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Research paper

PM_{10}-bound arsenic emissions from the artistic glass industry in Murano (Venice, Italy) before and after the enforcement of REACH authorisation

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ABSTRACT

The island of Murano (Venice, Italy) is famous worldwide for its artistic glass production. Diarsenic trioxide was a main ingredient of the raw glass mixture until 2015, when the authorisation process of European REACH Regulation (Registration Evaluation Authorisation of Chemicals) entered into force, effectively forbidding the use of arsenic. A total of 3077 PM_{10} samples were collected across the Venice area in 2013–2017. This period included the REACH Sunset Date (May 2015). High arsenic concentrations were recorded in Murano before the Sunset Date (average 383 ng/m^3), representing a serious concern for public health. Other sites in Venice complied with the EU target value. In 2013, concentrations were 36-folds higher than model estimation computed over the maximum-allowed emission scenario. Polar plot analysis indicated Murano as the major source of arsenic contamination. The concentration significantly dropped after the REACH implementation, thus meeting the European target values. However, high peaks of arsenic were still detected; inspections on raw and finished glass materials confirmed that some factories were still using arsenic. Results reported serious airborne arsenic pollution in Murano before the REACH implementation. This work represents an interesting case study on the effectiveness of the European REACH process.

1. Introduction

The artistic glass production in Venice (Italy) has a thousand-year history, dating back to the VII century BC. In 1291, all the workshops in the city centre were moved to the island of Murano (Fig. 1) in order to prevent outbreaks of fires due to the glassmaking activity, moreover, there was the aim to isolate and preserve "secret recipes" of glass composition, engineering and manufacturing. From that moment onward, the glass production was strictly confined to Murano, contributing to the technological development through centuries of research and experimentation (Tagliapietra, 1996; Toninato, 2003; Zecchin, 2003). The artistic glass sector in Murano underwent a serious decline during the last century due to market globalisation, the illegal competition of the counterfeit market, and the technological developments that has made this ancient artisan technique basically uncompetitive. Consequently, many factories decided to move their glass production to the mainland or other countries. Despite the rapid decline of the glass sector, Murano still hosts a large number of studio-workshops and small factories scattered on the highly populated island (~4500 inhabitants over 1.2 km^2).

The main raw materials used in the art glass production include silica sand (SiO_2), alkali feldspars, borax ($Na_2B_4O_7{\cdot}10H_2O$), and aluminium oxide (Al_2O_3). The glass mixture is mixed with alkali carbonates (Na_2CO_3, K_2CO_3) aiming to drop the melting temperature of the glass. Stabilisers (e.g., dolomite ($CaMg(CO_3)_2$), Pb_3O_4, and ZnO) are present to reinforce the glass structure and to improve its chemical and physical

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properties along with several dye elements added in different oxidation states (e.g. Ti, Cr, Mn, Fe, Co, Ni, Cu, Se, Ag, Cd, Au). The melted glass mixture generally presents gas bubbles originating from the decomposition of raw materials (e.g., added carbonates and dolomite) which release CO_2 to form CaO and MgO. Gas bubbles are then eliminated by adding the so-called refining agents (e.g., As_2O_3, Sb_2O_3, CaF, $NaNO_3$). Historically, every factory conserved a "secret recipe" to produce its own glass, however, arsenic trioxide was widely used (Apostoli et al., 1998; Rampazzo et al., 2008; Constantinescu et al., 2018). The transition between As(III) and As(V) at ~1200 °C releases oxygen stripping gases out from the glass mixture. Refining agents can be also added for secondary purposes, such as producing a more transparent glass, obtaining specific colours, or helping to remove unwanted colours of the raw glass after the addition of additives (Vogel, 1994).

For centuries, emissions from traditional furnaces were uncontrolled. Exhaust gases were released directly into the open air from the melting ovens through chimneys that were relatively low and had no abatement devices. The adoption of higher chimneys and stricter safety and security criteria started in the '50-'70s of the last century. The European Directives on air quality were implemented and local authorities were able to propose incentives for investing in new technologies since the early 2000s. However, these changes were difficult to implement, due to a unique urban structure with a high density of population, and without separation between residential and productive activities. Also, local cultural/artistic heritage constraints caused the use of suboptimal technical solutions (Spagnolo et al., 2018).

Consequently, arsenic contamination was found in water, sediment and biota surrounding Murano Island (Giusti and Zhang, 2002), and atmospheric pollution was pointed out in several studies (Guerzoni et al., 2005; Rossini et al., 2010; Stortini et al., 2009; Masiol et al., 2014; Valotto et al., 2014). The geochemical fingerprint of the glassmaking industry, made up of As, Cd and Se, was widely detected in atmospheric depositions across the Venice Lagoon (Guerzoni et al., 2005), PM_{10} (Rampazzo et al., 2008; Rossini et al., 2010), $PM_{2.5}$ (Stortini et al., 2009; Masiol et al., 2014), and PM_1 (Valotto et al., 2014). This pollution was also detected over a wide area encompassing the historic city centre of Venice, the mainland and the coastal area (Masiol et al., 2014). Generally, high concentrations of arsenic were reported in PM_{10} collected daily in the surrounding area of Murano (60–181 ng/m^3) (Rampazzo et al., 2008; Rossini et al., 2010) as well as in biological fluids of glassworkers (Apostoli et al., 1998).

Results of these studies raised serious concerns for public health since arsenic is classified as a "carcinogenic to humans" (group I) by the International Agency for Research on Cancer (International Agency for Research on Cancer IARC, 2009). As_2O_3 is also classified as carcinogenic for skin and lungs according to the European Classification, Labelling and Packaging Regulation (CLP EC Regulation 1272/2008) (European Commission EC, 2018). The World Health Organization reports an excess lifetime risk level of 1:10000 with an air concentration of about 66 ng/m^3 (World Health Organization WHO, 2000). These concentrations were comparable to previous studies in Murano (Rampazzo et al., 2008; Rossini et al., 2010). Following the biological evidence of adverse health effects due to airborne arsenic exposure, a target year average of 6.0 ng/m^3 arsenic in PM_{10} was fixed as a European air quality target value (Directive 2004/107) to be met by December 31, 2012 (European Parliament and Council of the European Union, 2004).

During 2013–2017, the Environmental Protection Agency for the Veneto Region (ARPAV) carried out some monitoring campaigns to investigate the impacts of the local glass industry on the air quality in Murano. In the meantime, the ban of As_2O_3 came into force in compliance with the European REACH Regulation EC 1907/2006. The REACH Regulation (Registration Evaluation Authorisation of Chemicals; EC 1907/2006) (The Comission of the European Communities, 2006) was implemented in 2006 aiming to assure a high- level protection of human health and the environment; it also aims to achieve earlier identification of the intrinsic properties of chemicals. The process included registration, evaluation, authorisation and eventual restrictions of certain substances in use. It also aimed to enhance the innovation and competitiveness of the EU chemical industry. Before any authorisation, a potential chemical substance was inserted in the so-called "Candidate List" for prioritisation and defined as Substances of Very High Concern (SVHC). Arsenic was classified as SVHC, thus the As_2O_3 use was limited while suitable alternatives were proposed and tested (Giubilato et al., 2016). The deadline for the use of arsenic, also legally referred to as the "Sunset Date", was set on May 21, 2015.

This study aims to: (i) estimate the dispersion of exhaust fumes from the authorised glass workshops and factories in Murano before the Sunset Date established by the application of the REACH authorisation through the implementation of an advanced non-steady-state air dispersion modelling system; (ii) compare the model results with the arsenic concentrations experimentally quantified in 3077 PM_{10} samples collected in 4 sites before and after the Sunset Date; (iii) investigate the source location of As by using polar plot analyses to detect the major source areas; (iv) to estimate the background As concentration in the area and understand the real impact of the glassmaking industry; (v) to verify the drop of concentrations after REACH authorisation implementation; and (vi) detect potential unauthorised use of As after the Sunset Date.

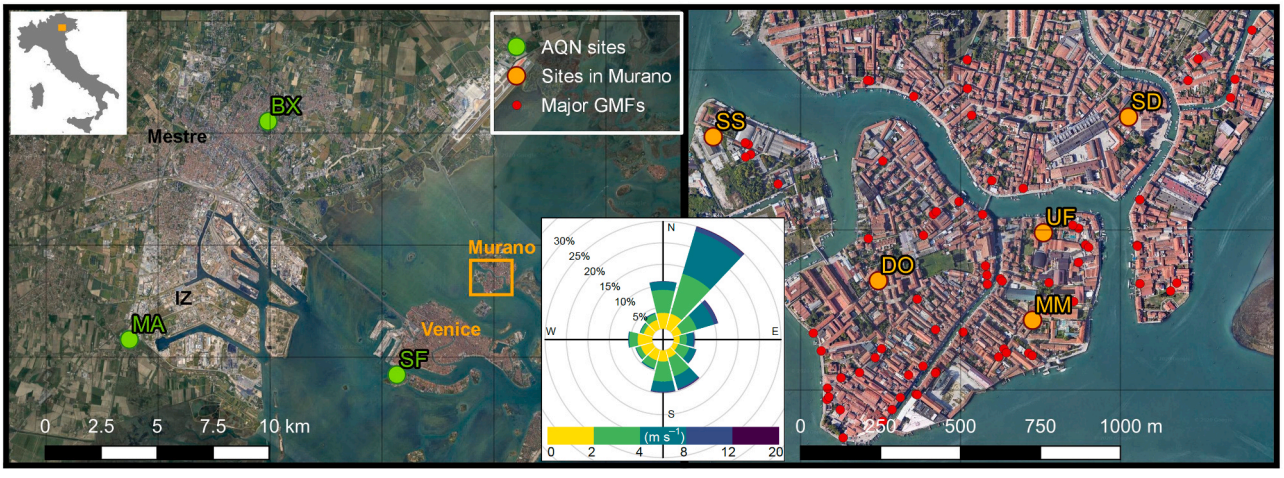

Fig. 1. Map of the study area (left) showing the city center of Venice, the mainland city of Mestre, the location of the main industrial zone (IZ) of Porto Marghera, and the Island of Murano. The southern part of Murano (highlighted on the left) is zoomed in the right panel. The wind rose (2013–2017 data) is also reported (centre).

2. Materials and methods

2.1. Modelling system

The CALMET-CALPUFF v.5.8 (Scire et al., 2000a, 2000b) is an advanced non-steady-state meteorological and air dispersion model system adopted by the U.S. Environmental Protection Agency. It is a suitable model for near-field application involving complex meteorological conditions such as overwater transport and coastal environments or light wind speed and calm wind conditions. Thus, this model represented a suitable solution to estimate the airborne arsenic dispersion in weather conditions typical of the Venice area and Po Valley (Benassi et al., 2011).

Information about the number and size of glassmaking factories (GMFs) active in Murano during 2013 was provided by the local authorities (Venice Board of Trade, the Italian Institute for Accident Insurance at Work, and the Metropolitan Authority of Venice). A total of 76 authorised GMFs were identified. As a precautionary emission scenario, it was assumed that during the melting-phase all chimneys serving the furnace were emitting at the standard emission limit set by the Italian permitting regulation (D.lgs 152/2006) for arsenic, that is 0.5 mg/Nm^3 (concentrations which are presented at normal pressure and temperature: 101.325 kPa and 273.15 K) for the stack flow as a whole, considering both particle and gas phase. Furnace stacks emissions were considered constant for all the 24 h since a different daily pattern was unknown (only half of the firms provided this information to the local Environmental Agency).

This hypothesis represents the maximum theoretical input of the GMFs emissions into the atmosphere considering the compliance to the standard authorisation. The model application did not consider emissions potentially occurring under conditions of not-steady state operation, such as anomalies or disservices. The assumption of such a high emission rate was checked to be coherent with the amount of raw arsenic used in the glass industry manufacturing.

A 20 × 20 km^2 computational domain was used for CALMET model with a resolution grid of 500 m centred in Murano. This domain was a downscaling of a regional domain with a 200 × 168 km^2 extension (4 km resolution grid), encompassing the mountains (Alps) and flatland (Po Valley) of the Veneto region (Sansone et al., 2005). The CALMET model was implemented from observed data recorded at surface meteorological stations of the regional area operated by ARPAV, the Italian Air Force Met Service, and a local station of a private industrial network (station EZI5 Ente Zona Industriale – Porto Marghera). Meteorological data over the Adriatic Sea were collected from the CNR research platform of the Municipality of Venice, located ~8 miles east from the coastline (Cavaleri, 2000). Upper air data were retrieved from three of the nearest RAOB Sounding Stations (Milan, Udine, and Bologna). Details are reported in Table S1.

2.2. Experimental and QA/QC

ARPAV manages a total of 4 air quality network (AQN) stations in the Venice area (Fig. 1, Table 1) used to routinely analyse As, Cd, Ni, Pb, and polycyclic aromatic hydrocarbons in PM_{10}. Ugo Foscolo (UF) is located in a residential area of Murano and is surrounded by several GMFs and should be considered as the reference site for the artistic glass pollution. Sacca Fisola (SF) is an urban background station located in the historical city centre of Venice. It is situated about 3 km SW from the southern border of Murano Island. Bissuola (BX) is an urban background station located in a public park in Mestre, the mainland conurbation of Venice (Fig. 1), and is considered the long-term reference station for air quality in the entire area. Malcontenta (MA) is a station located in a suburban area near the large industrial area of Porto Marghera which is the inner harbour of Venice devoted essentially to commercial and industrial operators.

The AQN sites were active between February 2013 and December 2017 except for MA (starting on January 2014; Table 1). Additional 4 sites (SD, DO, SS, and MM) were temporarily placed in Murano to catch specific possible point sources during shorter (4.5–10 months) sampling campaigns carried out after the Sunset Date (Table 1).

A total of 3077 PM_{10} samples were collected daily (24 h, starting at midnight) and analysed for arsenic. Samples were collected on quartz fibre filters (47 mm Ø, Whatman QMA, GE Healthcare, USA) using low-volume samplers (2.3 m^3/h) set according to the European standards UNI EN 12341:2001 and UNI EN 12341:2015. PM_{10} mass was gravimetrically measured (48 h conditioning at 20 ± 1 °C and 50 ± 5% RH). Arsenic was analysed according to the UNI EN 14902:2005 standard. Briefly, microwave-assisted (Digestion Rotor Mars X and Mars 5 – CEM, Italy) acid digestion was performed using 8 mL HNO_3 (Fluka ≥69% TraceSELECT, Honeywell Morris Plains, NJ, USA) and 2 mL of hydrogen peroxide (Fluka ≥30% TraceSELECT with declared As ≤ 0.1 μg/kg). The obtained solution was transferred in a 50 mL vessel with ultrapure water (<18.2 MΩ cm at 25 °C) and analysed with an ICP-MS with collision/reaction cells (Agilent 7700x, Santa Clara, CA, USA).

The limit of detection (LOD) of the method for arsenic was calculated according to the European standard (UNI EN 14902:2005) and corresponds to 1 ng/m^3. Data below LOD were set to LOD/2. The NIST SRM1648a "urban dust" was used as certified standard reference material. Recoveries were in the 85 – 115% range. During the 4 years of monitoring, ARPAV laboratory was accredited on EN ISO/IEC 17025:2005, and participated in several international proficiency tests; the median of the standard deviation of the analytical results was used to calculate the uncertainty of the method, i.e. CV% of 8.3% for the ICP-MS analysis.

2.3. In situ screening analysis

After the Sunset Date, on-field screening determination of arsenic was performed on 101 raw materials, unknown powders and raw glass

Table 1
Characteristics of sampling sites. BRN=number of analyzed samples.

				Sampling periods before Sunset Date		Sampling periods after Sunset Date	
Site ID	Site full name	Lat	Lon	Start	End	Start	End
Reference site for Murano							
UF	Scuola Ugo Foscolo	45.455	12.354	28–02–13	02–11–14	02–09–15	31–12–17
Air quality network							
SF	Sacca Fisola	45.428	12.313	28–02–13	02–11–14	02–09–15	30–12–17
BX	Parco Bissuola	45.500	12.261	02–03–13	02–11–14	02–09–15	30–12–17
MA	Malcontenta	45.438	12.206	19–06–14	01–11–14	03–09–15	22–12–17
Sites in Murano							
SD	Campo San Donato	45.458	12.357	–	–	15–07–16	15–05–17
DO	Calle Dietro gli Orti	45.454	12.350	–	–	01–07–16	16–05–17
MM	Calle Marco da Muran	45.454	12.354	–	–	18–05–17	31–12–17
SS	Sacca Serenella	45.457	12.345	–	–	26–05–17	28–12–17

mixtures, and finished glass items prepared by randomly selected GMFs. In-situ screening analyses were performed with a portable X-ray fluorescence spectrometer xSORT (SPECTRO Analytical Instruments GmbH, Kleve, Germany) equipped with a miniaturized X-ray tube 50 kV and Rh anode (European Chemicals Agency ECHA, 2016; MILIEU, 2012; Desroches et al., 2018). A content above 0.1% of arsenic was detected in 7 samples. These samples were then collected in 5 aliquots and sent to ARPAV labs for confirmation analysis according to the UNI EN 16170:2016 standard.

2.4. Data processing

Statistical analyses were performed using R 3.6.1 (R Core Team, 2019) and a number of packages, including "plyr" (Wickham, 2011), "zoo" (Zeileis and Grothendieck, 2005), "lubridate" (Grolemund and Wickham, 2011), "reshape" (Wickham, 2007), and "openair" (Carslaw and Ropkins, 2012). Wind speed and direction data were retrieved from a site located in the city centre of Venice, which should be considered as representative of the entire study area. Polar plot analysis (Carslaw et al., 2006) and conditional bivariate probability functions (CBPFs) (Uria-Tellaetxe and Carslaw, 2014) were used to locate the potential sources of arsenic. Essentially, these methods map the As concentration by wind speed and direction as a continuous surface; polar plots map the mean concentration, while CBPF maps assess the probability to exceed a threshold concentration (75th percentile, in this case) would have been exceeded. Since wind data was hourly-measured and PM_{10} samples were collected daily, these analyses were performed by applying the 24-h concentration for every hour in a day.

3. Results and discussion

3.1. Modelling simulation

North-easterly winds are dominant in the Venice area (Fig. 1), but sea breeze regimes occur during the warmest seasons leading to south-easterly winds during the daytime and from NE during the night-time (Fig. S1). Under this view, Venice downtown is downwind to Murano for most of the year. In addition, the area undergoes frequent periods of slow or no wind lasting for several consecutive days and frequent wintertime thermal inversions favouring the accumulation of locally emitted pollutants (Masiol et al., 2014; Pecorari et al., 2013; Squizzato and Masiol, 2015).

The model simulation was run before Sunset Date (2013) to verify compliance with the target value even when all GMF were contemporary working and to compare modelling outcomes against data from the UF site. Model results (Fig. 2) estimated that the target value for As (average annual mean 6.0 ng/m^3) will not be attained for the most of the Murano Island, while annual average concentrations exceeding 3 ng/m^3 (half target value) were estimated across most of the historical centre of Venice. The maximum concentration (23 ng/m^{3}As) was estimated in the South-East area of Murano, while the concentration estimated at the UF site location was 14.5 ng/m^3. Generally, the GMF emission dispersion extended toward South-West and North-West to Murano, following the two main wind regimes in the study area linked to sea-land breezes. Similar model outcomes (Rampazzo et al., 2008) were previously obtained using a simple Gaussian plume model to predict the main areas affected by the total suspended particles emitted from the glassmaking industry over a short period extending a few months (winter-spring 2001–2002).

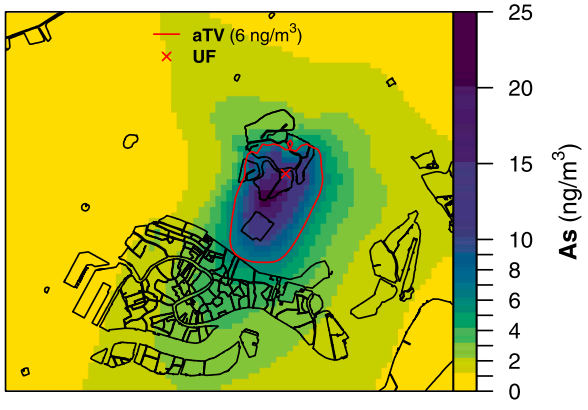

Fig. 2. Results of the CALMET-CALPUFF v.5.8 modelling system. The area with estimated concentration over the European annual target value (6 ng/m^3) is highlighted in red (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The dispersion calculations estimated that the maximum ground concentrations associated with a single chimney occurred in a limited spatial range (within 200 m), which was very close to the emission points. This result raised serious concerns for public health and reflects the suboptimal setups of the emission chimneys and mitigation measures as well as the peculiar weather condition in the area. The GMF chimneys are generally not very high (often protruding from the top of the factory roofs, up to 12 m above the ground) due to cultural/artistic heritage protection constraints.

In addition, the furnace flows are emitted at a relatively low temperature (around 100 °C). A large amount of ambient air is introduced into the ovens during the glass production by suction hoods placed in front of the furnaces. Fans are commonly used at low speeds to extract the fumes to the chimneys.

3.2. Experimental data

The model estimation was set to depict the worst emission scenario, as the 76 GMFs was considered to emit a maximum of authorised concentrations (0.5 mg/Nm^3). However, the average annual concentration experimentally measured in UF during 2013 was 528 ng/m^3 (Table 2), i.e. 88-folds higher than the European target value (Fig. 3) and 36-folds higher than the model estimation. The daily concentration measured at UF during 2013 exhibited a variable time-series (Fig. 4) depicting extremely high peaks exceeding 1 μg/m^3 measured during few days (N = 21); these high-concentration samples strongly affected the annual average. The annual average excluding the samples with concentrations >1 μg/m^3 was 139 ng/m^3, i.e. 23-folds higher than the annual target value. The maximum As concentration (5.3 μg/m^3 on a total of 67 μg/m^3 PM_{10}) was measured on October 10th, 2013, when the wind direction comes from the south (III and IV quadrants, Fig. S2). This result is extremely worrying and represents a serious concern for public health. This situation is even more serious considering that UF is placed in the backyard of a primary school. The model also predicted a concentration of 1.2 ng/m^3 at SF, while the average concentration in 2013 from experimental results was 4.2 ng/m^3 (4.7 ng/m^3 when considering the same sampling period as UF (Table 2).

The disagreements between the model outcomes and the experimental results can be explained with the presence of totally illegal GMFs or the incorrect use of abatement systems by those authorized. Additional sources of As in PM_{10}, $PM_{2.5}$ and PM_1 were extensively investigated in the Venice area with source apportionment studies. In addition to the GMFs source (Rossini et al., 2010; Stortini et al., 2009; Masiol et al., 2014), studies carried out on the mainland (Masiol et al., 2014; Valotto et al., 2014; Squizzato et al., 2016; Squizzato et al., 2014) also identified road traffic, fossil fuels combustion, and industrial processes in the industrial zone of Porto Marghera (Fig. 1), including a major thermoelectric power plant burning coal and waste-derived fuel, incinerators and other industrial emissions. The arsenic concentration measured at UF before the Sunset Date was then compared with samples collected at 3 AQN sites in the same period (Fig. 3). Results did not show anomalously high arsenic concentrations at other AQN sites (averages during the entire before Sunset Date period: SF 4.3 ng/m^3, BX 2.6 ng/

Table 2
Statistics for samples collected on periods with UF data available. LOD=limit of detection (1 ng/m^3); Data below LOD were set to LOD/2.

	2013				Before Sunset Date (2013–2015)				After Sunset Date (2015–2017)			
	N	Mean(± St.Dev)	Median	Min-Max	N	Mean(± St.Dev)	Median	Min-Max	N	Mean(± St.Dev)	Median	Min-Max
UF	122	528 (± 1019)	96	3–5280	241	383 (± 841)	70	2–5280	593	5.4 (± 6.7)	3	<LOD–47
SF	119	4.7 (± 5.4)	3	<LOD–41	235	4.3 (± 4.3)	3	<LOD–41	338	1 (± 0.9)	1	<LOD–5
BX	68	3.1 (± 4)	2	<LOD–21	140	2.6 (± 3)	2	<LOD–21	313	0.9 (± 0.7)	1	<LOD–5
MA	–	–	–	–	79	1.2 (± 1.3)	1	<LOD–9	102	0.7 (± 0.4)	1	<LOD–2
SD	–	–	–	–	–	–	–	–	293	1.9 (± 3.7)	1	<LOD–51
DO	–	–	–	–	–	–	–	–	311	5.4 (± 10)	3	<LOD–103
MM	–	–	–	–	–	–	–	–	225	3.5 (± 3.1)	3	<LOD–21
SS	–	–	–	–	–	–	–	–	207	1.4 (± 1.4)	1	<LOD–8

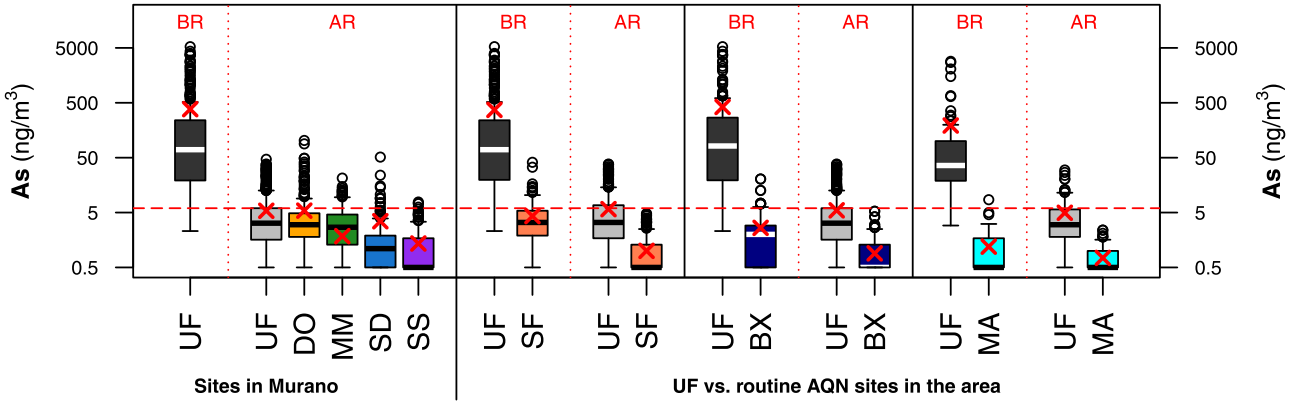

Fig. 3. Boxplots of the concentrations of PM_{10}-bound arsenic measured at each site before (BR) and after (AR) the REACH authorisation implementation, i.e. before/after the Sunset Date. Boxplots: line = median, box = inter-quartile range, whiskers = ± 1.5 *inter-quartile range; black dots = outliers and extremes, red crosses = arithmetic means.

m^3, MA 1.2 ng/m^3; Table 2). A more rigorous pairwise comparison amongst AQN sites was performed by accounting for days with data concurrently available for both sites. Results clearly show that the average As concentration were 86, 160 and 161 folds higher in UF than in SF, BX and MA, respectively (21, 41 and 72 folds higher when comparing the medians). Nonparametric Kruskal–Wallis and Wilcoxon tests on rank sums indicated that arsenic concentration measured at UF were always statistically different ($p < 0.05$) than in the other 3 AQN sites. Under this view, it is evident that GMFs are the dominant source of arsenic in Murano and in the whole Venetian area.

A deeper investigation on the potential source locations of airborne arsenic was assessed at each site by matching concentrations measured before Sunset Date with wind data and by applying polar plot and CBPFs analysis. Results (Figs. S3-S4) show that the higher average concentration of As in Murano occurs when winds blow from the south towards the UF site. On the contrary, the maximum concentrations at SF are measured with winds blowing from NNE, confirming that major sources of As lie in the southern part of Murano. Despite the distance up to 10 km away from Murano, increased concentrations of As were also measured at the two mainland sites (BX and MA) during low wind regimes blowing from Murano. This result confirms the potential influence of GMF emissions across the whole study area, as reported in previous studies (Masiol et al., 2014).

3.3. Implementation of the REACH Regulationregulation

PM-bound arsenic pollution has been analysed in several areas affected by industrial emissions across Europe (e.g., Sánchez-Rodas et al., 2007; Sánchez de la Campa et al., 2008, 2015, 2018, 2020; Šerbula et al., 2010; Cusack et al., 2012; García-Aleix et al., 2014; Pokorná et al., 2018; Goddard et al., 2019; Chen et al., 2016, 2012), but the analysis of the long-term trend of this element was limited by the relatively small number of stations in Europe before 2014 (Guerreiro et al., 2014). Most of the long-term trend studies reported significant decreases in arsenic concentration (Šerbula et al., 2010; Cusack et al., 2012; García-Aleix et al., 2014; Pokorná et al., 2018; Sánchez de la Campa et al., 2018; Goddard et al., 2019), mostly attributed to the adoption of best technologies, technological developments, and the implementation of European Directives. However, the evidence that the implementation of the REACH authorisation was able to successfully improve air quality in an industrial area is still lacking. Thus, data collected in Murano after the REACH implementation for arsenic (i.e. after the Sunset Date) are of extreme importance to verify the respect of the imposed ban in artistic glass production. Experimental results show a strong and statistically significant (Kruskal–Wallis ANOVA test) drop of concentrations recorded in UF, i.e. an average of 5.4 ng/m^3 complying with the EU target limit value of 6.0 ng/m^3. The EU target value was also attained at the other sites set in Murano after the REACH authorisation implementation (DO 5.4 ng/m^3, MM 3.5 ng/m^3, SD 1.9 ng/m^3, and SS 1.4 ng/m^3; Fig. 3). Apart from the sites in Murano, the arsenic concentrations also dropped all over the study area after Sunset Date, with statistically significant decreases recorded at the 3 AQN sites (SF, BX, MA). This result points out the extension of the GMF pollution, spanning over an area of ~100 km^2.

Despite these results show the positive feedback of the application of the REACH Regulation, time series (Fig. 3) still showed various high concentration peaks (maximum concentrations: DO 103 ng/m^3, SD 51 ng/m^3, UF 47 ng/m^3, MM 21 ng/m^3, and SS 8 ng/m^3). It was therefore evident that some firms were still using arsenic for glass production, probably utilising arsenic stocks purchased before the Sunset Date. Polar plot and CBPF analyses (Figs. S5-S8) showed that it was still possible to identify the southern part of Murano as a potential source location of arsenic, but the signal of GMF emissions in mainland sites was still not detected. In particular, the CBPF analysis on Murano sites (Fig. S8) showed a higher probability of a high concentration due to winds consistently blowing from the southern part of the island.

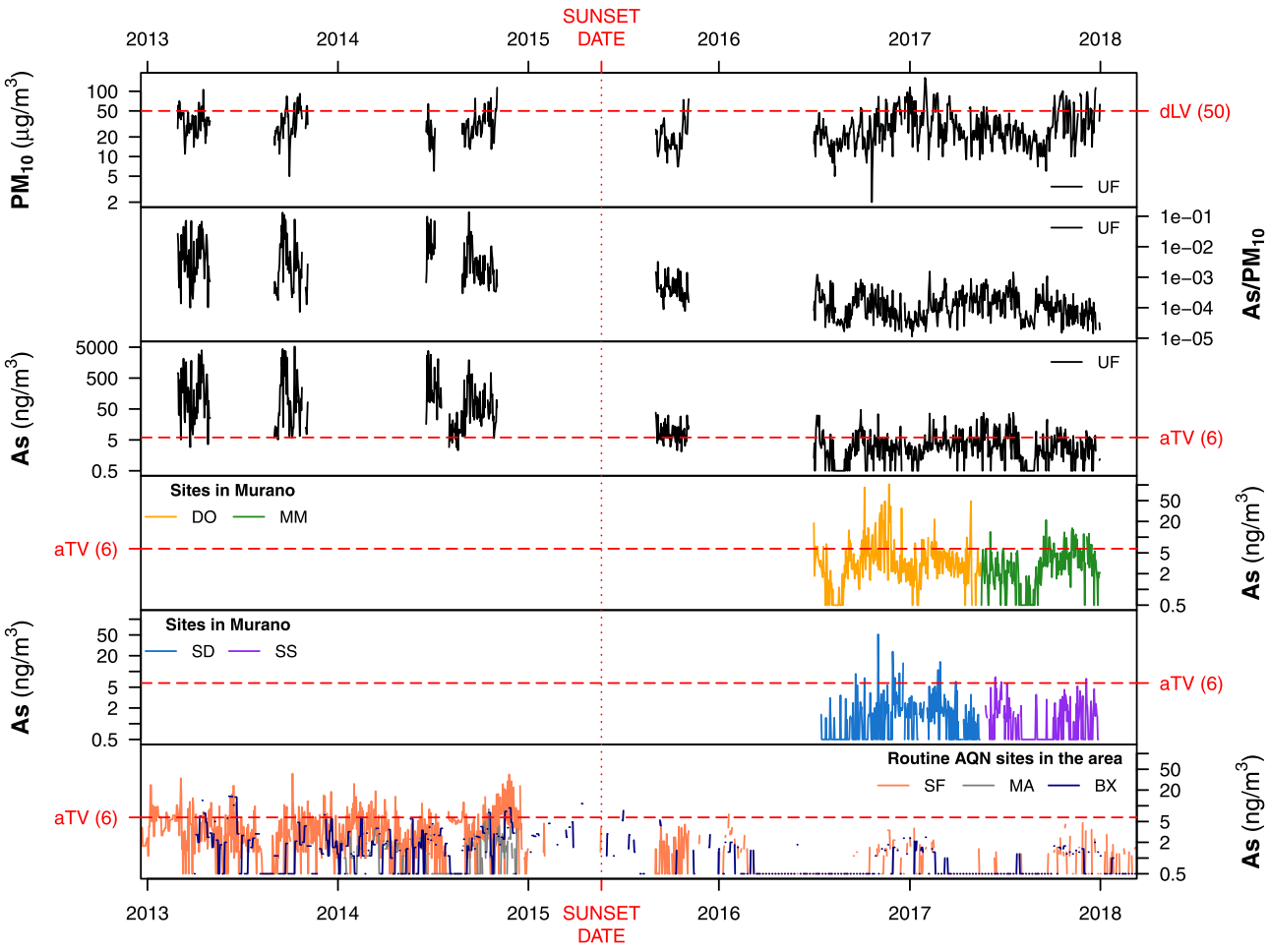

Fig. 4. Time-series showing the concentrations of PM10, arsenic and As/PM10 ratio measured at the UF site (3 plots on the top), sites located in Murano (4th plot) and AQN network sites (bottom plot).

However, the additional contribution of other locally-emitted arsenic sources (e.g., from the industrial zone of Porto Marghera) cannot be disregarded.

3.4. Veneto Regionregion action plan to ban of arsenic trioxide through inspections

At the beginning of 2015, some artistic glass production companies claimed As_2O_3 to be considered as "transported by an isolated intermediate", according to art. 3 point 15 of REACH Regulation, hence not under any process of authorisation. The official answer from the REACH competent authority (i.e. Regional Health Service), after consultation with the National REACH authority, was that "*As_2O_3 is included in Annex XIV and after the sunset date of May 21, 2015 the use of As_2O_3 in the production of artistic glass is then forbidden in EU because no one asked for the authorisation on the specific use*" (European Chemicals Agency ECHA, 2016).

At the same time, in order to understand the real amount of As used, the local administration of Venice asked the REACH competent authority to take actions in motoring the use of As_2O_3 in the artistic glass production. Moreover, according to information collected by the glass raw materials company suppliers, a total of ~5000–6000 kg As_2O_3 were ordered in 2013. Consequently, a monitoring campaign was carried out to investigate the use of As_2O_3. The enforcement of REACH authorisation was planned in a three-phases involving major stakeholders (i.e. glaziers): *i*) the census of GMFs in Venice area; *ii*) the implementation of a capillary informative campaign addressed to glassmakers, producers and factories (questionnaires, training meeting with trade associations and direct producers) about the new regulations, inspections and risks associated with the use of As; and *iii*) on-field inspections from December 1, 2015 until September 30, 2017.

Subsequently, each company identified was asked to fill in a questionnaire providing more details about their use of arsenic compounds and were informed about the state-of-the-art process dealing with the authorisation of As_2O_3. The results were: 104 companies answered, 35 of them involved in the artistic glass production including 18 that had used As_2O_3 until 2014. These last companies declared that they would use Antimony (III) oxide (Sb_2O_3), blast furnace slag, and a combination of cerium oxide, lithium oxide and sodium sulphate as an alternative substitution.

Meanwhile, the REACH competent authority invited glass masters and the owners of the glass factories to specifically dedicated meetings regarding the prohibition of the use of arsenic and the possible consequences if regulations were not followed. The companies were also informed that from December 2015 the health and environmental authorities would start random site inspections to control the presence of arsenic trioxide in the raw materials such as unknown powders and mixtures, and in mixtures prepared ahead for the furnace use located in the storehouses of glass producers and industries.

From December 2015 until 2017 nineteen inspections were conducted: one in 2015, thirteen in 2016 and five in 2017. In total 100 in-field screening analyses were performed with XRF and 7 laboratory analyses were conducted as confirmatory tests. In three cases, the use of As_2O_3, was confirmed by laboratory analyses. Details of the analyses are reported in Table S2 of the Supplementary Information.

4. Conclusions

During the millennial tradition of the Venetian artistic glass production in Murano, the protection of the environment and the protection of human health was generally disregarded. A large number of substances potentially harmful for human health like arsenic trioxide were widely utilised in glass production with suboptimal abatement or safety measures. With the introduction of European legislation on air quality and the consequent monitoring of atmospheric pollution, it became mandatory to evaluate the environmental effects of this peculiar and unique industrial production. The main findings can be summarised as follows:

- Before the Sunset Date, the PM_{10}-bound arsenic concentrations in Murano were not in compliance with the European Air Quality Directive. High concentrations of As (528 ng/m^3) were measured in 2013, i.e. 88-folds higher than the European target value. Other AQN sites in the Venice area met the European target values.
- A model set to depict the worst-case scenario (maximum allowed arsenic emission from all the authorised chimneys) failed to estimate the real concentration of As, that was 36-folds higher than the model output.
- The analysis of wind direction also indicted the island of Murano as the main source of arsenic.
- After Sunset Date, the arsenic concentration significantly dropped in Murano achieving the European target value. This positive feedback of the REACH enforcement confirmed a general decrease in the use of As in glass production.

The positive outcome of this case study was possible because of stakeholders involvement and the proactive involvement of local glaziers. Local administrations strongly supported multiple actions aiming to inform and educate about the dangers of the use of arsenic trioxide. The outcome of this study can help other administration to understand the methodology of intervention and to reduce the environmental impact of hazardous compounds. This study can be considered an interesting example of a good practice, supported by a large amount of validated experimental data, applications of a regulation aiming to protect human health as well as the environment.

Disclaimer

The views and conclusions expressed in this paper are exclusively of the authors and may not reflect those of ARPAV.

CRediT authorship contribution statement

Gianni Formenton: Conceptualization, Validation, Resources, Data curation, Writing - original draft, Supervision; **Maria Gregio**: Conceptualization, Investigation, Writing - original draft; **Giovina Gallo**: Validation, Investigation; **Francesca Liguori**: Conceptualization, Methodology, Software, Formal analysis, Writing - original draft, Writing - review & editing; **Massimo Peruzzo**: Conceptualization, Investigation; **Elena Innocente**: Formal analysis, Data curation, Writing - original draft, Writing - review & editing; R**oberto Lava**: Validation, Investigation; **Mauro Masiol**: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2020.124294.

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