

1 **Supplementary material 1.** Main facilities present in the industrial area of Porto Marghera registered in the E-PRTR for the 2009.

Facility Name	Parent Company Name:	Activity Name
AFV ACCIAIERIE BELTRAME SPA	AFV ACCIAIERIE BELTRAME SPA	Processing of ferrous metals
Alcoa Trasformazioni s.r.l. stabilimento di Fusina (VE)	ALCOA TRASFORMAZIONI S.R.L.	Production of non-ferrous crude metals from ore, concentrates or secondary raw materials
Arkema Srl - Socio Unico Stabilimento di Porto Marghera (VE)	Arkema Srl	Industrial scale production of basic organic chemicals
CENTRALE TERMOELETTRICA DI MARGHERA LEVANTE	EDISON	Thermal power stations and other combustion installations
CENTRALE TERMOELETTRICA DI MARGHERA AZOTATI	EDISON	Thermal power stations and other combustion installations
Impianto Depurazione di Fusina	Gruppo Veritas SpA	Urban waste-water treatment plants
IMPIANTO TERMOELETTRICO DI FUSINA	ENEL PRODUZIONE SPA	Thermal power stations and other combustion installations
IMPIANTO TERMOELETTRICO DI PORTO MARGHERA - VB DI FUSINA	ENEL PRODUZIONE SPA	Thermal power stations and other combustion installations
MONTEFIBRE S.p.A. Stabilimento di Porto Marghera	MONTEFIBRE S.P.A.	Industrial scale production of basic organic chemicals
Piattaforma Ambientale Servizi Porto Marghera S.c.ar.l.	SERVIZI PORTO MARGHERA S.C A R.L.	Disposal or recovery of hazardous waste
Pilkington Italia Spa	PILKINGTON ITALIA SPA	Manufacture of glass including glass fibre
Raffineria di Venezia	ENI S.P.A.	Mineral oil and gas refineries
SIMAR S.P.A.	SIMAR S.P.A.	Production of non-ferrous crude metals from ore, concentrates or secondary raw materials
Solvay Fluor Italia S.p.A.	Solvay S.p.A.	Industrial scale production of basic inorganic chemicals
Stabilimento di P.to Marghera	POLIMERI EUROPA SPA	Industrial scale production of basic organic chemicals
STABILIMENTO DI PORTO MARGHERA	SYNDIAL S.p.A.	Industrial scale production of basic inorganic chemicals
Vinyls Italia Stabilimento di Porto Marghera	Vinyls Italia S.p.A.	Industrial scale production of basic organic chemicals

Supplementary material 2. Instrumental parameters for microwave sample digestion.

Microwave digestion program	Time (min)	Power (W)
Step 1	5	250
Step 2	5	400
Step 3	2	600

Supplementary material 3. Limit of detection (LOD) for analyzed elements and ions.

LOD	ng m ⁻³	
As	0.2	75 ^a
Ni	2.9	60 ^a
Cu	1.4	63 ^a
Cd	0.2	111 ^a
Pb	0.8	208 ^a
Ba	10	137 ^a
V	0.2	51 ^a
Mn	1.3	257.610 ^b
Zn	22	206.200 ^b
Ti	8.3	336.121 ^b
Ca	1236	317.933 ^b
Mg	359	280.271 ^b
Al	440	396.153 ^b
Fe	57.7	238.204 ^b
K	183	766.490 ^b
S	363	180.669 ^b
Cl⁻	29	
NO₃⁻	49	
SO₄²⁻	23	
Na⁺	87	
NH₄⁺	9.3	
K⁺	38	

^a Selected atomic mass^b Selected wavelength

Supplementary Material 4. Comparison of mean elemental concentrations with previous studies. Fe and K are expressed in $\mu\text{g m}^{-3}$, other elements in ng m^{-3} .

Site ^a	City (Country)	Reference		As	Ni	Cu	Cd	Pb	Mn	V	Zn	Ti	Fe	K
IND	Venice (I)	This study	PM _{2.5}	1.5	6.4	9.3	1.5	15.9	7.1	6.7	59.0	20.2	0.2	0.4
UB	Venice (I)	Stortini et al. (2009)	PM _{2.5}	3.6	12.2		3.5	18.1	5.2	14.1	84.5	186.2	0.1	0.2
U	Palermo (I)	Dongarrà et al. (2007)	PM ₁₀	1.8	3.7	24.0		20.0	9.3	22.0				
UB	Trieste (I)	Cozzi et al. (2010)	PM ₁₀	0.7	4.8		0.4	24.7	8.5	14.6				
UB	Lecce (I)	Contini et al. (2010)	PM ₁₀		3.0	12.9		7.6	8.0	1.6	24.8	15.7	0.3	
UB	Santander (E)	Ruiz et al. (2011)	PM ₁₀	0.5	0.9	3.7	0.3	6.2	49.1	1.2		2.4		
UB	Castro (E)	Ruiz et al. (2011)	PM ₁₀	0.2	3.0	3.5	0.1	7.7	9.3	3.1		5.2		
UB	Torrelavega (E)	Ruiz et al. (2011)	PM ₁₀	0.2	2.8	18.9	0.2	12.5	23.7	2.0		5.4		
UB	Huelva (E)	Fernandez-Camacho et al. (2010)	PM _{2.5}	9.2	2.4	28.5	0.9	19.4	3.7	4.5	31.0	16.5	0.2	0.2
IND	Puertollano (E)	Moreno et al. (2010)	PM _{2.5}	1.0	3.1	12.1	0.1	9.3	3.2	5.5	30.1	12.4	0.1	0.3
IND	La Linea (E)	Moreno et al. (2010)	PM _{2.5}	0.5	13.5	6.1	0.2	9.7	8.5	22.4	48.8	7.2	0.1	0.1
IND	Algeciras (E)	Moreno et al. (2010)	PM _{2.5}	0.4	8.7	11.8	0.1	6.3	4.1	20.4	27.0	6.3	0.1	0.1
IND	Bailén (E)	Moreno et al. (2010)	PM _{2.5}	0.9	17.2	26.3	0.3	23.9	13.8	95.3	26.4	53.8	0.8	3.6
	Rural background (E)	Querol et al. (2007)	PM _{2.5}	0.3–0.3	2–4	9–40	0.2–0.2	6–7	3–3	3–4	17–27	4–8		
	Urban background (E)	Querol et al. (2007)	PM _{2.5}	0.3–0.7	1–4	3–44	0.2–0.4	6–20	2–10	1–9	11–72	6–18		
	Steel (E)	Querol et al. (2007)	PM _{2.5}	1.5	21.0	29.0	1.0	77.0	39.0	7.0	239.0	9.0		
	Stainless steel (E)	Querol et al. (2007)	PM _{2.5}	0.5	14.0	6.0	0.2	10.0	9.0	22.0	49.0	7.0		
	Copper metallurgy (E)	Querol et al. (2007)	PM _{2.5}	4.0	3.0	33.0	0.8	27.0	3.0	4.0	43.0	22.0		
	Petrochemical estates (E)	Querol et al. (2007)	PM _{2.5}	0.4–1.0	3–8	12–32	0.1–0.2	6–17	3–4	5–20	19–30	6–12		
UB	Dunkirk (F)	Alleman et al. (2010)	PM ₁₀	5.1	12.4	12.6	1.3	37.5	147.0	18.5	80.0		1.0	0.7

^a: IND, industrial; UB, urban background; U, urban.

References:

- Alleman L Y, Lamaison L, Perdrix E, Robache A, Galloo J-C. PM10 metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. *Atmos Res* 2010; 96:612–625.
- Contini D, Genga A, Cesari D, Siciliano M, Donato A, Bove M C, Guascito M R. Characterisation and source apportionment of PM10 in an urban background site in Lecce. *Atmos Res* 2010; 95:40–54.
- Cozzi F, Adami G, Barbieri P, Reisenhofer E, Apostoli P, Bovenzi M. Toxic elements content in PM10 samples from a coastal area of the Northern Adriatic Sea. *Cent Eur J Chem* 2010; 8:1014–1026.
- Dongarrà G, Manno E, Varrica D, Vultaggio M. Mass levels, crustal component and trace elements in PM10 in Palermo, Italy. *Atmos Environ* 2007; 41:7977–7986.
- Fernández-Camacho R, de la Rosa J, Sánchez de la Campa A M, González-Castanedo Y, Alastuey A, Querol X, Rodríguez S. Geochemical characterization of Cu-smelter emission plumes with impact in an urban area of SW Spain. *Atmos Res* 2010; 96, 590–601.

- Moreno T, Querol X, Alastuey A, de la Rosa J, Sánchez de la Campa A M, Minguillón M, Pandolfi M, González-Castanedo Y, Monfort E, Gibbons W. Variations in vanadium, nickel and lanthanoid element concentrations in urban air. *Sci Total Environ* 2010; 408, 4569–4579.
- Querol X, Viana M, Alastuey A, Amato F, Moreno T, Castillo S, Pey J et al..Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. *Atmos Environ* 2007; 41:7219–7231.
- Ruiz S, Arruti A, Fernández-Olmo I. Contribution of point sources to trace metal levels in urban areas surrounded by industrial activities in the Cantabria Region (Northern Spain). *Procedia Environmental Sciences* 2011; 4:76–86.
- Stortini AM, Freda A, Cesari D, Cairns WRL, Contini D, Barbante C, Prodi F, Cescon P, Gambaro A. An evaluation of the PM_{2.5} trace elemental composition in the Venice Lagoon area and an analysis of the possible sources. *Atmos Environ* 2009; 43:6296–6304.

Supplementary material 5. Percentage contributions of each group source in Venice on PM_{2.5} and analyzed elements (As, Cd, Cu, Ni, Pb, Zn) (ISPRA, 2013).

	Group source									
	01 - Combustion in energy and transformation industries	02 - Non-industrial combustion plants	03 - Combustion in manufacturing industry	04 - Production processes	05 - Extraction and distribution of fossil fuels and geothermal energy	06 - Solvent and other product use	07- Road transport	08 - Other mobile sources	09 - Waste treatment and disposal	10- Agriculture
PM _{2.5}	2.5	59.6	5.8	1.3	1.3		16.3	10.5	1.2	1.6
As	3.3	0.2	96.5					0.1		
Cd	1.9	54.9	26.9	2.6			5.4	0.8	7.5	
Cu	3.3	4.8	9.4				81.6	0.4	0.4	
Ni	13.8	55.3	22.9	0.4			2.8	4.3	0.5	
Pb	2.2	43.6	39.5				5.4	1.6	7.8	
Zn	2.4	14.1	63.1	0.4			17.4	0.6	2.0	