

PAHs AND TRACE ELEMENTS IN PM_{2.5} AT THE VENICE LAGOON

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Summary - The results of an experimental analysis carried out to investigate PM_{2.5} concentration levels and the content of polycyclic aromatic hydrocarbons, as well as inorganic trace elements in the atmospheric particles are presented. Measurements were taken with a micrometeorological station equipped with an optical PM_{2.5} detector, and simultaneously, particles were collected on filters for subsequent chemical analyses. The average value of daily PM_{2.5} concentration is 21.5 µg/m³ and real-time measurements indicate that the average concentration during the day (8 am to 8 pm) is about 25% lower than the nocturnal average. Short-time averages of PM_{2.5} decrease when the wind speed increases as consequence of the more efficient mixing. Meteorological measurements indicate the presence of a local daily (breeze) circulation with wind blowing from the Alps or the Adriatic Sea and, during this circulation, larger concentrations were observed, with wind coming from the Alps. Days of high PM_{2.5} concentration with dominant anthropic or with prevalent crustal contributions were identified.

Regarding trace metals, their average concentrations are comparable to those found in others urban areas, except for Cd (3 ng m⁻³), probably due to the presence of glassworks in Murano. The highest concentrations are observed for K (99 ng m⁻³) and Na (73 ng m⁻³), which are the main constituents of marine spray, while the lowest concentrations are observed for elements such as Cs and Co (respectively 0.01 and 0.02 ng m⁻³). Also the concentrations of PAH are comparable with those of other industrial areas, as their sum ranges from 0.16 ng m⁻³ to 3.73 ng m⁻³, but if considered as B(a)P toxicity equivalent, they are largely lower (0.036±0.026 ng m⁻³). From the analyses of discriminating ratios, it has been found that the main origin of PAH in PM_{2.5} samples may be petrogenic, probably related to the presence of refinery and petrochemical plants on the mainland, although the contribution of combustion processes cannot be excluded.

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INTRODUCTION

The dynamics and chemical composition of particulate matter in the atmosphere is an important topic of research. This is especially the case of the fine fraction of aerosol, like particles with sizes less than 2.5 μm (called $\text{PM}_{2.5}$), in both rural and urban environment, because it is recognized to be the most mobile and dangerous for its potential impact on human health.¹

The Venice Lagoon is a transitional environment surrounded both by the sea and a heavily populated mainland (about 800.000 inhabitants), where the aerosols emitted from the anthropic activities of the near industrial and urban district coexist and interact with marine originated particles. Particularly, the industrial emissions descend from the presence of the petrochemical industry of Porto Marghera, made up of a number of plants highly integrated each other, marked mainly for its chlorine chemistry and other important production cycles (caprolactam, acetonecyanohydrin, hydrochlorofluorine-carbides, hydroflorinecarbides and acrylic fibres). Apart from the petrochemical plants, the presence of refinery stations and industrial activity linked to the production and transformation of non-ferrous metal (especially aluminium, copper and zinc) produce a strong environmental impact, as well as the incinerators for chlorides and for sludge, the plant for chemical-physical and biological wastewater treatment and the thermo-electric power station. Moreover, it has to be considered the emissions deriving from the highly frequented street and highway nets in the mainland and from the ship traffic, both tourist and commercial, which affects the Venetian canals, and from the glass factories of Murano.

In recent years many studies have been performed to evaluate the impact of the aerosol on the Venice Lagoon by considering the fluxes of pollutants carried by atmospheric depositions^{2,3} and air masses coming from different sources.⁴ However, very little is known about the aerosol particulate matter, particularly with regard to the content of organic pollutants. The main aim of this study is to characterize the fine fraction of the aerosol ($\text{PM}_{2.5}$) collected in the Venice Lagoon in order to establish its content of trace metals and polycyclic aromatic hydrocarbons (PAH), and to link their variations with the local micrometeorology, directly measured in situ. To include in our study all the sources which influence the air quality of the Venice Lagoon, a sampling site located in the Northern part of the lagoon has been chosen, because it is well centred around both the anthropic and marine sources.

METHODS

Sampling

Samplings were performed from 5 July to 1 August 2004 at Mazzorbo (N 45° 29' 09.7" E 12° 24' 12.7", Figure 1), a small island in the heart of the North Lagoon between the islands of Murano and Torcello and in the neighborhood of Burano. This site is about 15 Km N-NE far from the industrial plants of Porto Marghera and the town of Mestre, and quite close from the town of Venice and the island of Murano, about 6 and 8 Km respectively.

$\text{PM}_{2.5}$ was collected with a low-volume sampler (38.33 L min^{-1} ; Sentinel PM-Charlie, TECORA) placed in a meadow facing towards the lagoon water, which was equipped alternatively with mixed cellulose ester filters and quartz fiber filters for metals and PAH analyses, respectively. Generally the sampler operated for periods of about 24 hours from 00.05 to 23.57, corresponding to about 55 m^3 of air collected, providing a total of 9 and 13 observations for PAH and elements, respectively. Further details on the sampling dates and main meteorological conditions are reported in Table 1.



FIGURE 1. - Map showing the position of the sampling site in the Venice Lagoon.

A micrometeorological measuring station for real-time detection of PM_{2.5} and of micrometeorological parameters was operating in the measurement site between 2 July and 18 July 2004. The measuring station consisted of a Gill R3 ultrasonic anemometer (operating at 100Hz in calibrated mode), an optical PM_{2.5} detector MIE pDR-1200 (MIE-Personal Data logging Real time Aerosol Monitor) and a Rotronic (Campbell Scientific MP100A) thermo-igrometer. The instruments were mounted on a horizontal bar placed at the top of a telescopic mast (Clark Mast SQT9/M) at 9.6 m above the ground. The pDR-1200 was placed inside a small aerated box fixed at the top of the mast and air samples were collected through a 40 cm tube. The aerosol sampling point was about 30 cm from the measuring volume of the ultrasonic anemometer. The pDR-1200 is an advanced instrument, operating at 1 Hz, to measure air particulate concentrations using diffusion of infrared radiation (880 nm) from particles. Measured diffused light is converted to mass concentration using the diffusion theory and the factory calibration by ISO test fine dust (specific gravity 2.5-2.6, MMD 2-3 μm).^{5,6} The pDR-1200 was working with active sampling using a BRAVO pump (TECORA) to collect continuously air at a flow-rate of 4 l/min, and was equipped with a 2.5 μm cut-off cyclone at the 4 l/min flow-rate used.

TABLE 1. - Sampling dates and relative average meteorological conditions.

Samples name	Date of collection	Average temperature (°C)	Average RH (%)	Wind direction	Average wind speed (m/s)	Rain (mm H ₂ O)
1 (PAH)	5 July 2004	26.0	63.6	S-SE	2.6	0
2 (PAH)	7 July 2004	25.2	66.1	NE	3.6	0
3 (PAH)	8 - 9 July 2004	26.1	63.5	SW-S-SE	3.0	0
4 (PAH)	10 - 11 July 2004	21.0	63.5	NNE-NE	4.6	0.6
5 (PAH)	12 - 13 July 2004	19.1	63.6	NNE-NE	2.8	6.8
6 (PAH)	14 - 15 July 2004	21.8	66.9	SSE-SE	2.8	0
7 (trace metals)	16 July 2004	24.2	77.1	S-SE	1.7	0
8 (trace metals)	17 July 2004	24.5	79.2	SE	1.8	0
9 (trace metals)	18 July 2004	25.1	76.0	NNE-SSE	2.4	0
10 (trace metals)	19 July 2004	25.5	73.5	NNE-SSE	2.1	0
11 (trace metals)	20 July 2004	28.4	60.4	S	2.5	0
12 (trace metals)	21 July 2004	27.2	68.6	NE-SSW	1.8	0
13 (trace metals)	22 July 2004	28.4	74.0	NE-SSW	2.3	0
14 (trace metals)	23 July 2004					
15 (PAH)	start 00.05 end 08.56 start 09.20 end 23.53	26.5 30.6	85.8 68.2	NE NE-SW	1.6 1.4	0 0
16 (PAH)	24 - 25 July 2004	25.5	74.4	NNE-NE	3.8	2.4
17 (PAH)	26 - 27 July 2004	23.8	66.2	NE	3.6	3.6
18 (trace metals)	28 July 2004	22.3	65.4	S-SSE	2.8	0
19 (trace metals)	29 July 2004	23.2	66.5	S	2.8	0
20 (trace metals)	30 July 2004	24.1	72.3	SSE	2.3	0
21 (trace metals)	31 July 2004	25.7	74.6	S	1.9	0
22 (trace metals)	1 August 2004	26.1	75.9	SSE-SSW	1.8	0

Trace element analysis

Mixed cellulose ester filters (47 mm diameter, 0.45 µm porosity, Pall corporation) for element sampling were washed with 5% diluted suprapur HCl (Merck) for 10 days and rinsed with ultrapure water. To assess the amount of particulate matter collected, the filters were weighed at constant humidity (40% RH) in a nitrogen box before and after sampling.

Sampled filters were digested with an ultrapure acid (Romil Ltd) mixture of HNO₃ (5 ml), HF (1 ml), HCl (0.5 ml) and H₂O (1.5 ml) in a microwave oven (Ethos 1600, Milestone) employing the following procedure: 10 min at 250W, 1 min at 0W, 20 min at 400W, 2 min at 0W, 20 min at 500W, 2 min at 0W, 3 min at 650W. The final solution was transferred into pre-cleaned LDPE bottles (30 ml) rinsing with Milli-Q water. Trace elements (Li, Na, Mg, Al, K, V, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Cd, Cs, Ba, Pb) were determined by Inductively Coupled Plasma Quadrupole Mass Spectrometer (ICP-QMS, Agilent 7500), applying an external calibration curve obtained with a multielement standard solution (ULTRAscientific).

Polycyclic Aromatic hydrocarbons analysis

Quartz fibre filters (47 mm diameter, about 1 µm porosity, Pall corporation) were baked at 400°C for 5 hours before use. To assess the amount of particulate matter, they were weighed before and after sampling, then stored at -20°C until the time of analysis. When the particulate matter collected on the filter was lower than 1 µg, two successive samples were joined together and analyzed as one.

Sampled filters were spiked with 50 ng of ¹³C-labeled phenanthrene (Phenanthrene ¹³C₆, Cambridge Isotope Laboratories) for quantitative purposes. The PAH were extracted by pressurized solvent extraction (One-PSE, Applied Separations) using a mixture of dichloromethane/*n*-hexane (3:1, v/v) with a static phase (10 min) at 100°C and 120 bar, repeated three times. The volume of sample extracts (about 90 mL) was reduced to 0.5 mL under a gentle nitrogen flow (Turbovap II, Zimark), after which the extracts were added with 4.5 mL of *n*-hexane before the clean up treatment, performed using an automatic system (Dioxin Prep, Fluid Management System Inc.). Samples were added to neutral silica columns and eluted with 30 mL of *n*-hexane and 20 mL of dichloromethane/*n*-hexane (1:1, v/v); the eluate volume was reduced to 100 µL and 13 PAH of the 16 EPA priority ones, corresponding to 13 chromatographic peaks (acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (Phe), anthracene (An), fluoranthene (Flt), pyrene (Py), benzo(a)anthracene (BaA), chrysene (Ch), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP) and benzo(g,h,i)perylene (BghiP)) were analyzed by a Hewlett Packard 5890 series II GC coupled with a MAT 95 XP, high resolution mass spectrometer (Thermo Finnigan).

Gas chromatographic separation was performed on a 60 m fused silica capillary column (J&W Scientific DB-5MS, 60m × 0.250 mm × 0.25 µm). The operating conditions were: injector temperature: 300°C; oven temperature program: 1.5 min at 70°C, 10°C min⁻¹ to 150°C, 10 min at 150°C, 3°C min⁻¹ to 280°C, 55 min at 280°C; carrier gas (helium): constant flow, 1 mL min⁻¹, injection mode: splitless (split valve open after 1 min) with purge flow 50 mL min⁻¹. Data were acquired in the electron impact (EI) mode (45eV) and high resolution (10000) with the Multiple Ion Detection (MID) technique, using the following mass ranges: 151.5-152.5, 153.5-154.5, 165.5-166.5, 177.5-178.5, 183.5-184.5, 201.5-202.5, 227.5-228.5, 251.5-252.5, 275.5-276.5.

Quality control

Quality control of the chemical analytical procedures was performed by evaluating their repeatability and recoveries with the analysis of standard reference materials, and by evaluating the potential sample contamination with the analysis of the field-blanks, consisting of pre-cleaned filters left in the sampler without air flowing and then processed in the same way as the samples.

The limit of detection (LOD) of both procedures was calculated as the average field blank value plus three times its standard deviation.

To estimate the repeatability and recoveries of trace metals, 4 aliquots (about 11 mg) of SRM-1648 (NIST) were analyzed. The relative standard deviation (RSD%) of the metal concentration ranged from 0.1% (Mg) to 20.3% (Cs) and was < 5% for 15 of the 19 elements. These results are comparable with those reported by Manoli et al.,⁷ who found an analytical precision better than 10% for all species. Heal et al.⁸ reported a RSD% value smaller than 7.6% for 10 of the 11 elements analyzed (18.2% for Ni).

Generally the recoveries are larger than 80%, ranging from 84% (V) to 105% (Na), and for 10 of the 14 elements are greater than 90%. They are in agreement with the studies of Yang et al.,⁹ who found recovery values around 90%, and of Pekney and Davidson,¹⁰ who reported a recovery of 100 ± 15% for all elements analyzed with the exception of Cr (59%) and Cs (82%).

The analysis of 6 field-blanks showed that the main contaminations concern K (1.0 µg), Fe (0.50 µg), Na (0.3 µg), Mg (0.36 µg) and Al (0.27 µg), whereas the lowest were found for Li (0.0004 µg), Rb (0.0004 µg), Cd (0.0009 µg) and Cs (0.0002 µg). If we consider the average volume of air collected (about 55 m³), these results are comparable with those reported in the literature, for example by Heal et al.,⁸ whose field blank values ranged between 0.01 ng m⁻³ (As) and 9.15 ng m⁻³ (Fe), and by Pekney and Davidson,¹⁰ who found field blank concentrations varying from 0.001 ng m⁻³ to 4 ng m⁻³.

From the comparison between the amount of trace elements in the samples and in the field blanks, considering the method repeatability and LOD (which ranged from 0.00049 µg for Cs to 1.5 µg for K), it emerges that all elements are present in quantities greater than LOD. However the field blanks are not negligible, because they account for 1% (Pb) to 60% (Co) of the sample amount. Thus, the metal concentrations in the samples must be corrected for the blank.

For PAH, the repeatability and recoveries of the method were evaluated by analyzing 5 aliquots (about 75 mg) of SRM-1649a Urban Dust (NIST), applying the analytical method previously reported. The relative standard deviation (RSD%) ranged from 6% (Phe) to 19% (BaP), and was < 15% for most PAH. Similar results were obtained by Gambaro et al.,¹¹ whose RSD% ranged between 5 to 24%, and by Panther et al.,¹² whose duplicate samples were within 20% of the sample concentration.

For all compounds the recoveries were greater than 65%; the lowest values were found for PAH with a small number of rings (F 68%, Phe 68%), while the highest were found for PAH with a larger number of rings (Ch 99%, BkF 137%). This is in agreement with the results of Guo et al.¹³ and Bi et al.,¹⁴ who reported the highest losses for the lightest compounds, varying from 39% (naphthalene) to 101% (BghiP). Cincinelli et al.¹⁵ also reported recoveries ranging from 60% to 80%, whereas Caricchia et al.¹⁶ found a mean recovery of 75%.

From the analysis of 8 field-blanks it was found that the greatest contamination concerns Py (28 ng) and Flt (6.2 ng), while the lowest concerns BkF (0.07 ng), BbF (0.11 ng), BaP (0.11 ng) and Ch (0.12 ng), in agreement with the results of Lee and Jones,¹⁷ whose blanks ranged between 0 and 0.2 ng m⁻³ (average air volume: 350 m³). The values of LOD, which varied from 0.13 ng (BkF and BaA) to 34 ng (Py), are comparable with those reported in the literature.^{13, 16, 17}

The comparison between PAH amounts in the samples, field blanks and LOD showed that all compounds are present in quantities greater than LOD, and the field blanks are not negligible, so that the concentrations in samples were corrected for the blanks.

Data analysis

Raw data series from the micrometeorological station are post-processed to evaluate the different parameters using 30 minutes averages in the streamlines reference system.¹⁸ The PM_{2.5} concentration signals are corrected for the effect of relative humidity (RH) and all the time-history

obtained (concentration, wind velocity and sonic temperature) is treated to limit the effect of slow changes in the measured quantities (with respect to the averaging time) by performing a linear detrend. The optical detectors of the kind used in this work can be used to monitor atmospheric aerosol, but they are affected by environmental relative humidity (RH), and their signal tends to increase at high values of RH.^{19, 20, 6} This effect is generated by the absorption of water vapour by the particles that change their dimensions and optical properties. In the case of the pDR-1200 detector, a previous analysis¹⁹ indicates that it is necessary to use a correction factor CF for values of the relative humidity RH larger than 70%. The correction factor used is reported in equation (1):

$$CF = \frac{C(RH)}{C(RH = 0.7)} = aRH^4 + bRH^3 + cRH^2 + dRH + e \quad (1)$$

where $a=4330.8282774$, $b=-13628.3399181$, $c=16102.7519624$, $d=-8456.2021129$ and $e=1664.7397809$ are coefficients calculated from the polynomial fit. All the decimal digits reported are necessary to achieve the correct representation of the correction curve. Its efficiency is evaluated comparing the optical measured concentrations with the daily concentrations measured with gravimetric detection in different measurement sites. Results, reported in Donato et al.¹⁹ indicate that with RH-correction the correlation coefficient between optical and gravimetric measurements is 0.94. This correlation is reasonably good and is similar to what has been reported in the scientific literature for the same instrument.²⁰

RESULT AND DISCUSSION

Local meteorology and aerosol concentrations

Results of 30 min average wind speed are reported in Figure 2(a). Figure 2(b) reports the wind direction as measured by the micrometeorological station. The meteorological data was integrated with results obtained by the meteorological stations and by the sodar-rass system managed by the Ente Zona Industriale Porto Marghera. The additional data correlated well with ours and cover the whole gravimetric sampling periods. During the measurement campaign the air temperature ranged between 15.1 °C and 32.4 °C, relative humidity ranged between 36% and 97%, and there were 4 days with precipitation higher than 1 mm H₂O (on 2, 13, 24 and 27 July).

The results show that the largest wind speeds are in the period before 14 July. The maximum peak during the whole measurement period is about 10 m/s (on 30 mins average), occurring on the afternoon of 13 July. There are also several wind velocity peaks over 8 m/s. The behaviour of wind direction highlights a local daily circulation (after 13 July), with wind blowing from NE during the night and from SE during the day. This is due to the presence of a circulation with wind coming from the Alps and the Adriatic sea.²¹ A comparison of our results with sodar measurements taken in the Venice Lagoon showed that this is a stable circulation up to at least 400 m above the ground. The transition from NE to SE usually occurs between 9 am and 11 am, while the opposite transition from SE to NE usually takes place between 11 pm and 1 am. In the period when circulation from NE and SE is present, the wind speed is generally lower (2.4 m/s on average between 13 July and 18 July with respect to 3.2 m/s on average between 2 and 12 July).

The PM_{2.5} average concentration was 21.5 µg m⁻³ with a standard deviation of 10.7 µg m⁻³, this range is in agreement with those reported for urban and sub-urban sites located at Spanish²² and Turkish coastal areas²³ and other European sites.²⁴ The PM_{2.5} daily concentrations obtained with gravimetric measurements and the RH-corrected optical measurements are reported in Figure 3(a) and Figure 3(b), respectively. The PM_{2.5} average concentration was 21.5 µg/m³ (with a standard deviation of 10.7 µg/m³), the minimum daily concentration was 5.3 µg/m³ and it was observed the

28th July. The maximum daily concentration was $54.8 \mu\text{g}/\text{m}^3$, observed on 23 July. There is a concentration peak on 8 July that was also observed with the optical measurements, and two similar peaks are present on 21 and 22 July. These results are in agreement with the average aerosol optical thickness (AOT) at 500 nm wavelength, obtained from the Aerosol Robotic Network (AERONET), which is 0.462 on 22 July and 0.436 on 23. On these days, the sky over Venice was cloud-free (as verified by examining meteosat pictures (<http://infomet.am.ub.es/infomet/arxiu/meteosat/>)); therefore the high AOT levels could be the consequence of a general polluted condition over the area. This is confirmed also by the air quality monitoring network managed by the Ente Zona Industriale Porto Marghera (<http://www.entezona.it>), which shows higher total suspended particulate (TSP) concentration levels on both days. Specifically the background station of Campagna Lupia (n. 26) shows daily TSP concentrations of 86 and $97 \mu\text{g}/\text{m}^3$, respectively on 22 and 23 July. Conversely, on 11 and 28 July, when the daily average $\text{PM}_{2.5}$ concentrations were low (see Fig. 3a), the AOT at 500 nm were respectively 0.209 and 0.238; the concentrations at station 26 were respectively $41 \mu\text{g}/\text{m}^3$ and $40 \mu\text{g}/\text{m}^3$.

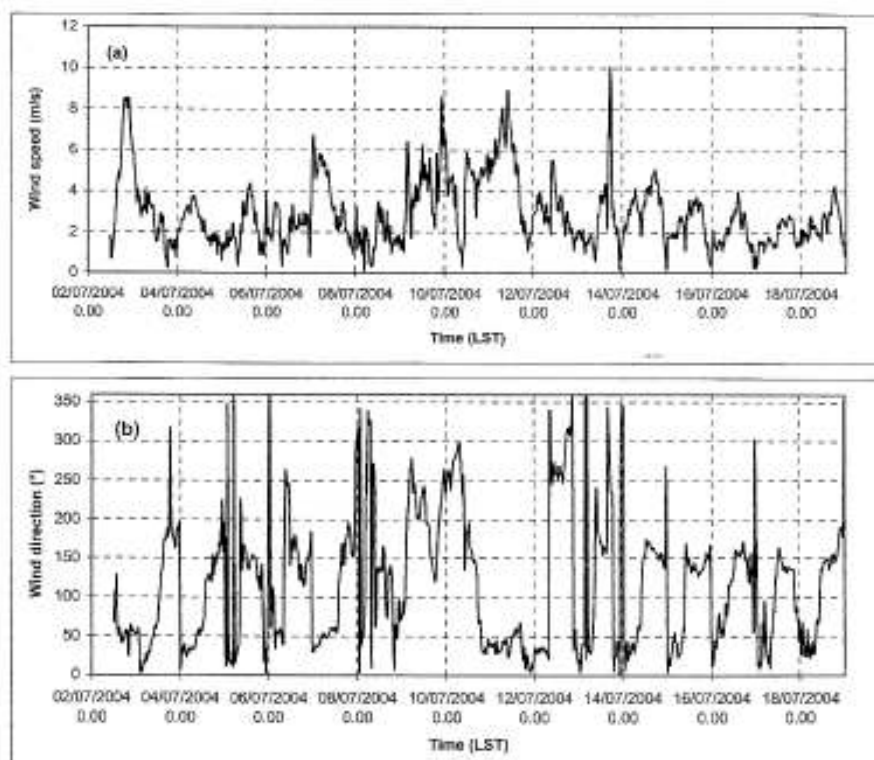


FIGURE 2. - Wind velocity (a) and wind direction (b) measured at the micrometeorological station. Data are reported as 30 min averages.

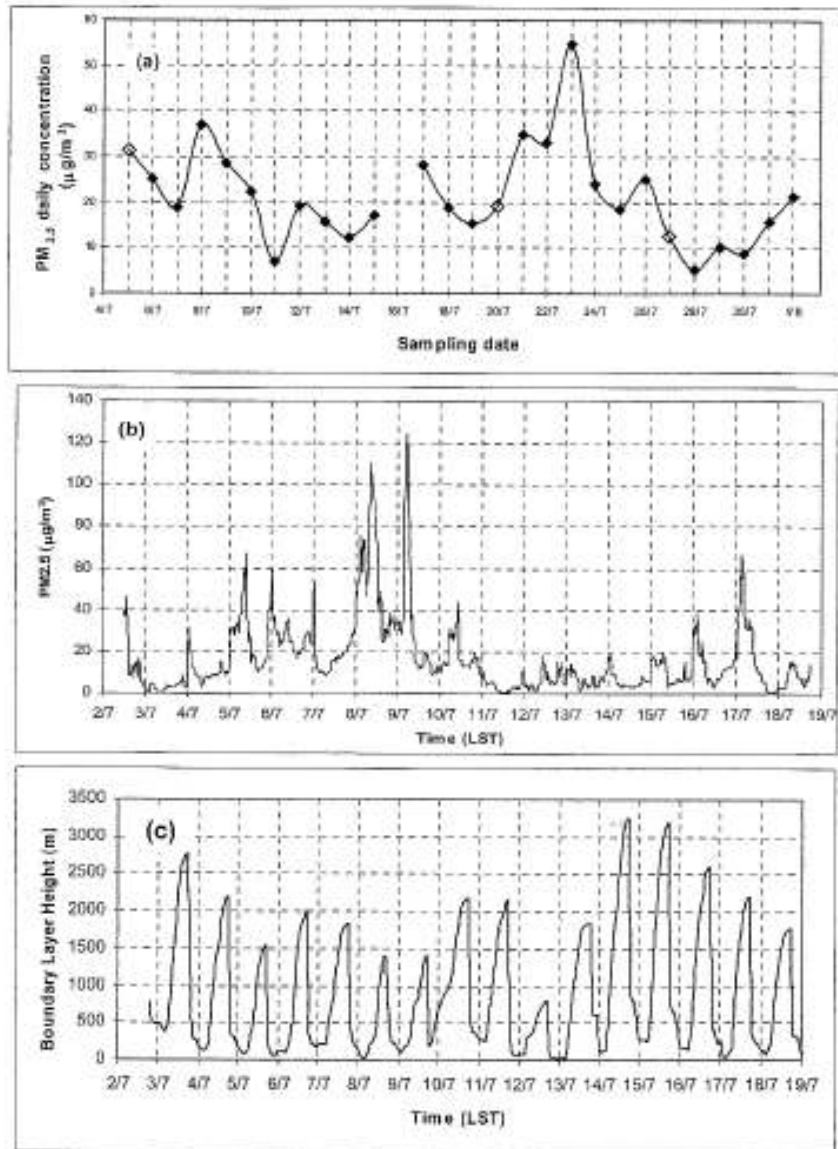


FIGURE 3. - Temporal trend of daily gravimetric measurements of PM_{2.5} (a), optical measurements (30 mins averages) of PM_{2.5} concentrations (b), where hollow marks correspond to days on which the sampling was about 12 hours because of maintenance of the equipment, and calculated Boundary-Layer Height on an hourly basis (c).

Compared to the daily gravimetric measurements, the optical ones provide greater detail. It was observed that typically the average concentration during the day (from 8 am to 8 pm) is about

25% lower than the average values measured during the night (from 8 pm to 8 am). Our results indicate a correlation of 30 min optical concentration measurements with wind velocity U so that, on average, the $PM_{2.5}$ concentration is reduced by about 38% for $U > 3$ m/s with respect to the values measured for $U < 3$ m/s. The analysis of the standard deviation σ_C of $PM_{2.5}$ concentration C evaluated on 30 min averages shows that the relative fluctuations σ_C/C are usually within 10% for concentration values larger than $25 \mu\text{g}/\text{m}^3$. Moreover a maximum peak was observed of about $125 \mu\text{g}/\text{m}^3$ (on 30 mins average), a short peak occurring 9 July. This peak takes place with a wind direction compatible with a short-range transport from the industrial area of Porto Marghera. Measured concentrations show peaks in the $PM_{2.5}$ level (about $100 \mu\text{g}/\text{m}^3$ in concentration) during the day of 8 July, which also presents a large daily average concentration. On this day the wind speed at 10 m is relatively low (about 2 m/s) and the wind direction is quite variable near the ground, with contributions from NE-NW and also from SE, but at 1500 m above the ground, as measured by the radio soundings in Udine, the wind is blowing mainly from SW. Therefore, the high concentration level could be due to a long range transport from the Po Valley or to Africa dust, which on this day was present at a high altitude over the northern part of Italy, and was brought towards the ground partly as consequence of convective mixing in the boundary layer.

In the period starting from 13 July, when the local daily (breeze) circulation is present, the $PM_{2.5}$ concentrations are correlated to wind direction. In this period maximum concentrations were found associated to a wind direction of about 50° corresponding to air masses coming from the Alps mainly during the night and early hours of the morning. Wind directions associated to air masses coming from the Adriatic Sea are characterised by lower levels of atmospheric $PM_{2.5}$.

Figure 3(c) reports the height of turbulent atmospheric boundary layer H . The values of H were calculated on an hourly basis, using data from the micrometrological station and from the sodar-rass (for nocturnal lapse-rate underneath and above the thermal inversion) as input parameters. We utilized a one-dimensional model for the calculation of time dependent boundary layer height, employing one point surface data as described in detail in Martano and Romanelli²⁵ and in Martano.²⁶ The implemented routine attempts to join together previously existing models for convective boundary layer growth,²⁷ stable boundary layer (SBL) decay²⁸ and surface inversion height development.²⁹ The calculated values of H show a typical diurnal cycle, increasing during daytime because of the heat flux from the surface (mixing height), and usually decreasing strongly during the night. The results indicate that maximum concentrations, generally found during the night, occur for low values of H . There are several cases (e.g. on 8 and 9 July), in which the temporal trend of H and $PM_{2.5}$ concentrations are strictly linked. In other cases, especially for low concentration values between 12 and 15 July, the temporal trends are different. This could be explained by the variable sources (that are not constant through the measurement periods), but also by the lower accuracy in aerosol measurements when small concentrations are involved.

Trace elements

Table 2 reports the average, maximum and minimum trace elements concentrations in $PM_{2.5}$ obtained in this study. The measured metal concentrations are found to differ by several orders of magnitude from one metal to another. The highest concentrations are observed for K (99 ng m^{-3}) and Na (73 ng m^{-3}), which are the main constituents of marine spray,³⁰ while the lowest concentrations are observed for elements such as Cs and Co (respectively 0.01 and 0.02 ng m^{-3}), which are present in very low concentrations in marine spray³⁰ and crustal material.³¹

Comparison with literature data shows that the observed average element concentration in $PM_{2.5}$ are very similar to values reported for other important cities of the world, such as Toronto,³² New York,³³ Budapest³⁴ for most of the elements. By contrast, the average concentrations observed for Cd in this study are higher than those found in literature, sometime even by three times; however, they are in agreement with values obtained in previous studies on $PM_{2.5}$ conducted in the

Venice Lagoon.³⁵ In particular, the authors reported that Cd and Se concentrations were linked to wind direction, and their source maybe the glass-works of Murano, because both elements are used to color glass products.

TABLE 2. - Average, standard deviation and range of concentrations of trace metals (ng/m³) during the sampling period.

	average	st. dev.	max	min
Li	0.05	0.03	0.11	n.d.
Na	73	16	111	46
Mg	12	5	23	5
Al	20	17	58	4
K	102	74	258	n.d.
V	5.1	3.2	9.5	0.1
Mn	2.6	1.7	5.8	0.9
Fe	37	25	88	n.d.
Co	0.03	0.03	0.10	n.d.
Ni	3	1	6	1
Cu	3	2	6	1
Zn	31	43	164	8
Rb	0.2	0.1	0.5	0.1
Sr	0.4	0.2	0.7	0.1
Cd	3	4	13	0
Cs	0.01	0.01	0.03	n.d.
Ba	1.4	0.8	2.9	0.3
Pb	10	11	45	2

n.d. means 'not detectable'

It is interesting to analyze the metal concentration trends in the light of the local micrometeorology. As previously mentioned, the maximum concentration of PM_{2.5} is actually observed on 23 July, even if the concentration on 22 July is much higher than the average value. On 23 July the wind direction near the ground is quite variable, while the dominant direction is from S at high altitude with a shift towards NW late in the evening. On 22 July the wind arrives prevalently from the S and SW at low and high altitude, possibly bringing a contribution of anthropic pollution from the Po Valley. On 23 July several metals and elements mainly of anthropic origin show a decrease, while the values of Fe and Mn (generally associated to mineral aerosol) are high on both days (22 and 23 July), indicating the possibility of a substantial contribution of crustal aerosol on 23 July, perhaps from long-range transport. In fact, Fe and Mn are highly correlated (correlation coefficient equal to 0.93) indicating that crustal material is a significant source and their concentration ratio is about 15 on both 22 and 23 July, while the ratio between Fe and a metal of anthropic origin like V changes from 9 to 17, going from 22 to 23 July.

Cs and Cd show different temporal trends from other elements and no significant correlation was observed with the other elements in trace. The Cd in particular shows the maximum peak on 17 July, unlike all other elements, even if a second smaller peak on 22 July is still present.

Pb presents a 0.99 correlation coefficient with Zn and both elements present a concentration peak 1 August. A smaller correlation coefficient equal to 0.77 was observed between Pb and Mn. Meteorological conditions on 1 August indicate a variable wind direction near the ground, with a

prevalence in the sector from SE to SW. At high altitude wind direction is in the sector between WSW and W early in the morning and during the day, subsequently, the wind rotates during the evening, with a dominant direction from the northern sector.

Results indicate that V is well correlated only with Ni (correlation coefficient equal to 0.87), and both present a decrease on 23 July and significant values on 22 July. These observations show that the elements as Pb, V, Ni, Zn, Cd and Cs seems to have an anthropogenic origin.

PAH concentrations

Table 3 reports the mean, maximum and minimum concentrations of PAHs in PM_{2.5}. Σ PAH (sum of 13 identified PAH) ranges from 0.16 ng m⁻³ to 3.73 ng m⁻³, with 4-ring compounds predominating over the others, varying from 38% to 87%. The main contributors to the total concentration are Py, Flt and Phe, on average about 44%, 13% and 12% of the total concentration, respectively, while Ace, An, F and BaA constitute less than 2% of Σ PAH. These results are in accordance with those previously found for the 'particulate' phase (>1 μ m) collected at 'marine' and 'industrial' sites of the Venice Lagoon by Gambaro et al.,¹¹ and are very similar to the summer values reported for the industrial area of Kwun Tong (Hong Kong) by Guo et al.¹³ but about one order of magnitude lower than concentrations found in central Taiwan by Fang et al.³⁶ and in California by Rinehart et al.³⁷ The concentration of BaP, which is an EPA priority pollutant classified as a probable human carcinogen, is 0.021 ± 0.021 ng/m³, much lower than values reported for other Italian^{15,16} and European^{38,39,40} cities. Presumably, it does not exceed the guideline fixed by the Italian Ministry of Environment for PM₁₀ (1 ng/m³), although it should be taken into account that BaP is a photosensitive compound and its concentrations are generally lower in summer than in other seasons due to the high sun irradiation.^{34,41,42,43} To better estimate the actual toxicity of samples, the other carcinogenic PAH were included, by considering the toxicity equivalent factors with respect to BaP proposed by Nisbet and LaGoy,⁴⁴ which many authors^{45,46,47} suggest as the most reliable. The Σ PAH BaP toxicity equivalents (BaP-TE) is 0.036 ± 0.026 ng/m³ and the maximum concentration (0.091 ng/m³) found on 24 July is lower than values reported in the literature.⁴⁵

The weekly evolutions of Σ PAH, Σ PAH BaP-TE and PM_{2.5} do not show similar trends, suggesting that they are emitted by different sources. Many factors influencing the PAH concentrations exist,⁴³ and they could be strongly affected by meteorological conditions and air mass circulation.¹⁷ From the analysis of the 48 hours backward trajectories (<http://www.arl.noaa.gov/ready/>), no particular event emerged, the circulation generally being from the Alps; only on 6 and 7 July, air arrived from the Balkan area and on 8 and 9 July from the Atlantic Ocean, crossing France and the Po Valley.

Several ratios between PAHs may be considered to evaluate their origin, as outlined by Yunker et al.⁴⁸ The main tool to discriminate between pyrolytic and petrogenic sources is to study simultaneously the ratios between the isomers with molecular weights 178 and 202.^{49,50,51,52} Considering our samples, both of these ratios show the presence of a petroleum source; in particular An/(An + Phe) (0.08 ± 0.05) is typical of crude oil, and Fl/(Fl + Py) (0.26 ± 0.08) of crude and diesel oils.⁴⁸ The petrogenic origin of PAH may be related to the presence of refinery and petrochemical plants on the industrial area in the mainland, whose impact is more evident in summer because of the absence of the typical winter source of PAH (burning of fossil fuel for residential heating). However, one cannot exclude the co-existence of parallel emissions from other processes, whose contribution may be investigated by analyzing the ratio between the sum of typically pyrogenic high molecular weight PAH (Σ COMB = Flt + Py + BaA + Ch + BbF + BkF + BaP + BghiP) and Σ PAH (Hwang et al., 2003). This ratio is 0.8 ± 0.1 , and the main contribution derives from Py and Flt. Zhou et al.⁴² found they were the predominant PAH in the fine particles at a urban site in Beijing (China) in summer, related to diesel vehicle exhaust and road dust

contaminated by incomplete petroleum residues and lubricating oil leakages. The contribution of vehicular emissions may be investigated as well by the BaP/(BaP+Ch) ratio: in our samples it is 0.42 ± 0.07 , characteristic of diesel emissions and roadway tunnel air, but also of wood and grasses combustion.⁴⁸

TABLE 3. - Average, standard deviation and range of concentrations of PAH (ng/m³) during the sampling period.

	average	st. dev.	max.	min.
Acenaphthylene	0.024	0.031	0.108	0.001
Acenaphthene	0.017	0.032	0.101	n.d.
Fluorene	0.027	0.039	0.117	n.d.
Phenanthrene	0.119	0.115	0.367	0.015
Anthracene	0.011	0.014	0.045	0.001
Fluoranthene	0.134	0.173	0.580	n.d.
Pyrene	0.504	0.705	2.240	n.d.
Benzo(a)anthracene	0.011	0.015	0.051	0.002
Chrysene	0.027	0.016	0.062	0.012
Benzo(b)fluoranthene	0.044	0.023	0.086	0.015
Benzo(k)fluoranthene	0.013	0.008	0.031	0.005
Benzo(a)pyrene	0.021	0.021	0.078	0.003
Benzo(g,h,i)perylene	0.028	0.015	0.056	0.012
ΣPAH	0.983	1.057	3.729	0.160

n.d. means 'not detectable'

As well as the study of the above ratios, the potential origin of PAH in PM_{2.5} collected in the Northern Lagoon of Venice was evaluated by applying the Principal Component Analysis (PCA), which is a multivariate statistical method used to reduce the dimensionality of a data set. The data matrix was composed by PAH concentrations as variables and by samples as objects. The first two principal components explain about 87% of the total variance, while the contribution of the others is negligible. In the plot of component weights (not shown), PAH appear divided into three main groups: the one in the left-upward of the graphic is constituted by the lightest PAH (molecular weight ≤ 202 , excluded An and with Phe quite external to the group), the second in the downward area composed by the heaviest PAH (molecular weight ≥ 228), and the third on the right made up by PM_{2.5} and An. These groups reflect the PAH chemical properties, such as volatility, and indirectly their main source, since the heaviest compounds are generally produced by combustion processes. However, it should be taken into account that the observed concentrations depend both on the kind and distance of the emission sources and depletion processes, such as the selective degradation undergone. In fact, it has been found that only heavy PAH (as previously defined) present a strong negative correlation with the solar irradiation (correlation coefficient = -0.67), and quite a significant correlation with the ozone concentration in air (correlation coefficient = -0.44), which is well represented by the PCA results.

CONCLUSIONS

The concentrations of PM_{2.5} collected in July 2004 at a site in the Venice Lagoon and its content of PAH and trace metals have been reported and discussed in the light of micrometeorological local parameters. In spite of the short sampling period and the small number of samples collected, some interesting findings did emerge. It has been found that the highest concentrations of fine aerosols coincide with episodes of long range transport from the Po Valley, or short range transport from the nearby industrial district on the mainland. Regarding trace metals, their concentrations in PM_{2.5} are comparable to those found in others urban areas, except for Cd, probably due to the presence of glass-works in Murano. Moreover, Cd, V, Pb and Zn present a different behaviour from other trace metals (Mn, Al, Li, Ni, K, Na, Mg, Rb, Ba, Co, Sr, Cu, Fe), which may reflect the different sources and transport paths undergone.

The concentrations of PAH are comparable with those of other industrial areas, but if considered as B(a)P toxicity equivalent, they are largely lower. From the analyses of discriminating ratios, it has been found that the main origin of PAH in PM_{2.5} samples may be petrogenic, probably related to the presence of refinery and petrochemical plants on the mainland, although the contribution of combustion processes cannot be excluded. A clearly different behavior is evident between low (≤ 202) and high (≥ 228) molecular weight PAH, which may be a consequence of their physical properties, as well as the emission from various sources or selective degradation (particularly by solar irradiation).

Received July 21st, 2006

Acknowledgements. This work was supported by Consortium for Coordination of Research Activities concerning the Venice Lagoon System (CORILA) under the Project "Balance of fluxes of organic and inorganic pollutants at the water-air interface of the lagoon of Venice" and by the National Research Council of Italy (CNR). The authors wish to thank Dr. I. Ongaro (Ca' Foscari University) for his support in sampling activities, Dr. S. Ferrari (CNR-ISAC) for her help in setting up part of the equipment, Dr. E. Mattiuzzo (Ca' Foscari University) for chemical analysis, the Ente Zona Industriale Porto Marghera for providing some meteorological data, and G. Zibordi for his effort in establishing and maintaining the Venice AERONET site.

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