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Toxic elements content in PM_{10} samples from a coastal area of the Northern Adriatic Sea

Research Article

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Abstract: PM_{10} samples were collected during winter and summer seasons at two different sites in the area of Trieste (Italy). The content of As, Cd, Cr, Mn, Ni, Pb and V in the PM_{10} samples was determined by inductively coupled plasma-mass spectrometry, with the purpose of evaluating the relevance of PM_{10} inhalation as a route of human exposure to these elements. The results showed that the ambient air concentration of the aforementioned elements were below the limits or target values for both sites and season. Site and season-specific correlation analysis was conducted for the identification of metals with similar origin: very good correlation for the couple Ni-V was found in both sites and seasons, showing the influence of combustion of heavy oils in PM_{10} composition. The inter-site and seasonal variability of both PM_{10} and metal concentrations were examined. A stronger impact by the vehicular traffic on the PM_{10} and metal concentrations was found for the urban site in both seasons. Because of the great importance of the "Bora" wind on the local climate, variability of PM_{10} and toxic elements concentration with wind were analysed, allowing determination of the effect of wind on dilution of the pollutants for the urban site during both seasons.

Keywords: *Particulate matter • Metals • Ambient air quality • ICP-MS • Bora wind*

1. Introduction

Among the many pollutants known to have adverse health effect, particular attention has been given to particulate matter of aerodynamic size less than 10 μm (PM_{10}). Several epidemiological studies have shown the negative effects of PM_{10} on human health [1-4]. PM_{10} has a variable and complex composition that includes a wide range of both organic and inorganic compounds. Moreover, they can also carry toxic pollutants, like heavy metals, that can be deposited in the respiratory tract during breathing [5,6].

Recent studies have related the PM_{10} induced toxicity *in vivo* and *in vitro* to the concentration of metals in PM_{10} [7].

The European Union set an annual limit value of 40 μg m^{-3} and a 24-h limit value of 50 μg m^{-3} (not to be exceeded over 35 times in a year) for PM_{10} (in force by January 2005).

Several metals and metalloids are present in the PM_{10} and some of them are well known for their peculiar toxicity. Arsenic (As), Cadmium (Cd), Chromo (Cr), Manganese (Mn), Nickel (Ni), Lead (Pb) and Vanadium (V) have been considered in this study.

Among all organic and inorganic arsenic compounds most of the toxic effects arise from exposure to the latter.

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Arsenic affects nearly all organ systems of the body since it targets a number of metabolic processes, and it is consider a human carcinogen, as it has been well documented [8].

Arsenic is ubiquitous in nature and is released to the atmosphere from both natural (*e.g.* volcanic activity, minor contributions by exudates from vegetation, windblown dusts) and anthropogenic sources (*e.g.* smelting of metals, combustion of fuels, especially of low-grade brown coal, use of pesticides) [9].

Cadmium is carcinogen and has adverse effects on kidney, bones, and lungs. Moreover, it has a very long biological half-life, estimated at more than 20 years in humans [9-11].

The main sources of airborne Cd are anthropogenic, mainly from smelting and refining of nonferrous metals, fossil fuel combustion and municipal waste incineration, while the natural sources of Cd are volcanic activities.

Chromium exists in the environment in two oxidation states: Cr(III) and Cr(VI). Cr(III) is recognized as a trace element that is essential to both humans and animals. However, Cr(VI) compounds are toxic and carcinogenic.

Natural sources like wind erosion of shale, clay and many other kinds of soil are the primarily sources for Cr(III), while anthropogenic sources such as fuel combustion (residential, commercial, and industrial), chrome plating and steel production release both Cr(III) and Cr(VI) into the atmosphere [12,13].

The main sources that release manganese into the atmosphere are both natural, like wind erosion and the suspension of soils, and anthropogenic, like metallurgical processes, production of batteries and combustion of fossil fuels (organic carbonyl compounds of Mn are used as fuel-oil additives, smoke inhibitors and anti-knock additives in petrol). Manganese is an essential trace element for all forms of life, however different studies have demonstrated that exposure to Mn could lead to neurotoxical effects with Parkinson-like symptoms [14], thus, the WHO (World Health Organization) – Europe in 2000 suggested a guideline annual limit value of 150 ng m^{-3} for this compound.

Nickel is known to be an allergenic agent, teratogenic and carcinogenic [15,16].

Combustion of fossil fuels produces the greatest contribution of nickel compounds in ambient air [17].

In 2003 the European Commission proposed a directive (2004/107/EC) concerning concentrations of Polycyclic Aromatic Hydrocarbon (PAHs) and toxic metals (As, Cd, Hg and Ni) in ambient air. The mean annual concentration target values proposed were respectively 6 ng m^{-3} for As, 5 ng m^{-3} for Cd and 20 ng m^{-3} for Ni.

Lead has deleterious effects on erythropoiesis, kidney function, and the central nervous system, especially in children [18].

After the ban of tetraethyl lead as an anti-knocking fuel addictive, the air concentration of this metal has decreased and is reported to be far from severe in air. However, vehicular traffic is still one of its important sources, besides industrial sources and fuel burning activities, since petrol can still contain up to 15 mg L^{-1} of lead [19-21].

The European Directive 1999/30/EC covering - beside other pollutants - particulate matter and Pb in ambient air, set an annual limit of 500 ng m^{-3} for Pb.

Besides vanadium ore refining and metallurgical works, the largest anthropogenic source of V is fossil fuel combustion, especially residual/heavy oils, which are known to be rich in this element. However, lighter distilled oil fractions used for transportation are known to have low V levels [22,23].

Vanadium compounds, and especially V_2O_5, are well known for causing irritation on the lungs, throat, eyes and nasal cavities. Moreover, some recent studies indicate a possible synergistic relationship between inhaled V and Ni [24].

The WHO – Europe in 2000 suggested a 24-h guideline limit value of 1 μg m^{-3} for V.

Our experimental activities have been conducted in the framework of the SITECOS (Integrated Study on national TErritory for the characterization and COntrol of atmoSpheric pollutants) PRIN project 2004–2006 [25-27].

The aim of the work is to present a first assessment of the concentrations of toxic elements in ambient air across the coastal area near the harbor of Trieste (Italy).

The study is relevant in this small territory (84 km^2) due to the presence of several human activities which have the potential for toxic element emissions to ambient air and consequent human exposure by inhalation. Moreover, we present an evaluation of variability of these metal and metalloids in PM_{10}, considering two different sites, two different seasonal situations, and effects of different meteorological conditions and weekly traffic patterns on air quality parameters.

2. Experimental Procedure

2.1. Sampling sites

The city of Trieste is located in the N-E of Italy (latitude: 45° 38′ N longitude: 13° 48′ E) in the northernmost part of the Adriatic and Mediterranean Sea, close to the

Slovenian border. The city has a population of about 200,000 inhabitants with densely populated areas.

The mild Mediterranean climate of Trieste is occasionally interrupted by very changeable cold and blustery weather brought it by a northern to north-eastern (meteorological wind direction) katabatic wind called the "Bora" on the Adriatic [28]. Bora can reach speeds up to 170 km h^{-1} and blow for several days.

The first sampling site represents an urban area characterized by the presence of mixed residential and commercial areas. In addition to typical urban diffuse and point sources of pollution, a number of specific point sources located near to the sampling site are considered. An integrated steel mill is considered a source of major concern for the inhabitants of the surrounding residential area since the coke plant (coke production: 450,000 tons $year^{-1}$) has relevant pollutant emissions in the atmosphere. Additionally, a solid waste incineration facility, a cement factory, and the activities of the harbor are approximately a kilometer close.

The second sampling site is located in the Municipality of Muggia - 3 km south from the first one – along the coast. The site has a low population density and no local pollution sources are evident. However, since the site is located less than 4 km from the pollution sources mentioned for the first site, it could be affected by these distant pollution sources.

The first and second sampling sites are conventionally named as urban site and coastal site, respectively.

The map of the city, the sampling sites, the meteorological station, the integrated steel mill plant, the solid waste incineration facility and the cement factory are shown in Fig. 1.

2.2. Sampling protocol and PM_{10} gravimetric analysis

The first sampling campaign was conducted between February 1st and March 5th, 2006 to cover the winter period, while the second sampling campaign was conducted from the June 20th to July 24th, 2006 to cover the summer period.

The daily sampling operations were performed each day for 24 h starting at 00:00 am, and simultaneously in both sites.

The first and second sampling campaigns are conventionally named as winter campaign and summer campaign, respectively.

All the samples were collected on 47 mm diameter polytetrafluoroethylene filters (Teflo™ by Pall Corporation) by two HYDRA Dual Sampler (FAI Instruments s.r.l. – Italy) sampling systems with an EN 12341 European PM_{10} sampling head. The flow rate was established in agreement with the EU regulations (1999/30/CE) and it was set at 2.3 m^3 h^{-1} with a nominal sampling volume of 55.2 m^3.

To obtain reliable mass measurements, the filters were conditioned for 48 h in an Aquaria® Activa Climatic electric chamber at a temperature of 20±1°C and humidity of 50±5%, before and after the sampling. And the net mass of PM_{10} was determined by weighing the filters before and after sampling using a Gibertini® Microcrystal 250 electronic microbalance with a reading precision of 0.001 mg.

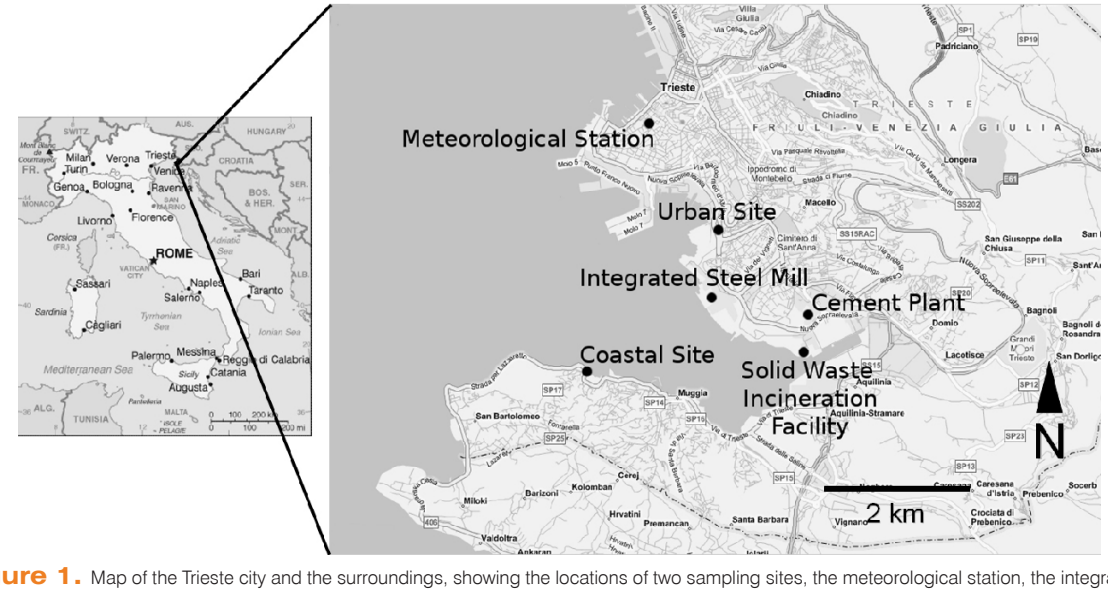

Figure 1. Map of the Trieste city and the surroundings, showing the locations of two sampling sites, the meteorological station, the integrated steel mill, the solid waste incineration facility and the cement factory

2.3. Sample preparation and chemical analysis

The filters were extracted by sonication using ultrapure 68% nitric acid (Carlo Erba SpA) [29].

This method does not dissolve aluminium silicate minerals, thus the concentration of Cr associated with Al-Si minerals may be underestimated since hydrofluoridric acid was not used in the extraction procedure either. However, it is known that the fraction of metals associated with Al-Si minerals is scarcely bioavailable [30].

The obtained solutions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using a Perkin-Elmer ELAN® DRC II spectrometer for all the elements.

The ICP-MS was calibrated using the "Perkin-Elmer calibration standard 3" with a metal concentration of 10 μg mL^{-1}. Every ten samples the response of the instrument was checked using the "NIST 1643 Trace Elements in Water" certified standard material.

Considering an average daily sampling volume of 55.2 m^3 the detection limits for each element were: 0.0018 ng m^{-3} for As, 0.0091 ng m^{-3} for Cd, 0.0018 ng m^{-3} for Cr, 0.0054 ng m^{-3} for Mn, 0.0091 ng m^{-3} for Ni, 0.0018 ng m^{-3} for Pb and 0.011 ng m^{-3} for V.

2.4 Statistical procedures

Data were summarized using the mean and the median as measures of central tendency, and also the standard deviation (SD) and the range as measures of dispersion.

Statistical analyses were performed on the data sets of both sites and seasons for detecting the presence of outliers, defined as values higher than 1.5 times the 95th percentile.

The Kalmogorov-Smirnov statistical test was employed to evaluate the normality of data distribution. Data were not normally distributed after logarithmic transformation, thus, the U Mann-Whitney test was used instead of a two-way ANOVA to assess intersite and seasonal data variability.

A Varimax-rotated Principal Component Analysis (PCA) was performed to qualitatively determine the

Table 1. Descriptive statistics of measured concentrations at both sites for winter (W) and summer (S) campaigns (all concentrations are in ng m^{-3} except PM10 mass concentration expressed in $\mu g\ m^{-3}$)

	Urban Site W (n=33)		Number of days with concentration over the EU or WHO limits	Coastal Site W (n=33)		Number of days with concentration over the EU or WHO limits	Urban Site S (n=35)		Number of days with concentration over the EU or WHO limits	Coastal Site S (n=35)		Number of days with concentration over the EU or WHO limits
	Mean	Median		Mean	Median		Mean	Median		Mean	Median	
	SD	Range		SD	Range		SD	Range		SD	Range	
PM_{10}	35.7	32.1	6 (18%)	30.1	26.1	3 (9%)	38.8	34.9	8 (24%)	30.5	29.0	2 (6%)
	20.1	6.1 - 84.4		17.8	8.6 -81.5		16.3	11.1 - 76.1		12.1	10.1 - 57.8	
As	0.72	0.57	-	0.7	0.6	-	0.79	0.79	-	0.70	0.60	-
	0.44	0.19 - 2.11		0.5	0.2 - 2.0		0.35	0.2 - 1.41		0.35	0.20 - 1.41	
Cd	0.36	0.37	-	0.52	0.23	-	0.28	0.20	-	0.24	0.20	-
	0.21	0.06-0.85		0.70	0.02 - 3.43		0.17	0.08 - 0.61		0.17	0.06 - 0.80	
Cr	1.89	1.67	-	0.8	0.8	-	2.3	1.6	-	0.66	2.0E-05	-
	1.19	0.181 - 5.11		0.6	1.8E-06 - 1.9		1.8	0.08 - 7.02		1.36	1.8E-06 - 5.61	
Mn	10.9	9.4	-	6.0	4.0	-	17.1	12.1	-	10.9	9.9	-
	6.9	1.5 - 26.4		4.7	0.4 - 16.4		10.6	1.98 - 49.32		5.4	3.95 - 22.1	
Ni	6.8	5.6	-	5.2	4.5	-	5.0	3.8	-	4.4	3.4	-
	4.7	1.1 - 19.2		2.9	1.3 - 11.4		3.9	9.1E-06 - 15.2		3.3	0.14 - 13.99	
Pb	17.4	15.1	-	31.9	36.4	-	13.3	11.9	-	17.4	16.1	-
	10.6	5.6 - 46.4		16.4	9.1 - 66.8		6.7	3.96 - 40.1		7.2	5.92 - 29.8	
V	13.3	7.6	-	10.6	9.3	-	15.1	14.1	-	18.5	18.1	-
	15.9	0.4 - 76.8		6.7	2.1 - 31.8		10.1	0.59 - 34.1		9.9	1.78 - 38.4	

sources of the contaminants in PM_{10}. The PCA attempts to explain the statistical variance in a number of original variances using a minimum number of significant components (factors) and with this rotation is widely used in the analysis of atmospheric aerosol [31].

Data were processed by means of the Statistica® and Excel® programs.

3. Results and Discussion

3.1. PM_{10}, trace metal concentrations and comparison with limit values and other sites

In Table 1 arithmetic means, standard deviations, medians and concentration ranges for PM_{10} and the analyzed metals are displayed together with the number of the days in which the EU or WHO limits were exceeded.

For $PM_{10,}$ the average concentrations do not exceed the EU annual limit value at either site during either season. However, at the urban site the seasonal mean was very close to this limit, especially in the summer. The percentages of daily PM_{10} concentrations higher than the 24-h limit were higher in the urban site for both seasons.

The above data – showing 14 exceedances in 68 days for the urban site - point to the need to pay attention to an airborne particulate matter pollution problem.

During this study, the measured concentrations for As and Cd were nearly one magnitude lower the limits mentioned in the introduction at both sites and seasons.

Table 2. Comparison of PM_{10} and elemental concentrations from different sites across Europe; all concentrations are in ng m^{-3} except PM_{10} mass concentration expressed in $\mu g\ m^{-3}$.

Site Type of Site Season	Trieste[1] Urban Winter	Trieste[1] Coastal Winter	Trieste[1] Urban Summer	Trieste[1] Coastal Summer	Milan[2] Urban Winter	Milan[2] Urban Summer	Palermo[3] Urban -	Udine[4] Urban Winter	Barcelona[5] Urban -
PM_{10}	35.7	30.1	38.8	30.5	110	74	36	41.6	49.8
As	0.72	0.70	0.79	0.70	-	-	1.5	-	-
Cd	0.36	0.52	0.28	0.24	-	-	-	0.29	-
Cr	1.89	0.8	2.3	0.66	14	<10	6.5	4.38	6.0
Mn	10.9	6.0	17.1	10.9	45	25	12	35.1	24
Ni	6.8	5.2	5.0	4.4	10	<6	5.5	3.07	7
Pb	17.4	31.9	13.3	17.4	310	120	18	27.6	149
V	13.3	10.6	15.1	18.5	9	<12	20	-	13

Site Type of Site Season	Tarragona[6] Urban Background -	Thessaloniki[7*] Urban Winter	Thessaloniki[7*] Urban Summer	Budapest[8] Urban Spring	Edinburgh[9] Urban -	Stockholm[10] Urban -	Chaumont[11] Rural above 1000 a.s.l. -
PM_{10}	37.4	92	74	48	14.2	36	10.8
As	0.8	1.9	1.5	1.40	0.37	0.77	0.18
Cd	0.3	0.94	0.61	-	0.34	0.31	0.11
Cr	3	12	9.3	8.9	1.6	3.7	-
Mn	9	27.7	24	30	2.94	18	2.4
Ni	4	11	9.7	3.2	3.43	3.9	1.3
Pb	26	78	63	24	14.1	15	5.4
V	8	43	36	2.9	1.14	3.3	0.8

[1]This work
[2]Marcazzan et al. (2001) Sampling years: 1997-1998; ED-XRF
[3]Dongarrà et al. (2007), Sampling year: 2005; HNO_3-$HClO_4$-HF; ICP-MS
[4]Cozzi et al. (2007), Sampling period: 2002-2003; HNO_3; ICP-AES+DPASV
[5]Querol et al. (2001); Sampling years: 1999-2000; HNO_3-HF-$HClO_4$; ICP-AES
[6]Querol et al. (2004); Sampling years: 2001-2002; HNO_3-HF-$HClO_4$; ICP-AES+ICP-MS
*[7]Voutsa et al. (2002), Sampling period: 1997-1998; HCl-HNO_3; FAAS+GFAAS; *Mean among three sites in the city*
[8]Maenhaut et al. (2005); Sampling years: 2002; PIXE+INAA
[9]Heal et al. (2005): Sampling years: 1999-2000; HCl-HNO_3; ICP-MS
[10]Furusjö et al. (2007); Sampling years: 2003-2004; HNO_3-HF; ICP-MS
[11]Hueglin et al. (2005); Sampling years: 1998-1999; HNO_3-H_2O_2; ICP-MS

Table 3. Results of Varimax-rotated principal component analysis for data from urban and coastal site; numbers typed in underlined italic letters denote loadings >0.5 and only factors loadings with moduli larger than 0.25 are shown

	Urban Site Winter & Summer			Coastal Site Winter & Summer		
	PC1	PC2	PC3	PC1	PC2	PC3
As	–	–	–	0.40	*0.75*	
Cd	*0.81*		0.35		*0.87*	
Cr	0.29	*0.87*				*0.91*
Mn		*0.83*	0.34	*0.74*		0.38
Ni	0.43	0.40	*0.73*	*0.54*	0.28	*0.66*
Pb	*0.89*				*0.82*	
V	0.19		*0.95*	*0.92*		
Variance (%)	60.5	14.5	11.9	46.0	21.0	11.7
Cumulative (%)	60.5	75.0	86.9	46.0	67.0	78.7

Ni concentrations were well below the limit, but only the maximum daily values were close to that limit.

Comparing our data with the EU limit, Pb appears not to be a problem for the air quality.

Regarding V and Mn, it is easy to see that the measured concentration for both sites and seasons were well below the WHO limits, especially for V.

Table 2 shows a comparison of PM_{10} and metals mean concentrations in the two sites and seasons with data collected across Italy and other European countries.

We chose other cities of Italy with a continental climate (like Milan and Udine) and a Mediterranean climate (like Palermo), other cities of the Mediterranean basin (like Barcelona, Tarragona and Thessaloniki), one central European city (Budapest), one on the Atlantic Ocean (Edinburgh), one in Northern Europe (Stockholm) and one remote site on the Swiss Jura (Chaumont).

Milan and Thessaloniki look the more polluted sites and in fact the PM_{10} and metal concentrations were higher compared with the Trieste sites measured in the reported study for both seasons (except for V in Milan); also Budapest and Barcelona had higher concentrations of PM_{10} and nearly all metals but to a minor extent.

Palermo, Udine, Tarragona and Stockholm had similar concentrations of PM_{10} but different metal concentrations. The city with more similar concentrations with both Trieste sites was Tarragona.

Edinburgh had the lower concentration for PM_{10}, As, Mn, Pb and V among the urban sites.

Chaumont, a remote site had not surprisingly lower concentrations of PM_{10} and metals than all other sites. We remark that V concentrations appear to be higher in Mediterranean coastal cities such as Thessaloniki, Barcelona, Palermo and Trieste, than in continental or northern cities as Edinburgh, Stockholm, but also Milan and Tarragona. A possible explanation links V concentration in air to heavy fuel emissions from marine traffic [32].

3.2 Site-specific associations

We explored the associations among the metals in each site and season using the Spearman non-parametric correlation coefficient (R critical=0.356 for n=33 with p=0.05; R critical=0.345 for n=35 and p=0.05).

During the winter season in the urban site the correlations among all the metals were generally good (R>0.70), except for As (R<0.40 with all the metals). Very good associations were found for the couples Cr-Mn (R=0.91, p<0.05) and Ni-V (R=0.90, p<0.05) suggesting common sources for each metals couple. For the couple Cr-Mn we assume the release from resuspended dust and steel mill emissions, while for Ni-V the most probable emission source could be heavy fuel combustion rich in those metals [33].

The summer season shown some change in these outline, the correlation among all analyzed metals drop below 0.70 except for the couple Cd-Pb (R=0.72, p<0.05) and Ni-V (R=0.87, p<0.05).

This seasonal difference can suggest an influence of the boundary layer that lifts during the summer season, promoting more efficient mixing and dispersion of the pollutants [34].

The situation of the coastal site during the winter season confirmed the strong correlation of the Ni-V couple (R=0.87, p<0.05). Like in the urban site, during the summer season the correlation among metals in general drops, suggesting again a seasonal influence. However, noTable exceptions are the couples Ni-V (R=0.64, p<0.05) and Ni-Mn (R=0.77, p<0.05).

Table 4. Site-specific average PM_{10} and trace metal concentrations in the two seasons, significance level of intersite variation tested by the non-parametric U Mann-Whitney test also displayed; numbers typed in underlined italic letters denote $p<0.05$

	Winter		
	Urban Site (n=33)	Coastal Site (n=33)	U Mann-Whitney Test
	Mean ± SD	Mean ± SD	
PM_{10} [$\mu g\ m^{-3}$]	35.7 ± 20.1	30.1 ± 17.8	0.188
As [ng m^{-3}]	0.72 ± 0.44	0.70 ± 0.50	0.858
Cd [ng m^{-3}]	0.36 ± 0.21	0.52 ± 0.70	0.665
Cr [ng m^{-3}]	1.89 ± 1.19	0.84 ± 0.60	*< 0.001*
Mn [ng m^{-3}]	10.9 ± 6.9	6.0 ± 4.7	*0.003*
Ni [ng m^{-3}]	6.83 ± 4.7	5.2 ± 2.9	0.352
Pb [ng m^{-3}]	17.4 ± 10.6	31.9 ± 16.4	*< 0.001*
V [ng m^{-3}]	13.3 ± 15.9	10.6 ± 6.7	0.646
	Summer		
	Urban Site (n=35)	Coastal Site (n=35)	U Mann-Whitney Test
	Mean ± SD	Mean ± SD	
PM_{10} [$\mu g\ m^{-3}$]	38.8 ± 16.3	30.5 ± 12.1	*0.038*
As [ng m^{-3}]	0.79 ± 0.35	0.70 ± 0.35	0.303
Cd [ng m^{-3}]	0.28 ± 0.17	0.24 ± 0.17	0.292
Cr [ng m^{-3}]	2.3 ± 1.8	0.66 ± 1.36	*< 0.001*
Mn [ng m^{-3}]	17.1 ± 10.6	10.9 ± 5.4	*0.007*
Ni [ng m^{-3}]	5.0 ± 3.9	4.4 ± 3.3	0.624
Pb [ng m^{-3}]	13.3 ± 6.7	17.4 ± 7.2	*0.010*
V [ng m^{-3}]	15.1 ± 10.1	18.5 ± 9.9	0.182

Table 5. Period-specific average PM_{10} and trace metal concentrations at the two sites, significance level of seasonal variation tested by the non-parametric U Mann-Whitney test also displayed; numbers typed in underlined italic letters denote $p<0.05$

	Urban Site		
	Winter (n=33)	Summer (n=35)	U Mann-Whitney Test
	Mean SD	Mean SD	
PM_{10} [$\mu g\ m^{-3}$]	35.7 ± 20.1	38.8 ± 16.3	0.316
As [ng m^{-3}]	0.72 ± 0.44	0.79 ± 0.35	0.086
Cd [ng m^{-3}]	0.36 ± 0.21	0.28 ± 0.17	0.457
Cr [ng m^{-3}]	1.89 ± 1.19	2.3 ± 1.8	0.696
Mn [ng m^{-3}]	10.9 ± 6.9	17.1 ± 10.6	*0.007*
Ni [ng m^{-3}]	6.8 ± 4.7	5.0 ± 3.9	0.084
Pb [ng m^{-3}]	17.4 ± 10.6	13.3 ± 6.7	0.199
V [ng m^{-3}]	13.3 ± 15.9	15.1 ± 10.1	0.148
	Coastal Site		
	Winter (n=33)	Summer (n=35)	U Mann-Whitney Test
	Mean SD	Mean SD	
PM_{10} [$\mu g\ m^{-3}$]	30.1 ± 17.8	30.5 ± 12.1	0.366
As [ng m^{-3}]	0.70 ± 0.5	0.70 ± 0.35	0.217
Cd [ng m^{-3}]	0.52 ± 0.70	0.24 ± 0.17	0.156
Cr [ng m^{-3}]	0.8 ± 0.6	0.66 ± 1.36	*0.003*
Mn [ng m^{-33}]	6.0 ± 4.7	10.9 ± 5.4	*< 0.001*
Ni [ng m^{-3}]	5.2 ± 2.9	4.4 ± 3.3	0.156
Pb [ng m^{-3}]	31.9 ± 16.4	17.4 ± 7.2	*< 0.001*
V [ng m^{-3}]	10.6 ± 6.7	18.5 ± 9.9	*< 0.001*

3.3 Identification of sources of contaminants

To further identify the contaminants sources, a Varimax-rotated PCA was applied to the element concentration data obtained at the urban and coastal sites, without seasonal distinction.

We extracted the factors which explain more than 5–10% of the total variance of the data sets, and which also explain together more than 75–85% of accumulated variance.

Arsenic was not included in the PCA for the urban site since it was not significantly correlated (R>0.50) with the other elements.

We compared the PCA results summarized in Table 3 with the emission profiles for the specific point sources [35] cited in chapter 2.1.

Three factors were obtained for the urban site representing 86.9% of the total variability for this site: the first factor accounting for 60.5% of the total variance was dominated by Cd and Pb that could be released from solid waste incineration activities.

Factor 2, explaining 14.5% of the total variance was dominated by Cr and Mn, suggesting resuspended dust and steel mill emissions as the main contributions to this factor.

Factor 3, with high factor loading for Ni and V, accounted for 11.9% of the total variance. Both Ni and V are related to heavy fuel combustion.

Similarly, for the coastal site we obtained three

Table 6. Traffic-specific average PM_{10} and trace metal concentrations at the two sites for the winter season, significance level of traffic conditions variation tested by the non-parametric U Mann-Whitney test also displayed; numbers typed in underlined italic letters denote $p<0.05$

	Urban Site Winter			Coastal Site Winter		
	Business (n=28)	Non-Business (n=5)	U Mann-Whitney Test	Business (n=28)	Non-Business (n=5)	U Mann-Whitney Test
	Mean SD	Mean SD		Mean SD	Mean SD	
PM_{10} [$\mu g\ m^{-3}$]	38.7 ± 20.2	18.8 ± 8.04	*0.0160*	31.4 ± 18.8	22.3 ± 8.16	0.3153
As [ng m^{-3}]	0.78 ± 0.44	0.37 ± 0.18	*0.0239*	0.76 ± 0.55	0.40 ± 0.15	0.0707
Cd [ng m^{-3}]	0.52 ± 0.67	0.37 ± 0.18	*0.0160*	0.52 ± 0.70	0.53 ± 0.78	0.5807
Cr [ng m^{-3}]	2.13 ± 1.13	0.18 ± 0.12	*0.0019*	0.92 ± 0.55	0.38 ± 0.56	*0.0445*
Mn [ng m^{-3}]	12.2 ± 6.65	3.38 ± 2.03	*0.0031*	6.57 ± 4.87	2.92 ± 1.34	0.1320
Ni [ng m^{-3}]	7.49 ± 4.79	3.12 ± 0.82	*0.0209*	5.49 ± 2.98	3.58 ± 1.17	0.1320
Pb [ng m^{-3}]	18.3 ± 11.0	12.2 ± 6.76	0.2094	31.5 ± 16.2	33.8 ± 19.2	0.8803
V [ng m^{-3}]	14.9 ± 16.8	4.50 ± 2.38	0.1196	11.1 ± 7.00	7.75 ± 4.56	0.3153

Table 7. Traffic-specific average PM_{10} and trace metal concentrations at the two sites for the summer season, significance level of traffic conditions variation tested by the non-parametric U Mann-Whitney test also displayed; numbers typed in underlined italic letters denote $p<0.05$

	Urban Site Summer			Coastal Site Summer		
	Business (n=30)	Non-Business (n=5)	U Mann-Whitney Test	Business (n=30)	Non-Business (n=5)	U Mann-Whitney Test
	Mean SD	Mean SD		Mean SD	Mean SD	
PM_{10} [$\mu g\ m^{-3}$]	40.5 ± 16.2	28.6 ± 14.2	0.1869	29.4 ± 11.1	29.0 ± 14.1	0.7414
As [ng m^{-3}]	0.79 ± 0.34	0.80 ± 0.45	0.8137	0.68 ± 0.34	0.76 ± 0.46	0.8137
Cd [ng m^{-3}]	0.29 ± 0.17	0.22 ± 0.16	0.4795	0.25 ± 0.18	0.19 ± 0.13	0.3961
Cr [ng m^{-3}]	2.47 ± 1.90	1.28 ± 0.59	*0.0006*	0.61 ± 1.31	2.00E-5 ± 2.00E-7	0.0897
Mn [ng m^{-3}]	17.7 ± 10.6	13.6 ± 10.9	*0.0004*	10.8 ± 5.24	8.41 ± 5.03	0.2997
Ni [ng m^{-3}]	5.21 ± 3.99	3.77 ± 3.44	*0.0026*	3.89 ± 2.64	3.67 ± 2.35	0.8875
Pb [ng m^{-3}]	13.7 ± 6.75	10.80 ± 6.76	*0.0010*	17.5 ± 6.98	17.6 ± 9.77	0.8875
V [ng m^{-3}]	14.7 ± 9.29	17.4 ± 15.2	0.6714	17.1 ± 8.89	20.8 ± 13.1	0.6041

factors representing 78.7% of the total variability for this site: the first factor accounting for 46.0%, had high factor loading for Mn, Ni and V most likely released by resuspended dust and heavy fuel combustion.

Factor 2, explaining 21.0% of the total variance was dominated by As, Cd and Pb, suggesting solid waste incineration activities as the main contribution to this factor.

Factor 3, with high factor loading for Cr and Ni, accounted for 11.7% of the total variance. Ni is related to emission from heavy fuel combustion while Cr is associated to resuspended dust and steel mill activities, suggesting for this factor a mixed contribution of these two sources.

Table 8. Spearman correlation coefficients between PM_{10}, trace metal concentrations and daily average values of wind speed (Ws) and relative humidity (RH) (Numbers typed in underlined italic letters denote $p<0.05$)

Ws ($m\ s^{-1}$)	Urban Site Winter	Coastal Site Winter	Urban Site Summer	Coastal Site Summer
PM_{10}	-0.72	-0.74	-0.65	-0.58
As	-0.09	-0.22	-0.41	-0.38
Cd	-0.62	-0.67	-0.40	-0.35
Cr	-0.58	-0.45	-0.37	-0.36
Mn	-0.63	-0.64	-0.59	-0.53
Ni	-0.64	-0.51	-0.84	-0.52
Pb	-0.60	-0.55	-0.35	-0.16
V	-0.70	-0.35	-0.79	-0.43

RH (%)	Urban Site Winter	Coastal Site Winter	Urban Site Summer	Coastal Site Summer
PM_{10}	0.28	0.28	0.37	0.46
As	0.02	0.11	0.14	0.11
Cd	0.27	0.24	0.14	0.14
Cr	0.03	0.39	0.12	0.07
Mn	0.22	0.04	0.23	0.39
Ni	0.17	0.14	0.39	0.48
Pb	0.07	0.16	0.06	0.31
V	0.40	0.11	0.30	0.28

3.4 Intersite variation of PM_{10} and metal concentrations

Variability between the two sites was examined in the two considered seasons using the non-parametric U Mann-Whitney test. This approach helps in subtracting a possibly confounding temporal factor by focusing on investigation of the impact of site-specific emission patterns and possible meteorological effects. Results are summarized in Table 4.

During the winter season mean PM_{10} and metal concentrations, with the exception of Cd and Pb, are higher in the urban site. However, the differences are only statistically significantly different for Cr, Mn and Pb.

Higher concentrations for Cr and Mn in the urban site can be attributed to a mix of industrial emissions like the integrated steel mill [36] and vehicular traffic (including road dust resuspension) [37].

Higher concentrations of Pb in the coastal site are not easily explained since the coastal site is not affected by any punctual source of lead. However, since sea salt spray has been reported as a natural Pb source [38], and due to the short distance between the sampler and the sea, we assume a marine aerosol influence on the Pb concentration.

During the summer season the situation is similar except for the PM_{10} concentration that now is statistically significantly higher in the urban site.

3.5 Seasonal variation of PM_{10} and metal concentrations

We examined the seasonal variations between the two seasons separately at the two considered sites, using again the non-parametric U Mann-Whitney test. With this analysis, we try to focus our attention on the investigation of the impact of seasonal-specific emission patterns (see Table 5).

At the urban site Cd, Ni and Pb have lower concentrations while PM_{10} and all the other metals have higher concentrations during the summer season. However, this difference is statistically significant only for Mn.

These results show that the urban site appears not to be affected by seasonal specific contribution to PM_{10} or metal concentrations in the air, such as domestic heating. However, it could be mainly affected by annually steady emission sources like industries and vehicles.

In the coastal site Mn, Pb and V concentrations were statistically different between the two seasons. As already stated above, the relatively high average value for Pb at the costal site in winter may be attributed to the sea spray contribution.

The higher concentrations of Mn in the summer season could be explained by the resuspension of road dust and vehicular emissions due to the dryer season and the increase of vehicular traffic near the coastal site; the site is situated close to one of the main roads used by tourists going to and returning from holiday resorts in Slovenia and Croatia.

With regard to V, the higher concentration during the summer period could be explained by an increase of heavy oil emission from marine traffic during the summer months in the near Porto San Rocco marina.

3.6 Business and non-business days variation of PM_{10} and metal concentrations

Road traffic is often indicated as an important contributor to the PM_{10} and metal concentrations, especially in a city environment like the Trieste area. In order to assess the impact of the vehicular traffic on the PM_{10}

Table 9. Wind-specific average PM_{10} and trace metal concentrations at the two sites for the winter season, significance level of wind conditions variation tested by the non-parametric U Mann-Whitney test also displayed; numbers typed in underlined italic letters denote $p<0.05$

	Urban Site Winter			Coastal Site Winter		
	Bora (n=8)	No Bora (n=25)	U Mann-Whitney Test	Bora (n=8)	No Bora (n=25)	U Mann-Whitney Test
	Mean SD	Mean SD		Mean SD	Mean SD	
PM_{10} [$\mu g\ m^{-3}$]	18.6 ± 8.00	41.1 ± 19.9	*< 0.001*	17.1 ± 7.61	34.2 ± 18.2	*0.002*
As [ng m^{-3}]	0.69 ± 0.29	0.73 ± 0.48	0.789	0.70 ± 0.33	0.70 ± 0.57	0.522
Cd [ng m^{-3}]	0.20 ± 0.08	0.42 ± 0.21	*0.003*	0.19 ± 0.08	0.63 ± 0.78	0.055
Cr [ng m^{-3}]	0.90 ± 0.40	2.21 ± 1.19	*< 0.001*	0.56 ± 0.57	0.93 ± 0.56	0.127
Mn [ng m^{-3}]	4.66 ± 2.16	12.9 ± 6.7	*< 0.001*	3.30 ± 2.23	6.89 ± 4.97	*0.049*
Ni [ng m^{-3}]	2.97 ± 1.33	8.07 ± 4.72	*< 0.001*	3.76 ± 1.65	5.66 ± 3.03	0.156
Pb [ng m^{-3}]	9.90 ± 3.01	19.8 ± 11.1	*0.003*	23.6 ± 13.12	34.5 ± 16.7	0.107
V [ng m^{-3}]	2.45 ± 2.32	16.8 ± 16.9	*< 0.001*	8.71 ± 3.77	11.2 ± 7.41	0.578

and toxic elements concentration, we have examined the variations of the PM_{10} and metal concentrations during the business (Monday to Saturday) and non-business days (Sundays) using the non-parametric U Mann-Whitney test. In this area, the industrial activities follow a 7-days duty cycle, while the vehicular traffic has different patterns during Sundays (comparing to the rest of the week).

Results are summarized in Table 6 for the winter season. These results show that in the urban site, PM_{10} and all the elements concentrations decrease during the non-business days; with statistically significant differences for PM_{10}, As, Cd, Cr, Mn and Ni.

On the contrary, in the coastal site we observed a statistically significant decrease only for the concentration of Cr.

This difference between the two sites could point to a stronger local impact of the vehicular traffic, direct exhaust pipe emission and abrasion/resuspension processes, on the pollutants concentration for the urban site.

During the summer season (Table 7), for the urban site we found a statistically significant decrease of the concentration for Cr, Mn, Ni and Pb, while in the coastal site neither the PM_{10} nor the element concentrations show a statistically significant variation during non-business days.

The results for the summer season confirm the stronger impact of the vehicular traffic on the urban site.

3.7 Meteorological study

Correlations among PM_{10}, metal concentrations and average daily wind speed (W_S) and relative humidity (RH) at the two sites for both seasons are presented in Table 8.

PM_{10} and metal concentrations are all negatively correlated with wind speed at both sites and seasons highlighting a dilution effect of the wind. The correlation is lower during summer season compared with the winter, possibly due to the already mentioned lifting of the boundary layer during the summer season. This phenomenon leads to a better mixing of the atmosphere and help to disperse pollutants with or without the help of the breeze. This is not true for V, Ni and especially As since their correlation with wind speed raises significantly during the summer season. A moderate correlation was found among PM_{10}, metal concentrations and humidity only for Ni (R=0.48) and PM_{10} (R=0.46) during summer season in the coastal site.

Due to the remarkable importance of the bora wind for the local meteorology, we examined the variations of the PM_{10} and metal concentrations during the blowing bora days and non-blowing bora days for the two seasons in the two studied sites. For this analysis we use the non-parametric U Mann-Whitney test. We followed the criterion chosen by Stravisi [39] to decide which days were bora blowing days: wind velocity > 5 m s^{-1} - ENE and E direction.

Results are summarized in Table 9 for the winter season and they are especially indicative for the urban

Table 10. Wind-specific average PM_{10} and trace metal concentrations at the two sites for the summer season, significance level of wind conditions variation tested by the non-parametric U Mann-Whitney test also displayed; numbers typed in underlined italic letters denote $p<0.05$

	Urban Site Summer			Coastal Site Summer		
	Bora (n=5)	No Bora (n=30)	U Mann-Whitney Test	Bora (n=5)	No Bora (n=30)	U Mann-Whitney Test
	Mean SD	Mean SD		Mean SD	Mean SD	
PM_{10} [$\mu g\ m^{-3}$]	23.4 ± 9.04	41.3 ± 16.0	*0.006*	15.5 ± 4.23	33.0 ± 11.1	*< 0.001*
As [$ng\ m^{-3}$]	0.52 ± 0.27	0.84 ± 0.34	*0.032*	0.44 ± 0.26	0.74 ± 0.34	*0.037*
Cd [$ng\ m^{-3}$]	0.19 ± 0.13	0.30 ± 0.17	0.161	0.19 ± 0.13	0.25 ± 0.17	0.262
Cr [$ng\ m^{-3}$]	1.40 ± 0.67	2.45 ± 1.91	0.325	1.99E-3 ± 1.30E-7	0.77 ± 1.44	*0.010*
Mn [$ng\ m^{-3}$]	8.00 ± 3.75	18.6 ± 10.6	*0.006*	6.76 ± 2.67	11.5 ± 5.43	0.074
Ni [$ng\ m^{-3}$]	0.88 ± 0.76	5.69 ± 3.69	*< 0.001*	2.29 ± 2.08	4.72 ± 3.35	0.082
Pb [$ng\ m^{-3}$]	9.14 ± 6.37	13.9 ± 6.64	0.082	15.9 ± 8.95	17.6 ± 7.01	0.396
V [$ng\ m^{-3}$]	1.31 ± 0.61	17.4 ± 8.99	*< 0.001*	13.5 ± 9.19	19.3 ± 9.92	0.243

site. These results show that all the concentrations have a statistically significative decrease during blowing bora days (with the exception of As), while for the coastal site all the parameters shown a decrease during the blowing bora days (except for As again) but this decrease is statistically significant only for PM_{10} and Mn.

This difference between the two sites could point to a dilution effect of the bora wind over local pollution sources for the urban site.

During the summer season (Table 10) PM_{10}, As, Mn, Ni and V in the urban site, and PM_{10}, As and Cr in the coastal site shown a statistically significant decrease during the blowing bora days. During summer – in comparison to the winter season - the bora influence is less marked for the urban site, while for the coastal site the influence seems stronger, especially for Cr, showing in 5 summer bora days concentrations below the LOD.

4. Conclusions

This is the first systematic study about toxic elements composition in PM_{10} in the province of Trieste, situated at the northernmost part of the Mediterranean basin. Two sites and two monthly campaigns in different seasonal situation have been considered. During the study period we registered several exceedences of the PM_{10} 24h limit value for both sites (urban site, exceeding the daily limit 14 days in 68, coastal site 5 days in 68). Our monitoring data contradict a common sense statement that points at worst situation for particulate matter during winter months when heating and mixing layer height contributes negatively to air quality compared to summer ones (percentage of days exceeding the PM_{10} daily limit in the urban site during winter campaign 18% versus 24% during summer campaign). This observation holds partly also for toxic elements pollution. The same is confirmed in this coastal area for PAHs data, here not reported.

Metal concentrations in all considered cases were found below the limits or target values, since the levels for Pb, Cd, Mn, Ni and V remained relatively low. This fact is of particular importance for the urban site, where on the contrary concentrations of Cr and Mn were statistically higher than those of the coastal site, in both winter and summer. On the other hand the statistically higher Pb concentration in the coastal site compared to the urban one in both seasons, could point at sea spray source influence.

Seasonal variations were statistically significant only for Mn in the urban site, while the seasonal influence was much more significant in coastal site, suggesting an almost constant effect of the pollution sources in the urban site.

A remarkable evidence is provided by the correlation analysis between metal concentrations, that underlines high correlation for the Ni-V couple ($R>0.70$) for both sites and seasons, suggesting a common source for these metals. Literature reports the combustion of heavy oils as a relevant source for Ni and V, and – considering the very high diffusion of natural gas for heating – marine

engines from harbor traffic, and eventually from engine production plant can play a role in enriching PM_{10} with these elements.

Not surprisingly we found that the impact of the vehicular traffic is stronger on the urban site in both seasons.

The meteorological study -besides the usual more or less pronounced negative correlation among wind speed in general and pollutants- have shown the relevant effects of the bora wind for the dispersion of pollutants. This holds especially for the urban site situated in a densely populated area of the city of Trieste.

Further studies are needed, aimed at better defining the contribution of marine traffic and sea spray to the particulate matter composition in this coastal area.

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