of measurements of atmospheric total gaseous mercury (TGM) at a remote site in Mt. Changbai area, Northeastern China. *Atmos. Chem. Phys.* 12, 4215–4226. <https://doi.org/10.5194/acp-12-4215-2012>.
- Fu, X., Maruszak, N., Heimbürger, L.-E., Sauvage, B., Gheusi, F., Prestbo, E.M., Sonke, J. E., 2016. Atmospheric mercury speciation dynamics at the high-altitude Pic du Midi Observatory, southern France. *Atmos. Chem. Phys.* 16, 5623–5639. <https://doi.org/10.5194/acp-16-5623-2016>.
- Gabrieli, J., Decet, F., Luchetta, A., Valt, M., Pastore, P., Barbante, C., 2010. Occurrence of PAH in the seasonal snowpack of the eastern Italian Alps. *Environ. Pollut.* 158, 3130–3137. <https://doi.org/10.1016/j.envpol.2010.06.042>.
- Gabrieli, J., Carturan, L., Gabrielli, P., Kehrwald, N., Turetta, C., Cozzi, G., Spolaor, A., Dinale, R., Staffler, H., Seppi, R., dalla Fontana, G., Thompson, L., Barbante, C., 2011. Impact of Po valley emissions on the highest glacier of the eastern European Alps. *Atmos. Chem. Phys.* 11, 8087–8102. <https://doi.org/10.5194/acp-11-8087-2011>.
- Gay, D.A., Schmeltz, D., Prestbo, E., Olson, M., Sharac, T., Tordon, R., 2013. The Atmospheric Mercury Network: measurement and initial examination of an ongoing atmospheric mercury record across North America. *Atmos. Chem. Phys.* 13, 11339–11349. <https://doi.org/10.5194/acp-13-11339-2013>.
- GMOS, S.O.P., 2011. Standard operational procedure, methods for the determination of TGM and GEM (last access July 2020). <http://www.gmos.eu/download/gmos-sop-tgm-gem/>.
- Gustin, M.S., Engle, M., Ericksen, J., Lyman, S., Stamenkovic, J., Xin, M., 2006. Mercury exchange between the atmosphere and low mercury containing substrates. *Appl. Geochem.* 21 (11), 1913–1923. <https://doi.org/10.1016/j.apgeochem.2006.08.007>.
- Gustin, M.S., Lindberg, S.E., Weisberg, P.E., 2008. An update on the natural sources and sinks of atmospheric mercury. *Appl. Geochem.* 23 (3), 482–493. <https://doi.org/10.1016/j.apgeochem.2007.12.010>.
- Gustin, M.S., Jaffe, D., 2010. Reducing the uncertainty in measurement and understanding of mercury in the atmosphere. *Environ. Sci. Technol.* 44, 2222–2227. <https://doi.org/10.1021/es902736k>.
- Gustin, M.S., Amos, H.M., Huang, J., Miller, M.B., Heidecorn, K., 2015. Measuring and modeling mercury in the atmosphere: a critical review. *Atmos. Chem. Phys.* 15, 5697–5713. <https://doi.org/10.5194/acp-15-5697-2015>.
- Han, Y.-J., Kim, J.-E., Kim, P.-R., Kim, W.-J., Yi, S.-M., Seo, Y.-S., Kim, S.-H., 2014. General trends of atmospheric mercury concentrations in urban and rural areas in Korea and characteristics of high-concentration events. *Atmos. Environ.* 94, 754–764. <https://doi.org/10.1016/j.atmosenv.2014.06.002>.
- Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., Nicolas, J., Pubeby, C., Radu, R., Schepers, D., Simmons, A., Soci, C., Abdalla, S., Abellan, X., Balsamo, G., Bechtold, P., Biavati, G., Bidlot, J., Bonavita, M., De Chiara, G., Dahlgren, P., Dee, D., Diamantakis, M., Dragani, R., Flemming, J., Forbes, R., Fuentes, M., Geer, A., Haimberger, L., Healy, S., Hogan, R.J., Hólm, E., Janisková, M., Keeley, S., Laloyaux, P., Lopez, P., Lupu, C., Radnoti, G., de Rosnay, P., Rozum, I., Vamborg, F., Villaume, S., Thépaut, J.-N., 2020. The ERA5 global reanalysis. *Q. J. R. Meteorol. Soc.* 146, 1999–2049. <https://doi.org/10.1002/qj.3803>.
- Hopke, P.K., Barrie, L.A., Li, S.-M., Cheng, M.-D., Li, C., Xie, Y., 1995. Possible sources and preferred pathways for biogenic and non-sea-salt sulphur for the high Arctic. *J. Geophys. Res.* 100 (16), 595–616. <https://doi.org/10.1029/95JD01712>.
- Horowitz, H.M., Jacob, D.J., Zhang, Y., Dibble, T.S., Slemr, F., Amos, H.M., Schmidt, J. A., Corbitt, E.S., Marais, E.A., Sunderland, E.M., 2017. A new mechanism for atmospheric mercury redox chemistry: implications for the global mercury budget. *Atmos. Chem. Phys.* 17, 6353–6371. <https://doi.org/10.5194/acp-17-6353-2017>.
- Huang, J., Kang, S., Yin, R., Ram, K., Liu, X., Lu, H., Guo, J., Chen, S., Tripathi, L., 2020. Desert dust as a significant carrier of atmospheric mercury. *Environ. Pollut.* 267, 115442. <https://doi.org/10.1016/j.envpol.2020.115442>.
- Kaiser, A., Scheffinger, H., Spangl, W., Weiss, A., Gilge, S., Fricke, W., Ries, L., Cemas, D., Jesenovec, B., 2007. Transport of nitrogen oxides, carbon monoxide and ozone to the alpine global atmosphere Watch stations Jungfraujoch (Switzerland), Zugspitze and Hohenpeissenberg (Germany), Sonnblick (Austria) and Mt. Kravec (Slovenia). *Atmos. Environ.* 41 (40), 9273–9287. <https://doi.org/10.1016/j.atmosenv.2007.09.027>.
- Kang, S., Zhang, Q., Qian, Y., Ji, Z., Li, C., Cong, Z., Zhang, Y., Guo, J., Du, W., Huang, J., You, Q., Panday, A.K., Rupakheti, M., Chen, D., Gustafsson, Ö., Thiemens, M.H., Qin, D., 2019. Linking atmospheric pollution to cryospheric change in the Third Pole region: current progress and future prospects. *Natl. Sci. Rev.* 6 (4), 796–809. <https://doi.org/10.1093/nsr/nwz031>.
- Karthik, R., Paneerselvam, A., Ganguly, D., Hariharan, G., Srinivasulu, S., Purvaja, R., 2017. Temporal variability of atmospheric Total Gaseous Mercury and its correlation with meteorological parameters at a high-altitude station of the South India. *Atmos. Pollut. Res.* 8, 164–173. <https://doi.org/10.1016/j.apr.2016.08.010>.
- Karuppasamy, M.B., Seshachalam, S., Natesan, U., Ramasamy, K., 2020. Characterization of atmospheric mercury in the high-altitude background station and coastal urban city in South Asia. *Intech* 1–16. <https://doi.org/10.5772/intechopen.94543>.
- Kellerhals, M., Beauchamp, S., Belzer, W., Blanchard, P., Froude, F., Harvey, B., McDonald, K., Pilote, M., Poissant, L., Puckett, K., 2003. Temporal and spatial variability of total gaseous mercury in Canada: results from the Canadian Atmospheric Mercury Measurement Network (CAMNet). *Atmos. Environ.* 37, 1003–1011. [https://doi.org/10.1016/S1352-2310\(02\)00917-2](https://doi.org/10.1016/S1352-2310(02)00917-2).
- Kentisbeer, J., Leeson, S.R., Malcolm, H.M., Leith, I.D., Braban, C.F., Cape, J.N., 2014. Patterns and source analysis for atmospheric mercury at Auchincorth Moss, Scotland. *Environ. Sci. Process. Imp.* 16, 1112–1123. <https://doi.org/10.1039/C3EM00700F>.
- Kentisbeer, J., Leeson, S.R., Clark, T., Malcolm, H.M., Cape, J.N., 2015. Influences on and patterns in total gaseous mercury (TGM) at Harwell, England. *Environ. Sci. Process. Imp.* 17, 586–595. <https://doi.org/10.1039/C4EM00652F>.
- Kim, K.H., Ebinghaus, R., Schroeder, W.H., Blanchard, P., Kock, H.H., Steffen, A., Froude, F.A., Kim, M.Y., Hong, S., Kim, J.H., 2005. Atmospheric mercury concentrations from several observatory sites in the Northern Hemisphere. *J. Atmos. Chem.* 50, 1–24. <https://doi.org/10.1007/s10874-005-9222-0>.
- Kirchgeorg, T., Dreyer, A., Gabrieli, P., Gabrieli, J., Thompson, L.G., Barbante, C., Ebinghaus, R., 2016. Seasonal accumulation of persistent organic pollutants on a high altitude glacier in the Eastern Alps. *Environ. Pollut.* 218, 804–812. <https://doi.org/10.1016/j.envpol.2016.08.004>.
- Klausen, J., Zellweger, C., Buchmann, B., Hofer, P., 2003. Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites. *J. Geophys. Res.* 108, 4622. <https://doi.org/10.1029/2003JD003710>.
- Kock, H.H., Bieber, E., Ebinghaus, R., Spain, T.G., Thees, B., 2005. Comparison of long-term trends and seasonal variations of atmospheric mercury concentrations at the two European coastal monitoring stations Mace Head, Ireland, and Zingst, Germany. *Atmos. Environ.* 39 (39), 7549–7556. <https://doi.org/10.1016/j.atmosenv.2005.02.059>.
- Kotnik, J., Sprovieri, F., Ogrinc, N., Horvat, M., Pirrone, N., 2014. Mercury in the Mediterranean, part I: spatial and temporal trends. *Environ. Sci. Pollut. Res.* 21, 4063–4080. <https://doi.org/10.1007/s11356-013-2378-2>.
- Kottek, M., Grieser, J., Beck, C., Rudolf, B., Rubel, F., 2006. World map of the Köppen-Geiger climate classification updated. *Meteorol. Z.* 15, 259–263. <https://doi.org/10.1127/0941-2948/2006/0130>.

- Lalonde, J.D., Poulain, A.J., Amyot, M., 2002. The role of mercury redox reactions in snow on snow-to-air mercury transfer. *Environ. Sci. Technol.* 36, 174–178. <https://doi.org/10.1021/es010786g>.
- Lan, X., Talbot, R., Castro, M., Perry, K., Luke, W., 2012. Seasonal and diurnal variations of atmospheric mercury across the US determined from AMNet monitoring data. *Atmos. Chem. Phys.* 12, 10569–10582. <https://doi.org/10.5194/acp-12-10569-2012>.
- Lee, D.S., Dollard, G.J., Pepler, S., 1998. Gas-phase mercury in the atmosphere of the United Kingdom. *Atmos. Environ.* 32 (5), 855–864. [https://doi.org/10.1016/S1352-2310\(97\)00316-6](https://doi.org/10.1016/S1352-2310(97)00316-6).
- Lin, H., Tong, Y., Yin, X., Zhang, Q., Zhang, H., Zhang, H., Chen, L., Kang, S., Zhang, W., Schauer, J., de Foy, B., Bu, X., Wang, X., 2019. First measurement of atmospheric mercury species in Qomolangma Natural Nature Preserve, Tibetan Plateau, and evidence of transboundary pollutant invasion. *Atmos. Chem. Phys.* 19, 1373–1391. <https://doi.org/10.5194/acp-19-1373-2019>.
- Lindberg, S.E., Brooks, S., Lin, C.-J., Scott, K., Meyers, T., Chambers, L., Landis, M., Stevens, R., 2001. Formation of reactive gaseous mercury in the Arctic: evidence of oxidation of Hg⁰ to gas-phase Hg-II compounds after Arctic sunrise, water air soil Pollut. Focus 1, 295–302. <https://doi.org/10.1023/A:1013171509022>.
- Loewen, M.D., Sharma, S., Tomy, G., Wang, F., Bullock, P., Wania, F., 2005. Persistent organic pollutants and mercury in the Himalaya. *Aquat. Ecosys. Health Manag.* 8 (3), 223–233. <https://doi.org/10.1080/14634980500220924>.
- Lu, J.Y., Schroeder, W.H., Keeler, G., 2003. Field intercomparison studies for evaluation and validation of the AESminiSampler™ technique for sampling and analysis of total particulate mercury in the atmosphere. *Sci. Total Environ.* 304 (1–3), 115–125. [https://doi.org/10.1016/S0048-9697\(02\)00561-2](https://doi.org/10.1016/S0048-9697(02)00561-2).
- Lu, J.Y., Schroeder, W.H., 2004. Annual time-series of total filterable atmospheric mercury concentrations in the Arctic. *Tellus B* 56 (3), 213–222. <https://doi.org/10.3402/tellusb.v56i3.16432>.
- Lucianetti, G., Penna, D., Mastrorillo, M., Mazza, R., 2020. The role of snowmelt on the Spatio-temporal variability of spring recharge in a Dolomitic mountain group. *Italian Alps, Water* 12 (8), 2256. <https://doi.org/10.3390/w12082256>.
- Mao, H., Cheng, I., Zhang, L., 2016. Current understanding of the driving mechanisms for spatiotemporal variations of atmospheric speciated mercury: a review. *Atmos. Chem. Phys.* 16, 12897–12924. <https://doi.org/10.5194/acp-16-12897-2016>.
- McClure, C.D., Jaffe, D.A., Gao, H., 2016. Carbon dioxide in the free troposphere and boundary layer at the Mt. Bachelor observatory. *Aerosol Air Qual. Res.* 16, 717–728. <https://doi.org/10.4209/aaqr.2015.05.0323>.
- Moore, C., Carpi, A., 2005. Mechanisms of the emission of mercury from soil: role of UV radiation. *J. Geophys. Res.* 110, D24302. <https://doi.org/10.1029/2004JD005567>.
- Munthe, J., Wängberg, I., Pirrone, N., Iverfeldt, Å., Ferrara, R., Ebinghaus, R., Feng, X., Gärdfeldt, K., Keeler, G., Lanzillotta, E., Lindberg, S.E., Lu, J., Mamane, Y., Prestbo, E., Schmolke, S., Schroeder, W.H., Sommar, J., Sprovieri, F., Stevens, R.K., Stratton, W., Tuncel, G., Urba, A., 2001. Intercomparison of methods for sampling and analysis of atmospheric mercury species. *Atmos. Environ.* 35, 3007–3017. [https://doi.org/10.1016/S1352-2310\(01\)00104-2](https://doi.org/10.1016/S1352-2310(01)00104-2).
- Naizta, L., Cristofanelli, P., Marinoni, A., Calzolari, F., Roccato, F., Busetto, M., Sferlazzo, D., Aruffo, E., Di Carlo, P., Bencardino, M., D'Amore, F., Sprovieri, F., Pirrone, N., Dallo, F., Gabrieli, J., Vardè, M., Resci, G., Barbante, C., Bonasoni, P., Putero, D., 2020. Increasing the maturity of measurements of essential climate variables (ECVs) at Italian atmospheric WMO/GAW observatories by implementing automated data elaboration chains. *Comput. Geosci.* 137, 104432. <https://doi.org/10.1016/j.cageo.2020.104432>.
- Obrist, D., Hallar, A.G., McCubbin, I., Stephens, B.B., Rahn, T., 2008. Atmospheric mercury concentrations at Storm Peak Laboratory in the Rocky Mountains: evidence for long-range transport from Asia, boundary layer contributions, and plant mercury uptake. *Atmos. Environ.* 42, 7579–7589. <https://doi.org/10.1016/j.atmosenv.2008.06.051>.
- Ou Yang, C.-F., Lin, N.-H., Sheu, G.-R., Lee, C.-T., Wang, J.-L., 2012. Seasonal and diurnal variations of ozone at a high-altitude mountain baseline station in East Asia. *Atmos. Environ.* 46, 279–288. <https://doi.org/10.1016/j.atmosenv.2011.09.060>.
- Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., 2006. Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020. *Sci. Total Environ.* 370 (1), 147–156. <https://doi.org/10.1016/j.scitotenv.2006.06.023>.
- Parisi, M.L., Ferrara, N., Torsello, L., Basosi, R., 2019. Life cycle assessment of atmospheric emission profiles of the Italian geothermal power plants. *J. Clean. Prod.* 234, 881–894. <https://doi.org/10.1016/j.jclepro.2019.06.222>.
- Parolini, M., Antonoli, D., Borgogno, F., Gibellino, M.C., Fresta, J., Albonico, C., De Felice, B., Canuto, S., Concedi, D., Romani, A., Rosio, E., Gianotti, V., Laus, M., Ambrosini, R., Cavallo, R., 2021. Microplastic contamination in snow from western Italian Alps. *Int. J. Environ. Res. Publ. Health* 18, 768. <https://doi.org/10.3390/ijerph18020768>.
- Pirrone, N., Costa, P., Pacyna, J.M., Ferrara, R., 2001. Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. *Atmos. Environ.* 35 (17), 2997–3006. [https://doi.org/10.1016/S1352-2310\(01\)00103-0](https://doi.org/10.1016/S1352-2310(01)00103-0).
- Poissant, L., Casimir, A., 1998. Water-air and soil-air exchange rate of total gaseous mercury measured at background sites. *Atmos. Environ.* 32, 883–893. [https://doi.org/10.1016/S1352-2310\(97\)00132-5](https://doi.org/10.1016/S1352-2310(97)00132-5).
- Prete, D., Davis, M., Lu, J., 2018. Factors affecting the concentration and distribution of gaseous elemental mercury in the urban atmosphere of downtown Toronto. *Atmos. Environ.* 192, 24–34. <https://doi.org/10.1016/j.atmosenv.2018.08.041>.
- Pyta, H., Widziewicz-Rzońca, K., Slaby, K., 2020. Inhalation exposure to gaseous and particulate bound mercury present in the ambient air over the polluted area of southern Poland. *Int. J. Environ. Res. Publ. Health* 17 (14), 4999. <https://doi.org/10.3390/ijerph17144999>.
- Reiter, R., 1990. The ozone trend in the layer of 2 to 3 km a.s.l. since 1978 and the typical time variations of the ozone profile between ground and 3 km a.s.l. *Meteorol. Atmos. Phys.* 42, 91–104. <https://doi.org/10.1007/BF01030581>.
- Scholtz, M.T., Van Heyst, B.J., Schroeder, W.H., 2003. Modelling of mercury emissions from background soils. *Sci. Total Environ.* 304, 185–207. [https://doi.org/10.1016/S0048-9697\(02\)00568-5](https://doi.org/10.1016/S0048-9697(02)00568-5).
- Schroeder, W.H., Anlauf, K.G., Barrie, L.A., Lu, J.Y., Steffen, A., Schneeberger, D.R., Berg, T., 1998. Arctic springtime depletion of mercury. *Nature* 394, 331–332.
- Schultz, M.G., Akimoto, H., Bottenheim, J., Buchmann, B., Galbally, I.E., Gilge, S., Helmig, D., Koide, H., Alastair, C., Lewis, A.C., Novelli, P.C., Plass-Dülmer, C., Ryerson, T.B., Steinbacher, M., Steinbrecher, R., Tarasova, O., Tørseth, K., Thouret, V., Zellweger, C., 2015. The Global Atmosphere Watch reactive gases measurement network. *Elem. Sci. Anth.* 3, 000067. <https://doi.org/10.12952/journal.elementa.000067>.
- Sheu, G.-R., Lin, N.-H., Wang, J.-L., Lee, C.-T., Ou Yang, C.-F., Wang, S.-H., 2010. Temporal distribution and potential sources of atmospheric mercury measured at a high-elevation background station in Taiwan. *Atmos. Environ.* 44 (20), 2393–2400. <https://doi.org/10.1016/j.atmosenv.2010.04.009>.
- Sheu, G.-R., Gay, D.A., Schmeltz, D., Olson, M., Chang, S.-C., Lin, D.-W., Nguyen, L.S.P., 2019. A new monitoring effort for Asia: the Asia Pacific mercury monitoring network (APMMN). *Atmosphere* 10 (9), 481. <https://doi.org/10.3390/atmos10090481>.
- Skov, H., Christensen, J.H., Goodsites, M.E., Heidam, N.Z., Jensen, B., Wählin, P., Geernaert, G., 2004. Fate of elemental mercury in the Arctic during atmospheric mercury depletion episodes and the load of atmospheric mercury to the Arctic. *Environ. Sci. Technol.* 38 (8), 2373–2382. <https://doi.org/10.1021/es030080h>.
- Slemr, F., 1996. Trends in atmospheric mercury concentrations over the Atlantic Ocean and at the Wank summit, and the resulting constraints on the budget of atmospheric mercury. In: Baeyens, W., Ebinghaus, R., Vasiliev, O. (Eds.), *Global and Regional Cycles: Sources, Fluxes and Mass Balances*. NATO-ASI-Series, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 33–84.
- Slemr, F., Scheel, H.E., 1998. Trends in atmospheric mercury concentrations at the summit of the Wank mountain, Southern Germany. *Atmos. Environ.* 32 (5), 845–853. [https://doi.org/10.1016/S1352-2310\(97\)00131-3](https://doi.org/10.1016/S1352-2310(97)00131-3).
- Slemr, F., Ebinghaus, R., Brenninkmeijer, C.A.M., Hermann, M., Kock, H.H., Martinsson, B.G., Schuck, T., Sprung, D., van Velthoven, P., Zahn, A., Ziereis, H., 2009. Gaseous mercury distribution in the upper troposphere and lower stratosphere observed onboard the CARIBIC passenger aircraft. *Atmos. Chem. Phys.* 9, 1957–1969. <https://doi.org/10.5194/acp-9-1957-2009>.
- Slemr, F., Weigelt, A., Ebinghaus, R., Kock, H.H., Bodevad, J., Brenninkmeijer, C.A.M., Rauthe-Schöch, A., Weber, S., Hermann, M., Becker, J., Zahn, A., Martinsson, B., 2016. Atmospheric mercury measurements onboard the CARIBIC passenger aircraft. *Atmos. Meas. Tech.* 9, 2291–2302. <https://doi.org/10.5194/amt-9-2291-2016>.
- Slemr, F., Brunke, E.-G., Labuschagne, C., Ebinghaus, R., 2008. Total gaseous mercury concentrations at the Cape Point GAW station and their seasonality. *Geophys. Res. Lett.* 35, L11807. <https://doi.org/10.1029/2008GL033741>.
- Spolaor, A., Angot, H., Roman, M., Dommergue, A., Scarchilli, C., Vardè, M., Del Guasta, M., Pedeli, X., Varin, C., Sprovieri, F., Magand, O., Legrand, M., Barbante, C., Cairns, W.R.L., 2018. Feedback mechanisms between snow and atmospheric mercury: results and observations from field campaigns on the Antarctic plateau. *Chemosphere* 197, 306–317. <https://doi.org/10.1016/j.chemosphere.2017.12.180>.
- Spolaor, A., Barbaro, E., Cappelletti, D., Turetta, C., Mazzola, M., Giardi, F., Björkman, M.P., Lucchetta, F., Dallo, F., Pfaffhuber, K.A., Angot, H., Dommergue, A., Maturilli, M., Saiz-Lopez, A., Barbante, C., Cairns, W.R.L., 2019. Diurnal cycle of iodine, bromine, and mercury concentrations in Svalbard surface snow. *Atmos. Chem. Phys.* 19, 13325–13339. <https://doi.org/10.5194/acp-19-13325-2019>.
- Sprenger, M., Wernli, H., 2015. The LAGRANTO Lagrangian analysis tool – version 2.0. *Geosci. Model Dev* 8, 2569–2586. <https://doi.org/10.5194/gmd-8-2569-2015>.
- Sprovieri, F., Pirrone, N., Bencardino, M., D'Amore, F., Carbone, F., Cinnirella, S., Mannarino, V., Landis, M., Ebinghaus, R., Weigelt, A., Brunke, E.-G., Labuschagne, C., Martin, L., Munthe, J., Wängberg, I., Artaxo, P., Morais, F., Barbosa, H.D.M.J., Brito, J., Cairns, W.R.L., Barbante, C., Diéguez, M.D.C., Garcia, P. E., Dommergue, A., Angot, H., Magand, O., Skov, H., Horvat, M., Kotnik, J., Read, K. A., Neves, L.M., Gawlik, B.M., Sena, F., Mashyanov, N., Obolkin, V., Wip, D., Feng, X. B., Zhang, H., Fu, X., Ramachandran, R., Cossa, D., Knoery, J., Mariuszczak, N., Nerentrost Mastromonaco, M., Norstrom, C., 2016. Atmospheric mercury concentrations observed at ground-based monitoring sites globally distributed in the framework of the GMOS network. *Atmos. Chem. Phys.* 16, 11915–11935. <https://doi.org/10.5194/acp-16-11915-2016>.
- Sprovieri, F., Pirrone, N., Bencardino, M., D'Amore, F., Angot, H., Barbante, C., Brunke, E.-G., Arcega-Cabrera, F., Cairns, W.R.L., Comerio, S., Diéguez, M.D.C., Dommergue, A., Ebinghaus, R., Feng, X.B., Fu, X., Garcia, P.E., Gawlik, B.M., Hageström, U., Hansson, K., Horvat, M., Kotnik, J., Labuschagne, C., Magand, O., Martin, L., Mashyanov, N., Mkololo, T., Munthe, J., Obolkin, V., Ramirez Islas, M., Sena, F., Somerset, V., Spandow, P., Vardè, M., Walters, C., Wängberg, I., Weigelt, A., Yang, X., Zhang, H., 2017. Five-year records of mercury wet deposition flux at GMOS sites in the Northern and Southern hemispheres. *Atmos. Chem. Phys.* 17, 2689–2708. <https://doi.org/10.5194/acp-17-2689-2017>.
- Stamenkovic, J., Lyman, S., Gustin, M.S., 2007. Seasonal and diel variation of atmospheric mercury concentrations in the Reno (Nevada, USA) airshed. *Atmos. Environ.* 41, 6662–6672. <https://doi.org/10.1016/j.atmosenv.2007.04.015>.
- Steffen, A., Lehnher, I., Cole, A., Ariya, P., Dastoor, A., Durnford, D., Kirk, J., Pilote, M., 2015. Atmospheric mercury in the Canadian Arctic. Part I: a review of recent field measurements. *Sci. Total Environ.* 509–510, 3–15. <https://doi.org/10.1016/j.scitotenv.2014.10.109>.

- Subir, M., Ariya, P.A., Dastoor, A.P., 2012. A review of the sources of uncertainties in atmospheric mercury modeling II. Mercury surface and heterogeneous chemistry – a missing link. *Atmos. Environ.* 46, 1–10. <https://doi.org/10.1016/j.atmosenv.2011.07.047>.
- Swartzendruber, P.C., Jaffe, D.A., Prestbo, E.M., Weiss-Penzias, P., Selin, N.E., Park, R., Jacob, D.J., Strode, S., Jaeglé, L., 2006. Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory. *J. Geophys. Res.* 111, 1–12. <https://doi.org/10.1029/2006JD007415>. D24301.
- Taurino, E., Bernetti, A., De Lauretis, R., Cordella, M., D'Elia, I., Di Cristofaro, E., Gagna, A., Gonella, B., Lena, F., Moricci, F., Pantaleoni, M., Pesci, E., Romano, D., Vitullo, M., 2019. Italian emission inventory 1990-2017, informative inventory report 2019, ISPRA Institute for environmental protection and research environmental assessment, control and sustainability department emissions, prevention of atmospheric impacts and climate change area air emission inventory unit. *Rapport 306/2019*, 1–198.
- Tekran, model, July 2012. 2537B ambient mercury Vapor Analyzer, user manual. Rev 3.12.
- Temme, C., Blanchard, P., Steffen, A., Banic, C., Beauchamp, S., Poissant, L., Tordon, R., Wiens, B., 2007. Trend, seasonal and multivariate analysis study of total gaseous mercury data from the Canadian atmospheric mercury measurement network (CAMNet). *Atmos. Environ.* 41 (26), 5423–5441. <https://doi.org/10.1016/j.atmosenv.2007.02.021>.
- Thermo Environmental Instruments Inc, 2000. Model 49C UV, Photometric O₃ Analyzer Instruction Manual P/N 9999, pp. 1–3. Franklin, MA.
- Tørseth, K., Aas, W., Breivik, K., Fjærraa, A.M., Fiebig, M., Hjellbrekke, A.G., Lund Myhre, C., Solberg, S., Yttri, K.E., 2012. Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. *Atmos. Chem. Phys.* 12, 5447–5481. <https://doi.org/10.5194/acp-12-5447-2012>.
- Travnikov, O., Iluyin, I., 2005. Regional Model MSCE-HM of Heavy Metal Transboundary Air Pollution in Europe MSC-E Technical Report 6/2005. Meteorological Synthesizing Centre-East, Moscow, Russia.
- Travnikov, O., Angot, H., Artaxo, P., Bencardino, M., Bieser, J., D'Amore, F., Dastoor, A., De Simone, F., Diéguez, M.D.C., Dommergue, A., Ebinghaus, R., Feng, X.B., Gencarelli, C.N., Hedgecock, I.M., Magand, O., Martin, L., Matthias, V., Mashyanov, N., Pirrone, N., Ramachandran, R., Read, K.A., Ryjkov, A., Selin, N.E., Sena, F., Song, S., Sprovieri, F., Wip, D., Wängberg, I., Yang, X., 2017. Multi-model study of mercury dispersion in the atmosphere: atmospheric processes and model evaluation. *Atmos. Chem. Phys.* 17, 5271–5295. <https://doi.org/10.5194/acp-17-5271-2017>.
- UNEP and, W.M.O., 2011. Integrated Assessment of Black Carbon and Tropospheric Ozone. United Nations Environment Programme, Nairobi Kenya.
- Vardè, M., Dallo, F., Cairns, W.R.L., de Blasi, F., Maffezzoli, N., Gabrieli, J., Cozzi, G., Cristofanelli, P., Naitza, L., Calzolari, F., Busetto, M., Davolio, S., Bonasoni, P., Barbante, C., 2019a. A survey of total gaseous mercury and ozone during spring and summer 2018 after characterization of air masses at the Col Margherita Atmospheric Observatory (2543 m a.s.l.) in the Italian Dolomites. In: *Proceedings of the EGU General Assembly 2019*, April 7–12, 2019. Wien, Austria, vol. 21. Geophysical Research Abstracts. <https://meetingorganizer.copernicus.org/EGU2019/EGU2019-17017-4.pdf>.
- Vardè, M., Servidio, A., Vespasiano, G., Pasti, L., Cavazzini, A., Di Traglia, M., Rosselli, A., Cofone, F., Apollaro, C., Cairns, W.R.L., Scalabrin, E., De Rosa, R., Procopio, A., 2019b. Ultra-trace determination of total mercury in Italian bottled waters. *Chemosphere* 219, 896–913. <https://doi.org/10.1016/j.chemosphere.2018.12.020>.
- Vardè, M., 2021. Studio della distribuzione di mercurio in matrici ambientali (Study of mercury distribution in environmental matrices). Ph.D. Thesis. Doctoral Degree Programme in Chemical Sciences, Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Ferrara, Italy. <http://hdl.handle.net/11392/2453488>.
- Vaselli, O., Higuera, P., Nisi, B., Esbric, J.M., Cabassi, J., Martínez-Coronado, A., Tassi, F., Rappuoli, D., 2013. Distribution of gaseous Hg in the Mercury mining district of Mt. Amiata (Central Italy): a geochemical survey prior the reclamation project. *Environ. Res.* 125, 179–187. <https://doi.org/10.1016/j.envres.2012.12.010>.
- Wahsha, M., Bini, C., Zilioli, D., Spiadorello, M., Gallo, M., 2014. Potentially harmful elements in terraced agroecosystems of NE Italy: geogenic vs anthropogenic enrichment. *J. Geochem. Explor.* 144 (B), 355–362. <https://doi.org/10.1016/j.gexplo.2014.01.012>.
- Wan, Q., Feng, X., Lu, J., Zheng, W., Song, X., Han, S., Xu, H., 2009. Atmospheric mercury in Changbai Mountain area, northeastern China I. The seasonal distribution pattern of total gaseous mercury and its potential sources. *Environ. Res.* 109, 201–206. <https://doi.org/10.1016/j.envres.2008.12.001>.
- Wang, T., Wong, H.L.A., Tang, J., Ding, A., Wu, W.S., Zhang, X.C., 2006. On the origin of surface ozone and reactive nitrogen observed at a remote mountain site in the northeastern Qinghai-Tibetan Plateau, western China. *J. Geophys. Res. Atmos.* 111, D08303. <https://doi.org/10.1029/2005jd006527>.
- Wängberg, I., Nerentorp Mastromonaco, M.G., Munthe, J., Gärdfeldt, K., 2016. Airborne mercury species at the Råö background monitoring site in Sweden: distribution of mercury as an effect of long-range transport. *Atmos. Chem. Phys.* 16, 13379–13387. <https://doi.org/10.5194/acp-16-13379-2016>.
- Wängberg, I., Munthe, J., Berg, T., Ebinghaus, R., Kock, H.H., Temme, C., Bieber, E., Spain, T.G., Stolk, A., 2007. Trends in air concentration and deposition of mercury in the coastal environment of the North Sea Area. *Atmos. Environ.* 41, 2612–2619. <https://doi.org/10.1016/j.atmosenv.2006.11.024>.
- Warneck, P., 1999. In: *Chemistry of the Natural Atmosphere*, 2nd ed. Elsevier, New York.
- Weiss-Penzias, P., Jaffe, D.A., Swartzendruber, P., Dennison, J.B., Chand, D., Hafner, W., Prestbo, E., 2006. Observations of Asian air pollution in the free troposphere at Mount Bachelor Observatory during the spring of 2004. *J. Geophys. Res.* 111, D10304. <https://doi.org/10.1029/2005JD006522>.
- Weiss-Penzias, P., Amos, H.M., Selin, N.E., Gustin, M.S., Jaffe, D.A., Obrist, D., Sheu, G.-R., Giang, A., 2015. Use of a global model to understand speciated atmospheric mercury observations at five high-elevation sites. *Atmos. Chem. Phys.* 15, 1161–1173. <https://doi.org/10.5194/acp-15-1161-2015>.
- Wernli, H., Davies, H.C., 1997. A Lagrangian-based analysis of extratropical cyclones. I: the method and some applications. *Q. J. Roy. Meteorol. Soc.* 123, 467–489. <https://doi.org/10.1002/qj.49712353811>.
- Witt, E.L., Kolka, R.K., Nater, E.A., Wickman, T.R., 2009. Forest fire effects on mercury deposition in the boreal forest. *Environ. Sci. Technol.* 43 (6), 1776–1782. <https://doi.org/10.1021/es802634y>.
- WMO, World Meteorological Organization, 2013. Guidelines for continuous measurements of ozone in the troposphere. GAW Report 209, WMO No 1110. http://library.wmo.int/doc_num.php?explnum_id=7814.
- Xin, M., Gustin, M.S., 2007. Gaseous elemental mercury exchange with low mercury containing soils: investigation of controlling factors. *Appl. Geochem.* 22, 1451–1466. <https://doi.org/10.1016/j.apgeochem.2007.02.006>.
- Yin, X., Kang, S., de Foy, B., Cong, Z., Luo, J., Zhang, L., Ma, Y., Zhang, G., Rupakheti, D., Zhang, Q., 2017. Surface ozone at Nam Co in the inland Tibetan Plateau: variation, synthesis comparison and regional representativeness. *Atmos. Chem. Phys.* 17, 11293–11311. <https://doi.org/10.5194/acp-17-11293-2017>.
- Yin, X., Kang, S., de Foy, B., Ma, Y., Tong, Y., Zhang, W., Wang, X., Zhang, G., Zhang, Q., 2018. Multi-year monitoring of atmospheric total gaseous mercury at a remote high-altitude site (Nam Co, 4730m a.s.l.) in the inland Tibetan Plateau region. *Atmos. Chem. Phys.* 18, 10557–10574. <https://doi.org/10.5194/acp-18-10557-2018>.
- Yu, B., Wang, X., Lin, C.-J., Fu, X.W., Zhang, H., Shang, L.H., Feng, X.B., 2015. Characteristics and potential sources of atmospheric mercury at a subtropical near-coastal site in East China. *J. Geophys. Res. Atmos.* 120, 8563–8574. <https://doi.org/10.1002/2015JD023425>.
- Žagar, D., Sirník, N., Četina, M., Horvat, M., Kotnik, J., Ogrinc, N., Hedgecock, I.M., Cinnirella, S., De Simone, F., Gencarelli, C.N., Pirrone, N., 2014. Mercury in the Mediterranean. Part 2: processes and mass balance. *Environ. Sci. Pollut. Res.* 21, 4081–4094. <https://doi.org/10.1007/s11356-013-2055-5>.
- Zhang, H., Fu, X.W., Lin, C.-J., Wang, X., Feng, X.B., 2015. Observation and analysis of speciated atmospheric mercury in Shangri-La, Tibetan Plateau, China. *Atmos. Chem. Phys.* 15, 653–665. <https://doi.org/10.5194/acp-15-653-2015>.
- Zhang, H., Fu, X., Lin, C.-J., Shang, L., Zhang, Y., Feng, X., Lin, C., 2016. Monsoon-facilitated characteristics and transport of atmospheric mercury at a high-altitude background site in southwestern China. *Atmos. Chem. Phys.* 16, 13131–13148. <https://doi.org/10.5194/acp-16-13131-2016>.
- Zysk, J., Wyrwa, A., Pluta, M., 2011. Emissions of mercury from the power sector in Poland. *Atmos. Environ.* 45 (3), 605–610. <https://doi.org/10.1016/j.atmosenv.2010.10.041>.