

Organic and inorganic persistent pollutants monitoring: emission source identification

Bonelli MG¹, Colombo A², Benfenati E², Lodi M², Rossetti G³, Manni A³

¹ Dept. ICMA, University of Rome "La Sapienza", Via Eudossiana 18, Rome, Italy, 00198

² Department of Environmental Health Sciences, Istituto di Ricerche Farmacologiche "Mario Negri", Via La Masa 19, Milan, Italy 20156

³ Chemical Research 2000 Srl, Via Santa Margherita di Belice 16, Rome, Italy, 00133

Introduction

Air quality and human health are closely bound: among the exposure paths, the inhalation of contaminated air and dusts is probably the major route of exposure to xenobiotics, second only to diet [1]. Air pollution is the result of the contribution of different emission sources and anthropogenic activities and is of high concern for international, national and local governments. The potential hazard of some toxic elements such as PCDD/Fs, PCB, PAH and metals (As, Cd, Cr, Ni, Hg and Pb) is well known [2,3].

In the present study, ambient air samples were simultaneously collected at six locations in Brescia, a city in the North of Italy whose large scale industrial development has resulted in an impact on the surrounding environment. Seven sampling points were chosen in the proximity of a chemical factory - the only Italian PCB producer operating from 1930 to 1984 - indicated as the principal responsible for PCDD/Fs and PCBs soil concentrations- that are higher than legal limits in surrounding areas [4]. The purpose of this study is to identify other source emissions different than the chemical factory that are accountable for air pollution in the considered site, using Principal Component Analysis (PCA).

Materials and methods

Heavy metals (As, Cd, Cr, Ni and Pb) were quantified on one tenth of each filter using an atomic absorption spectrometer equipped with a transversely heated graphite atomizer furnace (Analyst 600, Perkin Elmer, MA USA), after microwave acid digestion [5]. PAHs, PCBs and PCDDFs were extracted from the filters and the PUFs as previously reported [6]. The extract was injected into an automated clean up system consisting of a gel permeation chromatography (GPC) module (AccuPrep™ J2 Scientific, Columbia, MI, USA) coupled to an evaporator (AccuVap™) and three solid phase modules able to manage the acid silica/neutral silica, basic alumina and active carbon columns SPE purification. The extract, at a volume of 5 ml, was injected into the GPC system using dichloromethane as the mobile phase. The system used a 5 mL sample loop and a flow rate of 5 mL/min. The GPC column was calibrated according to US-EPA Method 3640A. The eluate was collected between 23 and 45 minutes and concentrated to a final volume of 5 ml. Ten percent of sample collected was then concentrated under nitrogen flow to 100 µL and submitted to instrumental analysis for PAHs. The remaining 90% was concentrated to 0.5 ml and then diluted with n-hexane to 5ml. The sample was submitted to an automated clean up using acid silica/neutral silica, basic alumina and active carbon columns [7]. PAHs were analyzed using a HRGC-NICI-LMRS equipped with a fused silica capillary column. PCDD/Fs and PCBs were quantified using a TRACE GC2000 coupled with a Mat 95 XP Mass spectrometer (Thermoquest, Bremen, Germany) operating in the electron impact ionization (EI+) mode.

Results and discussion

Ambient air was sampled (58 samples) at seven sites: CR, CR30, SPG, SK, IVC, QIM and SE. Table 1 shows the pollutants air concentration. Municipal solid waste incinerator (MSWI), chemical, metallurgical and steel plants,

cement factories, thermoelectric power station and vehicular traffic are the main emission sources in the study area. They have direct relationships with the analyzed contaminants [8,9] as reported in Table 2.

Table 1. PCDD/F, PCB, PAH and metals concentrations

Location	Hg ng/m ³	Cd ng/m ³	As ng/m ³	Pb ng/m ³	Cr ng/m ³	Ni ng/m ³	PCDD/Fs ¹ pg/m ³	PCBs ² pg/m ³	PAH ³ ng/m ³
CR	29.76	3.86	18.29	6.56	28.63	20.54	0.04	0.02	0.06
CR30	23.03	3.15	29.66	13.54	19.68	14.18	0.04	0.02	0.17
SPG	27.67	1.81	13.15	24.44	20.80	20.94	0.04	0.13	0.06
SK	40.77	3.21	23.06	14.07	23.03	21.35	0.05	0.02	0.08
IVC	31.44	2.05	9.44	17.04	18.79	10.98	0.03	0.03	0.11
QIM	24.06	2.89	20.33	28.63	16.77	27.37	0.05	0.14	0.05
SE	22.11	2.20	69.38	2.12	47.86	19.22	1.49	0.01	0.09

1 I-TEF WHO 2005; 2 I-TEF WHO 2005; 3 B(a)P EPA equivalent

Table 2. Relationships between emission sources and contaminants

Emission source	Typical emissions
Thermoelectric power stations	Ni
Municipal solid waste incinerators	Cd, Hg, PAH, PCB, PCDD/F
Vehicular traffic	Pb, PAH
Metallurgical and steel plants	As, PCDD/F
Carbon combustion plants	As, Cr, PCDD/F
Chemical plants	Hg, PCB

PCA technique was used to identify the different pollutant sources in the seven considered sites. Table 3 describes the analytical results. Four PCs have been calculated, identifying four different emission sources. PCs accounted for 69.3% of the cumulative variance. PC1 show a high positive correlation with As, Cr and PCDD/Fs, PC2 presents high positive correlation with Cd and PAH, PC3 “saturates” Ni, while PC4 is positively correlated with Hg and negatively correlated with PCBs. Pb shows a low negative correlation with PC3. Some of relationships between original variables and PCs are graphically represented in Fig. 1-4

Relationships shown in Table 2 and in Figures 1-4 suggest four pollutant’s emission typologies:

PC1: Carbon combustion plants, characterized by Cr, As and PCDD/F; PC2: Municipal solid waste incinerators, characterized by Cd, PAH; PC3: Thermoelectric power stations, characterized by Ni; PC4: Chemical farm, PCBs producer, characterized by Hg and PCB.

In addition, a score plot of the sampling sites with respect to PC1 (Fig. 5) shows that carbon combustion plants are the main emission sources for the SE site, while the other six locations are subjected to multisource atmospheric pollution.

Table 3 – Principal Components Analysis: rotated component matrix and variance explained

Element	PC1	PC2	PC3	PC4
Hg	-0,310	-0,214	0,072	0,769
Cd	0,055	0,836	-0,004	-0,021
As	0,760	0,322	0,001	-0,025
Pb	-0,312	0,054	-0,633	0,144
Cr	0,766	0,082	0,341	-0,147
Ni	-0,025	0,044	0,861	0,190
PCDD/F	0,836	-0,233	0,067	0,141
PCB	-0,368	-0,229	0,010	-0,729
PAH	0,018	0,764	0,006	0,012
<i>% variance</i>	<i>24,4</i>	<i>17,2</i>	<i>14,1</i>	<i>13,6</i>
<i>% Cum. variance</i>	<i>24,4</i>	<i>41,6</i>	<i>55,7</i>	<i>69,3</i>

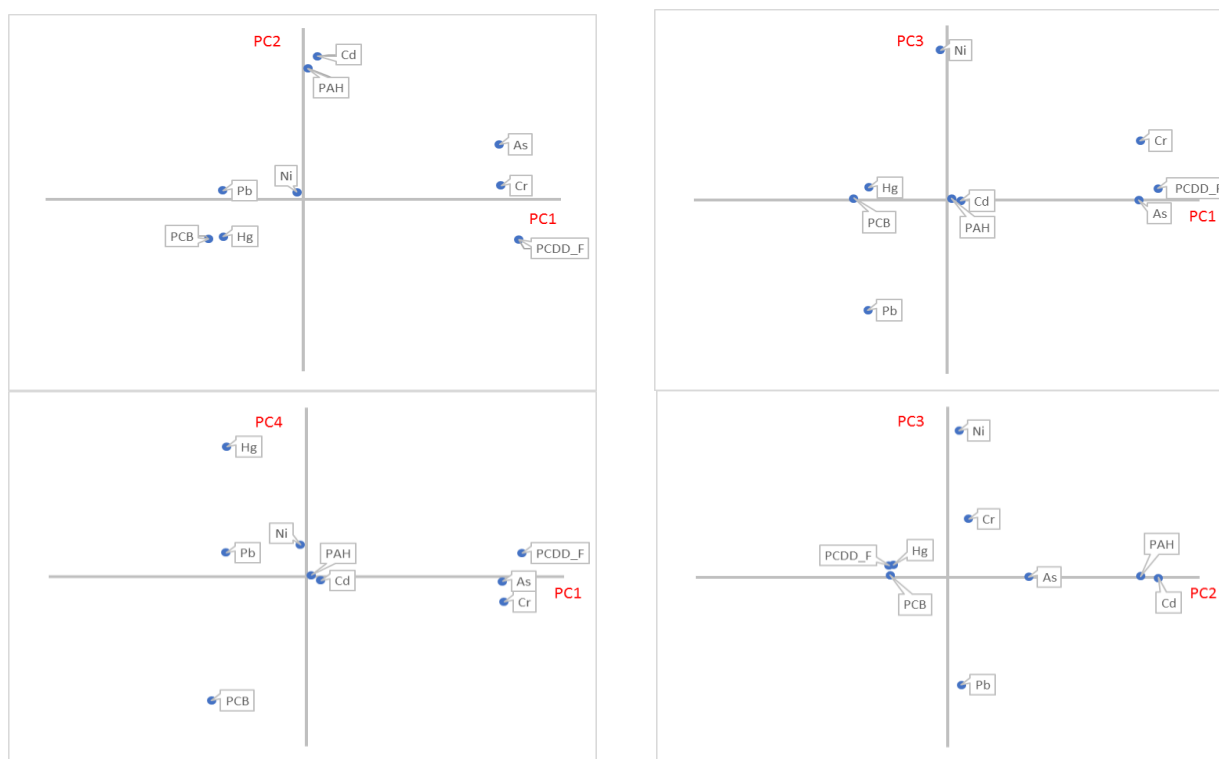


Fig 1-4 Component plots in rotated space: PC1-PC2; PC1-PC3; PC1-PC4; PC3-PC4

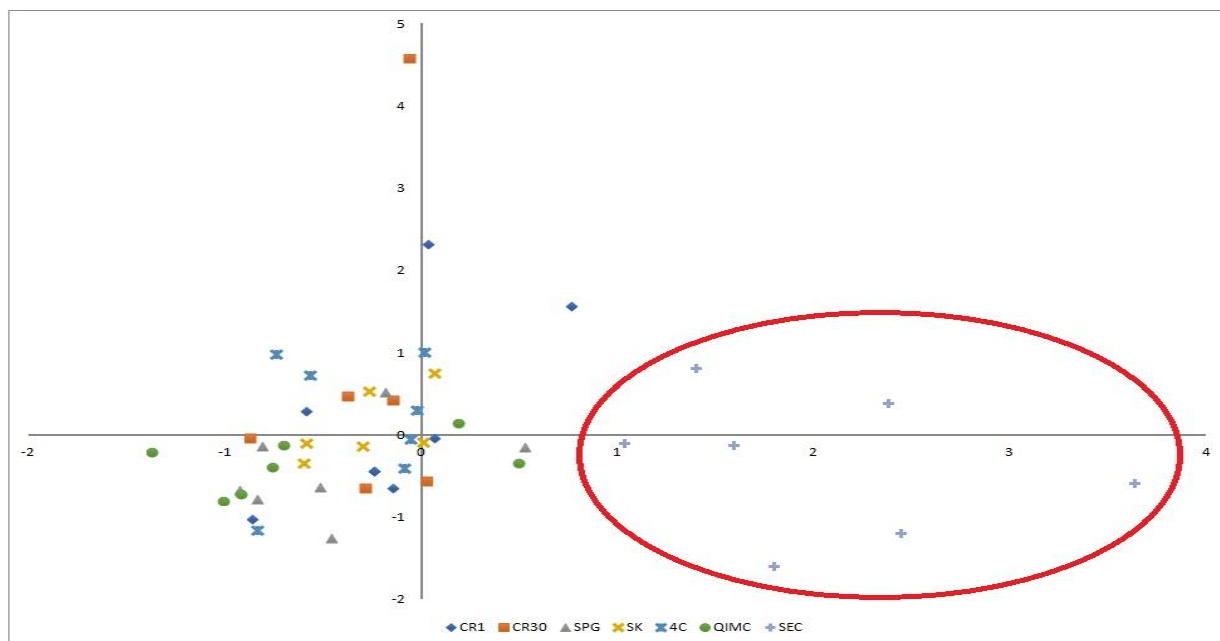


Fig. 5 Score plot in PC1 space: cluster identify PC1 (carbon combustion plants) such as a source *fingerprint* for SE

References

1. Teoldi F, Lodi M, Benfenati E, Colombo A and Baderna D (2017) *Sci Total Environ.* **579**, 1929-1939
2. Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N and Peterson RE (2006) *Toxicol. Sci.* **93**, 223-241
3. CONCAWE Review (1999), Vol. 8 N.2, Report No. 99/60, Brussels, Belgium
4. Turrio-Baldassarri L, Alivernini S, Battistelli CL, Carasi S, Casella M, Fochi I, Iacovella N, Indelicato A, La Rocca C, Mariani A and Scarcella C (2007) *Chemosphere* **67**, 1822–1830
5. Di Guardo A, Terzaghi E, Raspa G, Borin S, Mapelli F, Bessem C, Zanardini E, Moronini C, Colombo A, Fattore E, Davoli E, Ammiraglio S, Vanna MS, Anelli S and Nastasio P (2017) *Environ. Pollution* **223**, 367-375
6. Colombo, A., Benfenati, E., Mariani G., Lodi, M., Marras, R., Rotella, G., Senese, V., Fattore, E. and Fanelli, R., (2009) *Chemosphere* **77**, 1224-1229
7. Mariani G, Amalfitano L, Manni A, Mueller A, Skejo H and Umlauf G (2009): *Organohalogen compounds* **71**: 2796-2801
8. Marongiu A, Moretti M, Fossati G (2015) ARPA Lombardia Technical Report
9. Croce G (2013) Collana Ambiente ARPA Toscana, Scheda Informativa n.15