Nuclear techniques and the particulate matter pollution in big harbours

Original Citation:

Nuclear techniques and the particulate matter pollution in big harbours / V. Ariola; V. Bernardoni; G. Calzolai; M. Chiari; E. Cuccia; F. Lucarelli; F. Mazzei; S. Nava; P. Prati; G. Valli; R. Vecchi. - In: NUOVO CIMENTO DELLA SOCIETÀ ITALIANA DI FISICA. C, GEOPHYSICS AND SPACE PHYSICS. - ISSN 1826-9885. - STAMPA. - 031:(2009), pp. 527-534. [10.1393/ncc/i2008-10306-5]

Availability:
The webpage https://hdl.handle.net/2158/395620 of the repository was last updated on

Published version:
DOI: 10.1393/ncc/i2008-10306-5

IL NUOVO CIMENTO Online First
DOI 10.1393/ncc/i2008-10306-5

Nuclear techniques and the particulate matter pollution in big harbours

V. Ariola(1), V. Bernardoni(2), G. Calzolai(3)(4), M. Chiari(4), E. Cuccia(1),
F. Lucarelli(3)(4), F. Mazzei(1), S. Nava(4), P. Prati(1)(*), G. Valli(2)
and R. Vecchi(2)

(1) *Dipartimento di Fisica dell' Università and INFN - via Dodecaneso 33, 16146 Genova, Italy*
(2) *Istituto di Fisica Generale Applicata and INFN - Via Celoria 16, 20133, Milano, Italy*
(3) *Dipartimento di Fisica dell' Università - via Sansone 1, 50019, Sesto Fiorentino, Italy*
(4) *INFN - via Sansone 1, 50019, Sesto Fiorentino, Italy*

(ricevuto il 9 Dicembre 2008; approvato il 9 Febbraio 2009; pubblicato online il 3 Marzo 2009)

Summary. — The impact of big harbours on the air quality is an important issue both from the environmental and the economical point of view. The harbour of Genoa is the largest in Italy and one of the major ports of the Mediterranean. We have determined the fraction of Particulate Matter (PM) concentration in town due to the heavy oil combustion of the diesel engines of the vessels in the harbour. This turned out to be 12% in PM10 and 25% in PM2.5 and PM1, with about 85% of the PM from this source concentrated in particles with aerodynamic diameter, $D_{\mathrm{ae}} < 1\,\mu$m. We could also point out a link between concentration peaks of the tracers of heavy oil combustion (V and Ni) and the ferryboats traffic. The key tool in this work was the coupling between particular sampling devices and some Ion Beam Analysis (IBA) techniques, in particular Particle Induced X-ray Emission (PIXE), which belong to the broader category of nuclear techniques in applied physics.

PACS `92.60.Mt` – Particles and aerosols.
PACS `82.80.Ej` – X-ray, Mössbauer, and other γ-ray spectroscopic analysis methods.
PACS `29.20.Ej` – Linear accelerators.
PACS `07.88.+y` – Instruments for environmental pollution measurements.

1. – Introduction

In recent years, atmospheric aerosols have been studied extensively and strong relationships among heterogeneous chemistry, cloud formation and climate forcing have been observed [1, 2]. Effects on the health of human beings are also well established and, for

---

(*) E-mail: `prati@ge.infn.it`

instance, in accordance with the European Directive 1999/30/EC, the annual average concentration of PM10 (PM10 = atmospheric particulate matter with aerodynamic diameter $D_{\mathrm{ae}} \leq 10\,\mu\mathrm{m}$) in Europe should be lower than $40\,\mu\mathrm{g\,m}^{-3}$. The recent European Directive 2008/50 confirms the limits on PM10 but also introduces for PM2.5 (PM2.5 = atmospheric particulate matter with $D_{\mathrm{ae}} \leq 2.5\,\mu\mathrm{m}$) a limit of $20\,\mu\mathrm{g\,m}^{-3}$ to be reached in the year 2020. Moreover, recent works indicate the finer fraction of PM as the most dangerous for human health [3-10].

Up to now PM concentrations are routinely monitored, but the measurement of elements and compounds concentration is very important for several reasons. Elements and/or compounds can trace specific emissions and the knowledge of the chemical composition of particulate matter can be used to evaluate the impact of the various sources on air quality. Several "source apportionment" strategies have been developed during time and receptor models [11] are presently one of the most used approaches. They usually give three kinds of information: the number of (major) sources of particulate matter, the source profiles and the mass contribution of each source to total PM. The models single out groups of elements with correlated concentration time trends which are then associated to real-world sources on the basis of their composition (source profile). Among anthropogenic sources, we focus here on heavy oil combustion which has quite clear tracers as V-Ni [12, 13].

Major sources of heavy oil combustion are, at least in Italy, oil-fired power plant, domestic heating, industrial vehicles and the diesel engines of ships, so that big harbours can produce significant pollution levels, in particular because the vessels keep turned on their auxiliary engines during the berth. A complete discussion on the types of fuels used for marine diesels is beyond the scope of this work but the impact of ships emissions is a worldwide recognized problem and it has been considered also in terms of climate forcing at planetary level [14-16].

To resolve the contribution of each source to total PM concentration we used the receptor model known as Positive Matrix Factorization, PMF [17]. PMF is a variant of factor analysis [18, 19] which constrains factor loadings and factor scores to non-negative values. The basic inputs to PMF and to any other receptor model are the concentration of the elements and/or compounds measured as a function of time. In this respect, nuclear techniques and, in particular, Ion Beam Analysis (IBA) at particle accelerators, are powerful tools. They give the possibility to measure in short times the composition of large numbers of PM samples. In some cases and with particular sampling techniques [20, 21] IBA is the unique possible analytical tool.

In this paper we discuss how the contribution of the harbour emissions to PM concentration in the city of Genoa has been determined exploiting IBA and other techniques.

2. – Material and methods

2·1. *PM sampling.* – Genoa is the most populated costal town in the northwest of Italy (about 700000 inhabitants), grown in the centuries around the largest Italian harbour, with significant steelworks in the surrounding, and largely influenced by Mediterranean climate. The topography of the area (a chain of steep hills, up to 1000 m a.s.l., lays immediately behind the coast with the urban area developed as a narrow line along the sea) produces a quite complex meteorological regime characterized by sudden changes in wind direction and speed. PM data, collected in the past by local authorities, show non-correlated concentration trends in different parts of this 40 km long city.

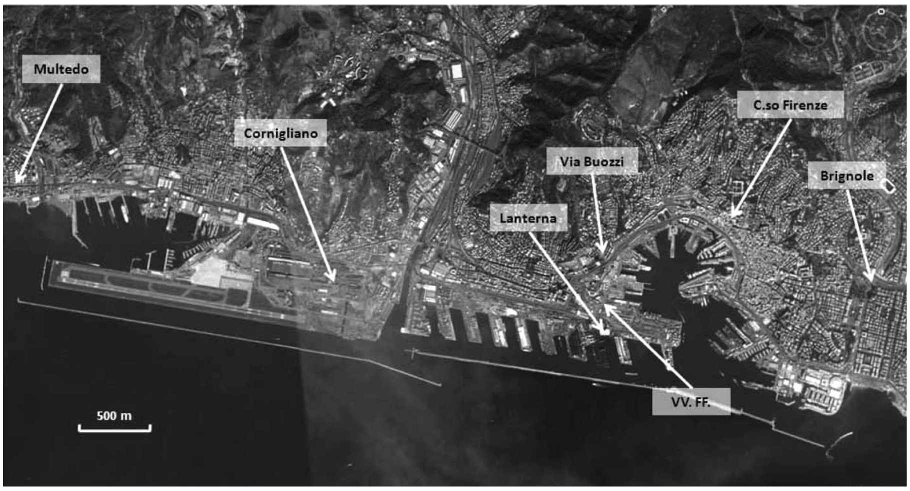

Fig. 1. – Map of the urban area of Genoa with the positions of the sampling sites.

We carried out monitoring campaigns in several sites (fig. 1) from May 2002 to August 2008: the maximum distance between any site and the sea was about 1 km.

For most of the time we used sequential PM samplers, equipped with inlets to select PM10, PM2.5 or PM1 (PM1 = particulate matter with $D_{\mathrm{ae}} \leq 1\,\mu\mathrm{m}$). In two sites (Buozzi and VVFF, see fig. 1) of the most recent campaigns we also used, for short periods, a two-stage continuous streaker sampler. This sampler and the control unit, which we developed for it, have been fully described elsewhere [22]. Briefly, the streaker consists of a pre-impactor that intercepts particles with aerodynamic diameter, $D_{\mathrm{ae}} > 10\,\mu\mathrm{m}$, a thin Kapton foil that collects particles with $2.5\,\mu\mathrm{m} < D_{\mathrm{ae}} < 10\,\mu\mathrm{m}$ and of a Nuclepore filter (pores size: $0.4\,\mu\mathrm{m}$) that intercepts all smaller particles with efficiency very close to 1. The impaction plate and the filter are paired on a cartridge which rotates semi-continuously for a week driven by a stepper motor. The sampling produces therefore a circular deposit (streak) on the two stages. The streaks are 3 mm and 8 mm high, in the Kapton foil and in the Nuclepore filter, respectively; the sucking orifice coupled to the Nuclepore filter has a rectangular shape ($2 \times 8\,\mathrm{mm}^2$). Air flow through the streaker is kept at $1\,\mathrm{l\,min}^{-1}$ by a mass flowmeter [22] to maintain the cut-off diameter at $2.5\,\mu\mathrm{m}$.

In the VVFF site (fig. 1) we also ran for two weeks in July 2008 a multi-stage inertial impactor [23, 24]. With an impactor, particles are collected in different stages according to their D_{ae}. We used the SDI (Small Deposit Area) by DEKATI [25]. This is a 12 stage impactor with the following cut-off diameters (in μm): 8.57, 4.12, 2.70, 1.68, 1.070, 0.804, 0.598, 0.349, 0.235, 0.1548, 0.0897, and 0.0479. During the two weeks at VVFF, we repeated several times the sampling varying the collection time from 12 hours to about 3 days: with cascade impactors each set of collection substrates is used for just one sampling. PM was collected on Kapton foils coated with APIEZON grease to avoid the rebouncing effect: these foils were provided mounted on plastic rings (external diameter = 25 mm, internal diameter = 12.6 mm) by PIXE International [26]. During the sampling, PM is collected on each stage according to the number and diameter of the respective inlets. This produces various inhomogeneous deposition patterns as shown in the four examples given in fig. 2 where the PM collected on the impaction stages look distributed in 3, 17, 28 and 54 small spots, respectively.

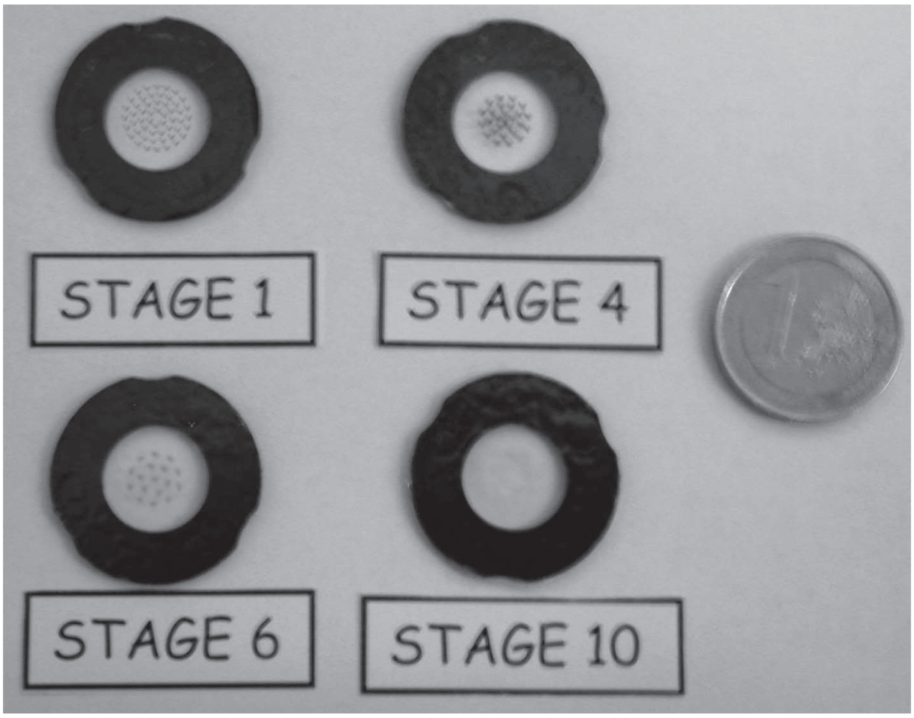

Fig. 2. – Pictures taken after the sampling of some Kapton foils positioned in different stages of the SDI impactor: PM is collected as small spots distributed on the surface of the foils according to number, diameter and position of the inlets.

2˙2. *Laboratory analyses.* – The PM concentration was determined using 47 mm Teflon membranes with 2 μm pore size. Sampling time was always 24 hours beginning at midnight. Filters, pre-conditioned for 2 days in a controlled room (temperature: $20 \pm 1\,^{\circ}$C, relative humidity: $50 \pm 5\%$), were weighed using an analytical balance (sensitivity: 1 μg); electrostatic effects were avoided using a de-ionizing gun.

The elemental composition of PM collected on daily basis on Teflon filters was detected by ED-XRF at the Physics Department of the Genoa University using an ED-2000 spectrometer by Oxford Instruments [13, 27]. X-ray spectra were fitted for 25 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Mo, Ba, Pb) using AXIL software package [28]. The elemental thickness (μg cm^{-2}) was obtained by comparing the filter yields with a sensitivity curve measured in the same geometry on a set of thin standards certified within 5% (Micromatter Inc.). Minimum Detection Limits (MDL) ranged from 1 to 10 ng m^{-3} and the uncertainties on measured values were on average 10%. However, uncertainties up 30% were registered for elements with concentration lower than 50 ng m^{-3} and on Na and Mg, due to corrections for self-absorption effects.

A PIXE analysis [29] was performed on streaker deposits, using the external beam facility of the 3 MV Tandem accelerator of INFN LABEC laboratory at the Physics Department of the Florence University [30]. PIXE spectra were fitted for 25 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Mo, Ba, Pb) using the GUPIX software package [31] and the elemental concentrations were

TABLE I. – *Summary of the average results on heavy oil combustion obtained since the year 2002 in several sites in the urban area of Genoa. In the last column, the ratio between the concentration of* V *and* Ni, *attributed by PMF to heavy oil combustion, is shown.*

Site	Period	PM Fraction	PM (μg/m^3)	Contribution of heavy oil combustion to PM (μg/m^3)	V/Ni
Brignole	1/5/02 → 30/6/04	PM_{10}	41 ± 1	9.7 ± 1.8	3.0 ± 0.9
C.so Firenze	17/10/04 → 11/6/05		25 ± 1	2.2 ± 0.8	3.0 ± 0.7
Multedo	2/12/04 → 31/1/05		41 ± 1	3.6 ± 0.9	3.8 ± 1.1
Lanterna	20/7/05 → 4/2/06		30 ± 1	1.9 ± 0.7	2.9 ± 0.9
Cornigliano	13/1/06 → 28/4/06		43 ± 1	5.4 ± 0.7	2.2 ± 0.8
Via Buozzi	23/10/06 → 1/9/07		40 ± 1	5.3 ± 0.7	3.1 ± 0.7
VV. FF.	12/3/08 → 2/9/08		24 ± 1	2.9 ± 0.6	2.3 ± 0.3
Cornigliano	21/5/05 → 2/7/05	$PM_{2.5}$	19 ± 1	7.6 ± 0.6	3.3 ± 0.6
Multedo	11/6/05 → 4/7/05		20 ± 1	2.7 ± 0.5	3.5 ± 0.8
Lanterna	16/9/05 → 21/1/06		17 ± 1	1.6 ± 0.3	2.8 ± 0.6
Via Buozzi	16/5/07 → 3/10/07		23 ± 1	6.8 ± 0.6	2.7 ± 0.5
C.so Firenze winter	21/12/03 → 29/2/04	PM_1	10 ± 1	2.0 ± 0.6	3.0 ± 1.0
C.so Firenze summer	22/6/04 → 21/9/04		17 ± 1	5.0 ± 1.0	3.2 ± 1.2
Multedo	11/2/05 → 4/4/05		18 ± 1	2.7 ± 0.5	3.7 ± 1.2
Cornigliano	17/3/05 → 18/5/05		17 ± 1	10.2 ± 0.3	2.0 ± 0.6

obtained via a calibration curve from a set of thin standards (Micromatter Inc., US). Minimum Detection Limits (MDL) of each element varied from 1 to 10 ng m^{-3}. Total mass concentration cannot be measured on streaker frames.

PIXE was also used to analyze the Kapton membranes used in the SDI impactor (fig. 2). In this case the beam was collimated to form a 1 mm × 1.7 mm homogeneous spot and the sample was moved to scan uniformly a part of the foil larger than the deposition area. In this way an average "effective thickness" was measured and absolute concentration values were obtained via the calibration curve as described above.

2˙3. *Statistical analysis*. – PMF was applied to the data sets of elemental concentrations in the PM10, PM2.5 and PM1 size fractions corresponding to the sampling periods and sites quoted in table I. The PMF methodology has been described in detail by its developers [32] and it has been adopted in several studies for receptor modelling of airborne PM and for a successfully assessment of particle source contributions [33-36]. Concentrations values and their associated errors were here treated according to the methodology suggested by Polissar *et al.* [37]. To reduce the influence of extreme values on the PMF solution, the robust mode was used, *i.e.* a high uncertainty has been attributed to outliers [37]. The determination of the optimal solution was performed following Lee *et al.* [38] and the PMF diagnostics therein described. It is worth noting that PMF is a descriptive model and there is no objective criterion to choose the best solution [32]. In this work the final solutions were determined by choosing those which were more stable with respect to different input options and those with the most physically meaningful profiles. Once the major sources of ambient PM were identified, their apportionment was obtained including PM mass concentration as an independent variable in PMF model analysis [36]. In this case, the PM mass data were down-weighted in the analysis by setting the uncertainties to 5 times their actual value. Further technical details on the PMF analysis are given in [13] and references therein.

3. – Results and discussion

The long campaign produced results which have been partially published elsewhere [13, 27, 39]: we focus here on the apportionment of heavy oil combustion (mainly obtained by daily sampling with Teflon filters) and on the tracks of ships emission singled out by streaker sampling.

In table I we summarize the V to Ni concentration ratio and the contribution of heavy oil combustion to PM concentration calculated by PMF, using the data collected in all sites (fig. 1). The V : Ni concentration ratio turns out to be very stable in all sites, periods and PM fractions: its overall average value is 3.0 ± 0.5; similar values have been found in other works [12]. Concentration ratios V : Ni = 3.5–4 have been very recently measured in tests with different ships engines and fuels, sampling directly at the exhausts of the auxiliary engine used in the harbours [40]. The contribution of heavy oil combustion to PM concentration is, according to the PMF analysis and on average, about 12% in PM10 and about 25% in PM2.5 and PM1. A particularly high contribution to PM1 (about $5\,\mu\mathrm{g\,m}^{-3}$) was found in the summer data set of C.so Firenze (table II): this could be in relation with the meteorological conditions (which in Genoa are, on average, more stable in summer than in winter) and to the notable increase of traffic of passenger ships in the harbour during the holidays period (about 35%). It should be noted that significant stationary sources (*e.g.*, power plants) that burn residual oil are not present in the urban area of Genoa, so it seems that the harbour activity is the dominant source of heavy oil combustion.

The same indication comes from hourly data, obtained in two one-week long campaigns carried on in July 2007 and July 2008 in two sites located nearby the harbour. The first site (Buozzi, July 2007, see fig. 1) was immediately behind the harbour precinct along one of the major roads in town. The streaker was positioned at about 2.5 m above ground. The second site (VVFF, July 2008, see fig. 1) was again in the blind alley but it was on the roof of a public building also serving as a parking, the height from ground was about 15 m. In fig. 3a and 3b the time series of V and Ni concentration, measured in Buozzi and VVFF, respectively, and obtained by the PIXE analysis of the Nuclepore stages of the streaker samplers, are shown. In both cases, the concentrations of the two elements are correlated ($R^2 = 0.81$, and 0.63, respectively) and the V : Ni average concentration ratio is about 2.5. Both elements show concentration peaks at the hours between 8–9 a.m and 8–10 p.m: these are the times of arrival and departure of the ferryboats which connect Genoa with some Mediterranean islands (Sardinia, Sicily, Corsica). The number of daily trips increases during summer. The peak hours in fig. 3 could look the same of traffic rush hours: as a matter of fact the tracers of traffic (Cu, Zn among the elements detected by PIXE) have concentration peaks at slightly different moments (not shown here) and they do not show any correlation with the V and Ni time series (correlation coefficient between V or Ni and Cu is always smaller than 0.2).

The two sites have about the same distance to the harbour but a completely different position with respect to urban traffic. In PM10, the average Cu concentration was about

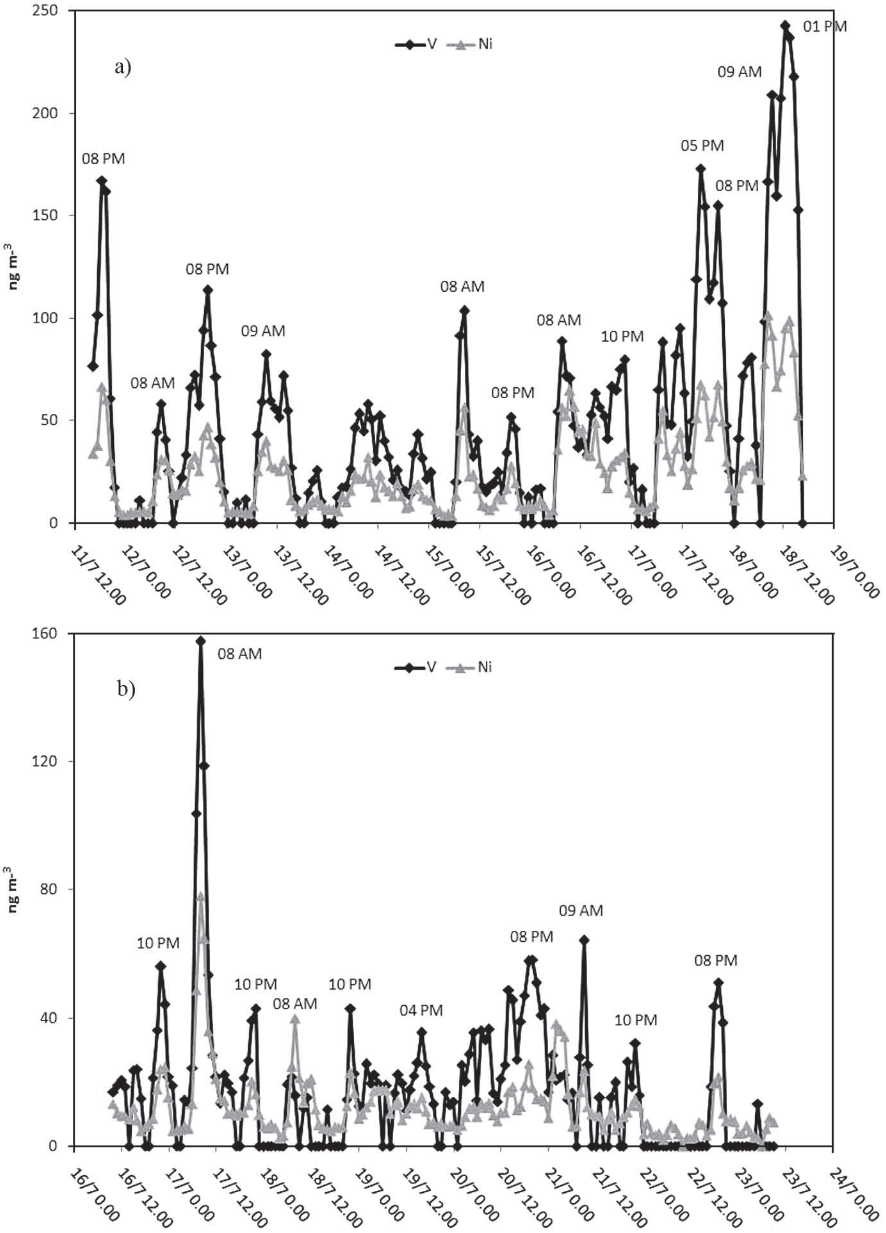

Fig. 3. – Concentration time series of V and Ni in the fine fraction of PM10, obtained by the PIXE analysis on the Nuclepore filter of the two-stage streaker sampler; a) site "Buozzi", July 2007; b) site "VVFF", July 2008.

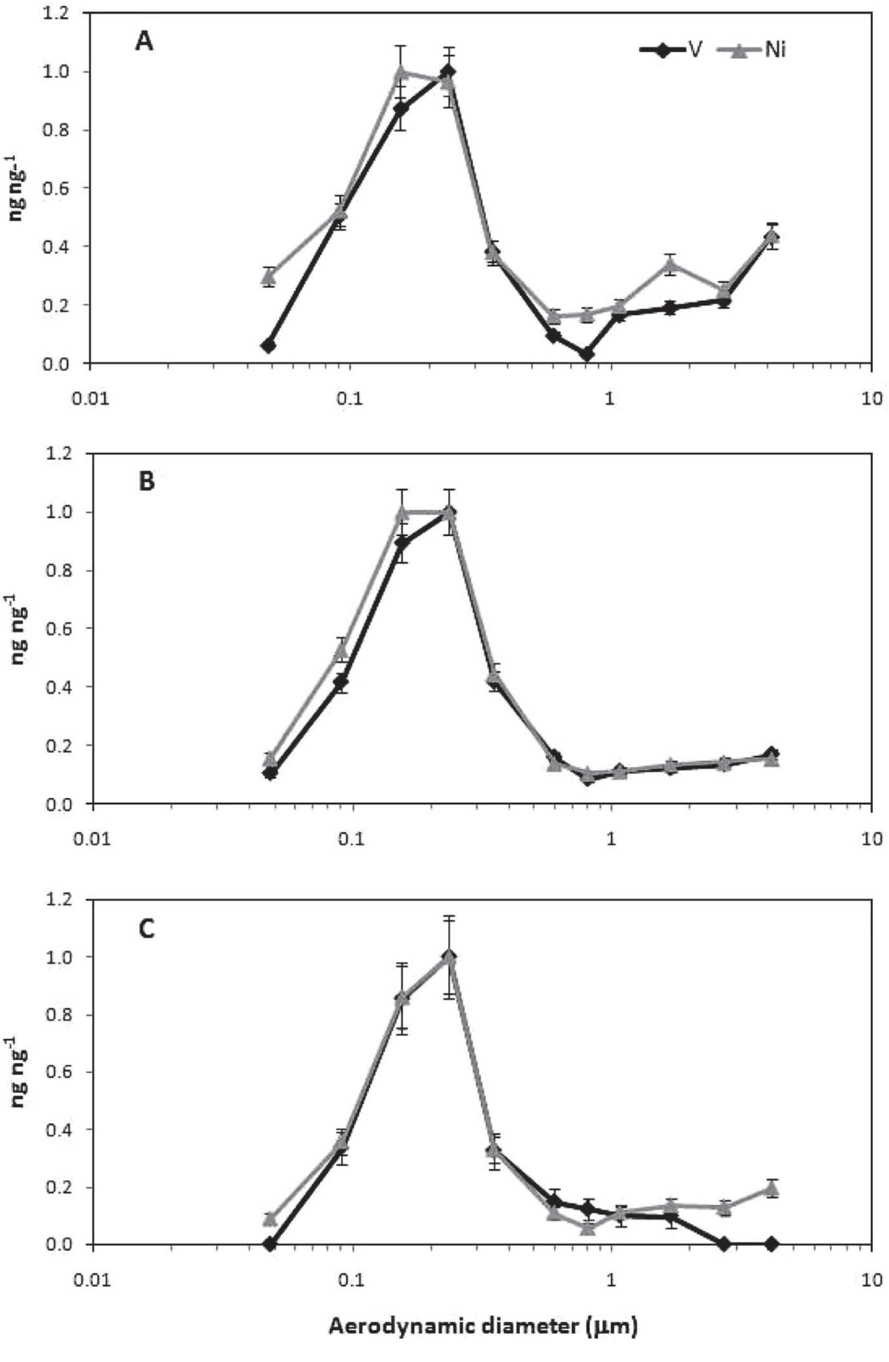

Fig. 4. – Mass distribution of V and Ni measured by SDI impactor + PIXE analysis at the VVFF site in July 2008 with three different samplings. A: from 14 July 12.15 pm to 16 July 9.35 am; B: from 18 July 10.35 am to 21 July 9.15 am; C: from 21 July 9.45 am to 22 July 9.15 am. Plotted data are the distribution of the V or Ni mass detected on the twelve stages of the SDI impactor *vs.* the cut-off diameters listed in the text.

$80\,\mathrm{ng\,m^{-3}}$ and $20\,\mathrm{ng\,m^{-3}}$ respectively in Buozzi and VVFF, the latter being less sensitive to vehicle emissions. A different figure emerges for V and Ni: their concentration in PM10 turns out to be the same in the two sites (about $40\,\mathrm{ng\,m^{-3}}$ and $17\,\mathrm{ng\,m^{-3}}$, respectively for V and Ni).

The data in fig. 3 concern the fine fraction of PM10: actually the concentration of V and Ni in the coarse fraction of PM10 was small. This was confirmed also by the analysis of the samples collected by the SDI impactor. We analyzed three series of 12 samples corresponding to samplings in different periods as detailed in fig. 4, where the measured size-distributions of V and Ni are shown. The three sampling produced stable results even if with some fluctuations: about 85% of the mass of V and Ni was concentrated in particles with $D_{\mathrm{ae}} < 1\,\mu\mathrm{m}$ with the remaining but non-negligible part in the coarse fraction of PM10. Similar distributions have been reported in the literature [41, 42]. This result is in agreement with the increase of the loading of heavy oil combustion in PM2.5 and PM1 with respect to PM10 discussed above (around a factor 2). As a matter of fact, several studies (*e.g.*, [27]) showed that in Genoa the ratios PM10 : PM2.5 and PM2.5 : PM1 are around 2 and 1, respectively.

4. – Conclusions

The contribution of heavy oil combustion to PM concentration by vessels anchored and/or in transit in the harbour of Genoa was measured in the frame of a wider campaign of characterization of the aerosol sources in town. Various time- and size-resolved sampling methods were adopted and PIXE analysis was a key tool to extract reliable information. IBA techniques offer a unique possibility to analyze large numbers of unconventional samples (*i.e.* streaker and impactor stages and others) with good sensitivity (in the order of $\mathrm{ng\,m^{-3}}$). The work is in progress to single out from the very large data set possible tracks of other PM source related to the harbour activity as for instance goods handling.

* * *

This work has been partly supported by Amministrazione Provinciale di Genova—Assessorato all'Ambiente and by INFN. We are particularly indebted with Dr. E. Daminelli for his continuous and precious collaboration.

REFERENCES

[1] Charlson R. J., Schwartz S. E., Hales J. M., Cess R. D., Coakley J. A. jr., Hansen J. E. and Hoffman D. J., *Science*, **255** (1992) 423.

[2] Seinfeld J. H. and Pandis S. N., *Atmospheric Chemistry and Physics* (Wiley, New York) 1998.

[3] Schwartz J., Dockery D. W. and Neas L. M., *J. Waste Manag. Assoc.*, **46** (1996) 927.

[4] Maynard R. L. and Howard C. V., *Particulate Matter: Properties and Effects upon Health* (Bios Scientific Publisher, Oxford) 1999.

[5] Wichmann H. E. and Peters A., *Philos. Trans. R. Soc. London, Ser. A*, **358** (2000) 2751.

[6] Samet J., *Inhal. Toxicol.*, **12** (Suppl. 1) (2000) 19.

[7] Chow J. C., Engelbrecht J. P., Freeman N. C. G., Hashim J. H., Jantunen M., Michaud J. P., De Tejada S. S., Watson J. G., Wei F., Wilson W. E., Yasuno M. and Zhu T., *Chemosphere*, **49** (2002) 873.

[8] Chow J. C., Engelbrecht J. P., Watson J. G., Wilson W. E., Frank N. H. and Zhu T., *Chemosphere*, **49** (2002) 961.

[9] Stieb D. M., Judek S. and Burnett R. T., *J. Air Waste Manag. Assoc.*, **52** (2002) 470.

[10] Fernandez A., Wendt J. O. L., Wolski N., Hein K. R. G., Wang S. and Witten M. L., *Chemosphere*, **51** (2003) 1129.

[11] Gordon G. E., *Environ. Sci. Technol.*, **22** (1988) 1132.

[12] Hedberg E., Gidhagen L. and Johansson C., *Atmos. Environ.*, **39** (2005) 549.

[13] Mazzei F., D'Alessandro A., Lucarelli F., Nava S., Prati P., Valli G. and Vecchi R., *Sci. Total Environ.*, **401** (2008) 81.

[14] Corbett J. J. and Koehler H. W., *J. Geophys. Res.*, **108** (2003) 4650, doi: 10.1029/2003JD003751.

[15] Endresen Ø. E. Sørgård J. K., Sundet S. B., Dalsøren I. S. A., Isaksen T. F. and Berglen G., *J. Geophys. Res.*, **108** (2003) 4560, doi: 10.1029/2002JD002898.

[16] Lack D. B., Lerner B., Granier C., Baynard T., Lovejoy E., Massoli P., Ravishankara A. R. and Williams E., *Geophys. Res. Lett.*, **35** (2008) L13815, doi: 10.1029/2008GL033906.

[17] Paatero P. and Tapper U., *Environmetrics*, **5** (1994) 111.

[18] Heidam N. Z., *Atmos. Environ.*, **16** (1982) 1923.

[19] Thurston G. D. and Spengler J. D., *Atmos. Environ.*, **19** (1985) 9.

[20] Prati P., Zucchiatti A., Lucarelli F. and Mandò P. A., *Atmos. Environ.*, **34** (2000) 3149.

[21] Bukowiecki N., Hill M., Gehrig R., Lienemann P., Zwicky C. N., Hegedu S. F., Falkenberg G., Weingartner E. and Baltensperger U., *Environ. Sci. Technol.*, **39** (2005) 5754.

[22] Formenti P., Annegarn H. J., Prati P., Zucchiatti A., Lucarelli F. and Mandò P. A., *Physica Medica*, **XIII** (1997) 101.

[23] Hillamo R. and Kauppinen E. I., *Aerosol Sci. Technol.*, **14** (1991) 33.

[24] Marple V. A., Rubow K. L. and Behm S. M., *Aerosol Sci. Technol.*, **14** (1991) 434.

[25] Maenhaut W., Hillamo R., Mäkelä T., Jaffrezo J. L., Bergin M. H. and Davidson C. I., *Nucl. Instrum. Methods B*, **109/110** (1996) 482.

[26] PIXE International Corporation, P.O. Box 7744, Tallahassee, FL 32316, USA.

[27] Ariola V., D'Alessandro A., Lucarelli F., Marcazzan G., Mazzei F., Nava S., Garcia Orellana I., Prati P., Valli G., Vecchi R. and Zucchiatti A., *Chemosphere*, **62** (2006) 226.

[28] Van Espen P., Nullens H. and Adams F., *Nucl. Instrum. Methods*, **142** (1977) 243.

[29] Johansson S. A. E., Campbell J. L. and Malmqvists K. G., *Particle-Induced X-ray Emission Spectrometry* (John Wiley & Sons) 1995.

[30] Calzolai G., Chiari M., García Orellana I., Lucarelli F., Migliori A., Nava S. and Taccetti F., *Nucl. Instrum. Methods B*, **249** (2006) 928.

[31] Maxwell J. A., Teesdale W. J. and Campbell J. L., *Nucl. Instrum. Methods B*, **95** (1995) 407.

[32] Paatero P., *Chemometrics and Intelligent Laboratory Systems*, **38** (1997) 223.

[33] Kim E., Larson T. V., Hopke P. K., Slaughter C., Sheppard L. E. and Claiborn C., *Atmos. Res.*, **66** (2001) 291.

[34] Liu W., Hopke P. K., Han Y. J., Yi S.-M., Holsen T. M., Cybart S., Kozlowski K. and Miligan M., *Atmos. Environ.*, **37** (2003) 4997.

[35] Ramadan Z., Song X. H. and Hopke P. K., *J. Air Waste Manag. Assoc.*, **50** (2003) 1308.

[36] Qin Y., Kim E. and Hopke P. K., *Atmos. Environ.*, **40** (2006) 312.

[37] Polissar A. V., Hopke P. K., Paatero P., Malm W. C. and Sisler J. F., *J. Geophys. Res.*, **103** (1998) 19045.

[38] Lee E., Chan C. K. and Paatero P., *Atmos. Environ.*, **33** (1999) 3201.

[39] Mazzei F., Lucarelli F., Nava S., Prati P., Valli G. and Vecchi R., *Atmos. Environ.*, **41** (2007) 5525.

[40] Nigam A., Welch W., Wayne Miller J. and Cocher III D. R., in *Proceedings of the VII International Aerosol Conference, Sept. 10-15 2006, St. Paul, Minnesota*, pp. 1531-1532.

[41] Buerki P. R., Gaelli B. and Nyffeler U. P., *Atmos. Environ.*, **23** (1989) 1659.

[42] Wang X., Sato T. and Xing B., *Chemosphere*, **65** (2006) 2440.