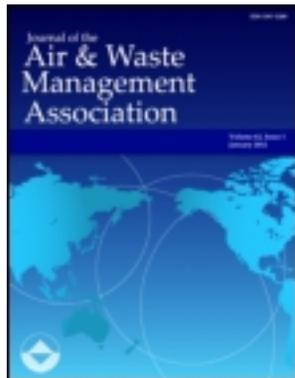


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Temporal and spatial variations of polycyclic aromatic hydrocarbon concentrations around a coke oven plant

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From 1995 to 2004, in Genoa, Italy, daily concentrations of twelve polycyclic aromatic hydrocarbons (PAHs) were measured in particulate phase (PM10), around a coke oven plant in operation from the 1950s and closed in 2002. The study permitted to identify the coke oven as the main PAH source in Genoa, causing constant exceeding of benzo(a)pyrene (BaP) air quality target (1.0 ng/m³) in the urban area till 1,900 meters distance downwind the plant. For this reason the plant was closed. Distance and daily hours downwind the coke plant were the main sources of variability of toxic BaP equivalent (BaP_{eq}) concentrations and equations that best fitted these variables were experimentally obtained. During full plant activity, annual average BaP_{eq} concentrations, measured in the three sampling sites aligned downwind to the summer prevalent winds, were: 85 ng/m³ at 40 m (site 2, industrial area), 13.2 ng/m³ at 300 m (site 3, residential area) and 5.6 ng/m³ at 575 m (site 4, residential area).

Soon after the coke oven's closure (February 2002) BaP_{eq} concentrations (annual average) measured in residential area, decreased drastically: 0.2 ng/m³ at site 3, 0.4 ng/m³ at site 4. Comparing 1998 and 2003 data, BaP_{eq} concentrations decreased 97.6% in site 3 and 92.8% in site 4.

Samples collected at site 3, during the longest downwind conditions, provided a reliable PAH profile of fugitive coke oven emissions. This profile was significantly different from the PAH profile, contemporary found at site 5, near the traffic flow.

This study demonstrates that risk assessment based only on distance of residences from a coke plant can be heavily inaccurate and confirmed that seasonal variability of BaP_{eq} concentrations and high variability of fugitive emissions of PAHs during coke oven activities require at least one year of frequent and constant monitoring (10-15 samples each month).

Implications: Around a coking plant, polycyclic aromatic hydrocarbons (PAHs), concentrations depend mainly on downwind hours and distance. Equations that best fit these variables were experimentally calculated. Fugitive emissions of an old coke oven did not comply with the threshold BAP air concentration proposed by the World Health Organization (WHO), up to 1,900 m distance. The study identified the PAH profile of fugitive emissions of a coke oven, statistically different from the profile of traffic emissions. During its activity, in the Genoa residential area, 575 m away from the plant, 92.8% of found PAHs was due to coke oven emission only.

Supplemental Materials: Supplemental materials are available for this article. Go to the publisher's online edition of the *Journal of the Air & Waste Management Association* for information about samples analyses, statistical analyses and regression models figure.

Introduction

In 2000, in the 15 European Union countries, 42 coke ovens were active (six in Italy) and their annual coke production was 81,030 ktonnes (TNO and AEA Technologies, 2001). Coke ovens are relevant pollution sources. The air pollution around coke oven plants is mainly caused by the continuous fugitive emissions of volatile coal components from leaking doors and top lids that occur during the cyclic operation of coal charging and coke discharging. Mean emission factors (mg/tonne of coke)

of total PAHs 16 (U.S. EPA, 1984) estimated for an old European coke oven were 2,653 mg from leaking doors, 4.0 mg from charging hole lids, and 341 mg as contained smoke emissions from battery under firing (Fisher, 2003).

Polycyclic aromatic hydrocarbons (PAHs) emitted into the atmosphere during coke preparation have received great attention (Bjørseth et al., 1978; Kesik and Janik-Spiechowicz, 1997; Liberti et al., 2006), as they are persistent organic pollutants with well-documented carcinogenic and mutagenic effects on humans (IARC, 1983).

The U.S. Environmental Protection Agency (EPA) designated 32 PAH compounds as priority pollutants, and benzo[a]pyrene (BaP) was recognized as the most carcinogenic PAH. Italian laws (D.M. November 25, 1994) set air quality targets for BaP: 2.5 ng/m³ as an annual average concentration in ambient air until 1999; 1.0 ng/m³ since 2000. The same target for annual BaP concentration (1.0 ng/m³) was proposed by the European Union and World Health Organisation.

PAHs are semivolatile organic compounds that distribute themselves between gas and solid phase, with a relationship governed by temperature and with partition coefficients higher for low-molecular-weight PAHs (Cincinelli et al., 2007).

The more volatile and light PAHs have lower toxicity (Nisbet and LaGoy, 1992), but they dominate the gas-phase factor (Stracquandano and Trombini, 2006; Tsapakis and Stefanou, 2005).

Epidemiologic studies proved an excess risk for coke oven workers: lung and kidney cancer (Bieniek et al., 2004; IARC, 1984; Kesik and Janik-Spiechowicz, 1997).

People living near coke ovens could be at risk too, because they might inhale the same pollutants as coke oven workers, albeit at lower concentrations (Ciaparra et al., 2009; Liberti et al., 2006).

Several studies were carried out to evaluate the health outcomes of coke oven emissions on exposed populations, but most of them failed to find conclusive evidences (Aylin et al., 2001; Bhopal et al., 1994; Bottle and Wakefield, 2004; Dolk et al., 2000; Parodi et al., 2003). Our institute monitored PAH concentrations around Genoa (Italy) coke oven plant for 13 years and used these data to evaluate possible health effects on population living near this plant (Parodi et al., 2005).

The obtained data set on air pollution was used to reach the following aims:

- (1) Verify the respect of BaP air quality targets in the residential area.
- (2) Identify main variables influencing PAH concentrations: coke oven maintenance, distance from the plant, wind

direction, presence of other PAH sources (traffic, steel factory emissions, urban heating).

- (3) Test and propose a monitoring strategy suitable to correctly quantify PAH exposures of population living around a coke oven.

Materials and Methods

Studied area

The Genoa industrial district is located in North Italy, along the Liguria Sea coast for about 1.5 km west of the town. In the 1950s, an integrated steelworks factory was built there on an embankment in front of a suburb (15,000 residents) called Cornigliano.

The nearest houses, less than 50 m from the industrial area boundaries, are 250 m north-west away from the coke oven center (Figure 1).

This area is characterized by a Mediterranean climate with mild winters; prevailing winter winds blow from NE and NNE; sea breezes from SSE characterize summer periods. The insert in Figure 1 shows annual wind directions and frequencies.

Genoa coke oven description and history

The coke oven, located on the east side of the Genoa steelworks facility (Figure 1), was a construction 174 m long, 14 m large, and 5 m high. At the beginning of this study, four batteries (30 ovens each) were in operation, and 134 ovens were daily charged and discharged, producing 1,810 tonnes of coke.

The Genoa coke oven can be classified as a well-maintained, “old design” plant.

According to the Environmental Department of Genoa Province, the main sources of its fugitive BaP emissions (56.8%) occurred during coal charge and from leaks of charge lids and doors. Temperatures of these emissions were between 40

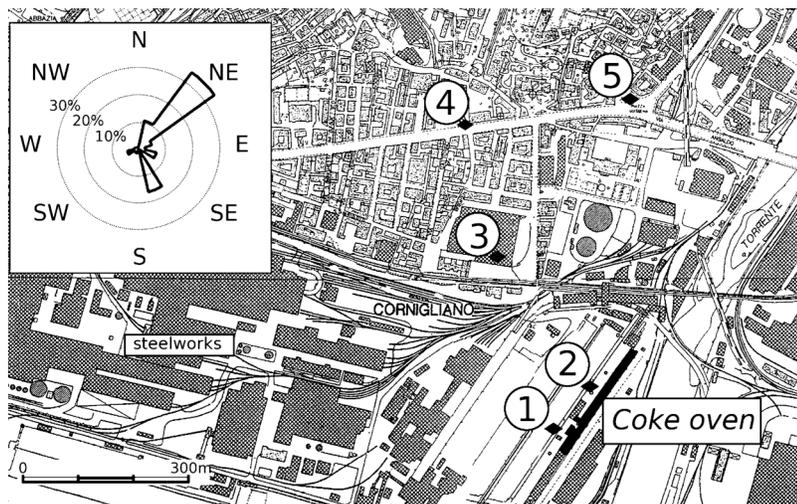


Figure 1. Map of the Cornigliano district with industrial and residential buildings. In black rectangle, the location of the coke oven plant. Numbers indicate the sampling sites used to monitor PAH concentrations inside the industrial area (sites 1 and 2), inside the urban area (sites 3 and 4), and along the sidewalk of the thoroughfare crossing the district (site 5). Insert shows the wind directions and frequencies of prevailing winds, registered in the meteorological station in 1998; calms (wind speed ≤ 0.5 m/s) accounted for 6.3% of the total hourly data.

and 90°C. Percentages of BaP emissions, occurring during coke discharge and coke quenching, were 37.7% and 4.3% and temperatures of these two emissions were, respectively, 800 and 100°C. The rest of the BaP emissions derives from depression systems. Genoa coke oven emitted PAHs into the atmosphere, at 200–300°C, by four stacks (70 m high) that collected smokes produced by battery burners. Their emissions per hour (sum of 10 PAHs: 10.8 g/hr) were negligible, compared to estimated total BaP fugitive emissions (BaP: 6.08 g/hr).

During the sampling period, several technical measures were taken to reduce coke oven emissions. From September 1996, distillation time was increased from 21 hr 30 min to 23 hr 15 min to reduce the number of daily coal charges and coke discharges. From August 1996 to August 1997, all the 240 oven door frames were progressively replaced. Lid sealing and surface cleaning, after coal charges, were regularly carried out.

Public authorities decided to close the coke oven: In 1999, the first southern battery was closed, the second southern battery followed in April 2001. In February 2002, with the closure of the remaining two batteries, the coke plant of Genoa was definitively closed.

Airborne sample collection and analyses

The monitoring network

Air monitoring started in 1995 and were carried out by three and then five sampling stations. Figure 1 shows their positions. A meteorological station, located on a nearby hill, completed the monitoring network.

Sites 1 and 2 were inside the industrial area, near the south and north sides of the coke plant, respectively, about 20 m away from the oven doors (machine pushing side) and about 70 and 30 m from the geometric center of the coke oven, respectively. These two sites were activated to monitor effects on air quality of coke oven maintenances, in particular door frames replacement.

Sites 3 and 4 were on the roofs of two civilian buildings (about 10 m height), 300 and 575 m away from the geometric center of the coke oven, respectively. These sites were selected to monitor coke oven impact in a residential area without a strong influence of traffic emissions.

Sites 2, 3, and 4 were also selected as aligned to the coke oven center, during prevailing SSE winds, when the residential area was downwind the fugitive emissions of the coke oven.

Site 5, 550 m away from the coke plant, was chosen as a ground-level site along the main street crossing the entire Cornigliano district, a canyon street with buildings along both sides. Site 5 was 4 m distant from heavy traffic flow, about 35,000 vehicles per day.

PM₁₀ airborne particle collection

Samples of airborne particulate matter (PM₁₀) were collected on glass fiber filters for 24 hr by high-volume samplers (General Metal Works, volumetric flow: 67.8 m³/hr). In 1995 and 1996, during the preliminary sampling phase, three to five randomly selected samples per month were collected from sites 3, 4, and 5. From November 1996, the collection frequency at sites 3 and 4

was increased to 15 monthly samples to comply with Italian legislation (D.M. November 25, 1994). At site 5, the sampling frequency remained constant at 25–30 samples per year, throughout the entire study period.

At sites 1 and 2, equipped with low-volume samplers (Tecora, volumetric flow: 2.3 m³/hr), daily filters were collected in both sites between March 1997 and December 2001, to control effects of extraordinary maintenances ordered by public authorities.

Sampler failures and other technical problems occurring during the analytical chain prevented the complete fulfilment of the planned monitoring frequency. The number of daily samples collected and analyzed in each site during the *preliminary monitoring phase* (1995–1996) was 46 at site 3, 45 at site 4, and 64 at site 5. During the *intensive monitoring phase*, from November 1996 to April 2004, the number of analyzed samples was 1,473 at site 1, 1,466 at site 2, 990 at site 3, 1,008 at site 4, and 166 at site 5.

Sample analyses. The extraction and analysis of PAHs by capillary gas chromatography (GC) with quality controls are described in a Supplement File, Appendix A. In brief, each filter was extracted by ultrasound sonication with cyclohexane, the solvent was concentrated by evaporation, and the PAH fraction was separated by an SPE column. PAH analyses were performed on a Perkin Elmer PE-5 capillary column (length 30 m) with flame ionization detection.

The following PAHs were quantified: phenanthrene (PHE), anthracene (AN), fluoranthene (FA), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benzo[fluoranthenes] (BF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno(1,2,3-cd)pyrene (IP), dibenzanthracenes (DBA), and benzo[ghi]perylene (BPE). BF is the sum of benzo[b]fluoranthene, benzo[j]fluoranthene, and benzo[k]fluoranthene. DBA is the sum of dibenz[a,h]anthracene, dibenz[a,c]anthracene, and dibenz[a,j]anthracene. All these isomers were not separated completely by the gas chromatographic method.

In this study, toxic equivalence factors (TEFs) proposed by Nisbet and LaGoy (1992) were used to estimate the carcinogenic potency of the analyzed PAH mixtures, with the exclusion of BeP, not evaluated in the Nisbet list. A TEF of 0.1 was assigned to DBA, according to Collins (Collins et al., 1998) since its three isomers were not resolved in our GC separation method. All PAH concentrations were reported as BaP toxic equivalent (BaP_{eq}).

Explorative evaluations and statistical analyses

Three different data sets, obtained during different periods of Genoa coke oven history, were submitted to statistical analyses (details in Supplement Data):

- *Preliminary* data: from January 1995 until October 1996.
- *Full activity* data: from August 1997 until July 1999.
- *Closure* data: 24 months after the coke oven closure, April 2002–March 2004.

An explorative principal component analysis (PCA) was applied on the preliminary data set to find main sources of variability in samples collected at sites 3, 4, and 5. PCA was applied to daily PAH concentrations, absolute values, and normalized to BeP

Table 1. Yearly average of BaP and BaPeq (ng/m³) in PM10 samples collected in the five monitoring sites during the coke oven activity, a year after its closure and six years later (2008)

Site	1995 “Preliminary”			1998 “Full activity”			2003 “Closure”			2008	
	N	BaP	BaPeq	N	BaP	BaPeq	N	BaP	BaPeq	N	BaP
1	—	—	—	357	29.6 (3.3)	48.0 (4.0)	—	—	—	—	—
2	—	—	—	357	57.2 (7.5)	95.6 (8.5)	—	—	—	—	—
3	25	11.5 (2.8)	18.0 (4.4)	143	9.7 (1.2)	14.7 (1.8)	77	0.22 (0.04)	0.35 (0.10)	40	0.16 (0.02)
4	38	3.7 (0.6)	5.7 (0.8)	153	4.9 (0.5)	6.3 (0.7)	46	0.28 (0.06)	0.45 (0.10)	46	0.28 (0.04)
5	34	2.5 (0.4)	3.9 (0.7)	22	1.3 (0.1)	2.1 (0.2)	16	0.45 (0.10)	0.75 (0.20)	42	0.58 (0.09)

Notes: N: number of monitored days; in parentheses, standard errors of the means.

concentrations. Details may be found in Supplement Data, Appendix B.

PAH profiles and diagnostic ratios were obtained through ratios of each PAH with BeP concentration contemporary measured (Sanderson et al., 2004). This method was applied to the full activity data set sampled at sites 3 and 5.

In Supplement Data, Appendix C, methods used for statistical comparison of PAH profiles and diagnostic PAH ratios are given.

Results

Annual BaP and BaPeq concentrations

Table 1 summarizes the mean annual BaP and BaPeq concentrations and their standard errors found, from 1995 to 2008, under different coke oven operating conditions: low maintenance (1995), best possible maintenance (1998), and after the coke oven closure (2003–2008).

During 1995, in urban sites 3 and 4, the Italian air quality target for BaP (2.5 ng/m³ during this year) was not respected, and this fact supported the decision of public authorities to control more frequently the air quality around the coke oven and to oblige owners to apply all possible practices useful to reduce fugitive emissions.

During 1998, with the four batteries in full activity, longer distillation time, the replacement of all door frames, and with stringent control of all applicable rules to reduce fugitive emissions (Aries et al., 2007), mean BaP and BaPeq concentrations decreased slightly (–15.6%) only at site 3, but this difference was not statistically significant.

Particularly high were the annual BaP (57.2 ng/m³) and BaPeq (95.6 ng/m³) concentrations found during 1998 at site 2 and at site 1 (BaP: 29.6 ng/m³; BaPeq: 48.0 ng/m³), both inside the industrial area, near the coke oven, a clear indication that its fugitive emissions were a relevant PAH source.

Therefore, notwithstanding maximum efforts to reduce coke oven emissions, annual concentrations again exceeded the BaP air quality target in the two urban sites. These results and the more stringent air quality target for BaP (1.0 ng/m³), effective since 2000, convinced public authorities of the unavoidable necessity to close the coke oven.

Since the coke oven closure occurred in February 2002, from the last available monitoring data in 2008 (Table 1), the BaP air quality target (1 ng/m³) was always respected in the three urban sites.

PAH concentrations measured after the coke oven closure confirmed the relevant impact of this plant on the under-wind residential area. Comparing 1998 and 2003 data, BaPeq concentrations decreased 97.6% at site 3 and 92.8% at site 4.

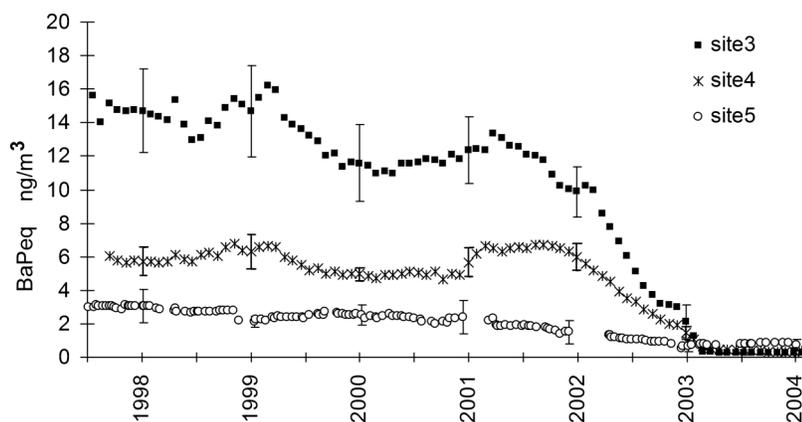


Figure 2. Annual moving averages at sites 3, 4, and 5 of BaPeq daily concentrations. Concentrations are expressed as BaPeq nanograms per cubic meter, updated every 4 weeks. Time axis is labeled at the start of each year, and annual moving average values are drawn at the end of their reference periods. The 95% confidence intervals for the annual means are traced onto the graphs at the end of every year.

During 2003, within the Cornigliano steelwork, two blast furnaces and one electric oven for steel production were still operating. The results obtained during the closure period in Table 1 show that PAH emissions from these residual industrial plants had negligible effects on air quality of sites 3 and 4.

Time trends of BaPeq in urban sites

The annual moving averages (AMAs) of BaPeq (arithmetic mean of all daily BaPeq values received during the previous 12 months, dated according to the last day of the involved period), from July 1997 to March 2004, found at sites 3, 4, and 5, placed in the residential area, are shown in Figure 2.

The highest annual BaPeq concentrations (12–16 ng/m³) were always found at site 3, the urban site nearest to the coke oven.

Similar AMA trends were observed at sites 3 and 4, with relative maximum during 1999 and the last months of 2001, probably due to increase of coke oven emissions caused by technical problems during the progressive coke oven closure, a complex and potentially dangerous procedure.

After the complete coke oven closure (February 2002), AMAs of both sites 3 and 4 declined steadily.

It is important to observe that the effects of coke oven closure on PAH pollution were very rapidly measured: From the day after the closure (February 7, 2002), to April 29, 2002, BaP concentrations of all 38 daily samples collected at site 3 were constantly between 0.1 and 0.6 ng/m³.

During the coke oven activity, the lowest BaPeq concentrations were always found at site 5, close to the traffic flow. At site 5, a constant decrease of BaPeq concentrations was observed during the studied period and mean annual BaP concentrations were below air quality target since 2001, with the coke oven still partially functioning. The progressive replacement of EURO 0 vehicles, without catalytic converters, with less polluting gasoline and diesel vehicles, started in Italy in 1993, explained this PAH concentration trend.

Downwind coke oven hours during samplings and BaPeq concentrations

Sectors of residential areas downwind of the coke oven were from ESE to S for site 3, and from east-southeast to south-southeast for site 4. Site 5 was downwind of the coke oven with south-southwest winds only, a wind direction rare in Genoa (see wind rose in Figure 1).

The explorative PCA (Supplement, Appendix B) provided one significant principal component, composed of the daily concentration of PAHs and highly correlated with the number of hours downwind to the coke oven, that explained 85.6% of the variance. The possible relationship between the number of hours downwind to the coke oven during samplings at sites 3 and 4 and BaPeq concentrations was investigated for the two years (1998–1999) belonging to the full activity period. Regression models applied at samples collected during this period at sites 3 ($n = 280$) and 4 ($n = 296$) are shown in Appendix D, Figures SD1 and SD2.

The equations that best fit the experimental data are:
Site 3:

$$\ln(\text{BaPeq}) = 1.8024 (0.0677) + 0.3295 (0.0115) \times \text{hr} - 0.0131 (0.0013) \times \text{hr}^2 \quad (1)$$

with $R^2 = 0.77$.

Site 4:

$$\ln(\text{BaPeq}) = 1.2747 (0.0642) + 0.1789 (0.0107) \times \text{hr} - 0.0053 (0.0012) \times \text{hr}^2 \quad (2)$$

with $R^2 = 0.55$.

In these equations, hr is the number of hours downwind the coke oven during the daily sampling, BaPeq the daily average value of BaPeq, and parentheses, the standard error on coefficients.

Spatial variations of BaP and BaPeq concentrations

At residential sites 3 and 4, considered to be receiving PAHs from mixed urban and industrial sources, the net value of BaP or BaPeq thought to be emitted by coke oven only (*coke BaP*, *coke BaPeq*) was estimated by subtracting from the measured annual concentration during the full activity period (August 1997–July 1999) the local average urban background, calculated as the mean concentration during daily samplings with zero downwind hours (0.6 and 1.1 ng BaPeq/m³, respectively, resulting from eqs 1 and 2).

The weighted regressions of logarithmically transformed annual coke BaP, coke BaPeq concentrations at sites 2, 3, and 4 and their distances (km) from the coke oven center, are significant ($R^2 = 0.91$, $p < 0.01$, 5 degrees of freedom) and follow an inverse distance power law:

$$\text{cokeBaP} \left(\text{ng/m}^3 \right) = 2.0 \text{ d}^{-1.1} \quad R^2 = 0.91 \quad (3)$$

$$\text{cokeBaPeq} \left(\text{ng/m}^3 \right) = 2.8 \text{ d}^{-1.1} \quad R^2 = 0.91 \quad (4)$$

Obviously, the exponent in these equations is related to the meteorological conditions during the examined biennium.

PAH fingerprints variability

At site 3, 31 samples, collected during the full activity period, were in the high BaPeq deciles group. Their mean BaPeq concentration and standard deviation was 61 ± 6.1 ng/m³.

Their PAH profile is shown with gray bars in Figure 3a. In the same figure, the white bars show the PAH profile of the samples collected in the same site 3 and grouped in the low BaPeq deciles (range: 0.45–0.73 ng/m³).

Student's *t*-test with Bonferroni correction found these two PAH profiles significantly different.

The high BaPeq deciles samples had significantly higher ($p < 5 \times 10^{-8}$) BaA/BeP and BaP/BeP ratios and significantly lower ($p \leq 5 \times 10^{-4}$) PHE, AN, FA, PY, DBA, and BPE ratios. No significant differences ($p > 0.015$) were found for the CHR, BF, and IP ratios. Comparison of site 3 high decile and site 5 contemporary fingerprints highlights an abundance of BPE in site 5 profiles, and an abundance of FA, BaA, BF, and BaP in site 3 profiles.

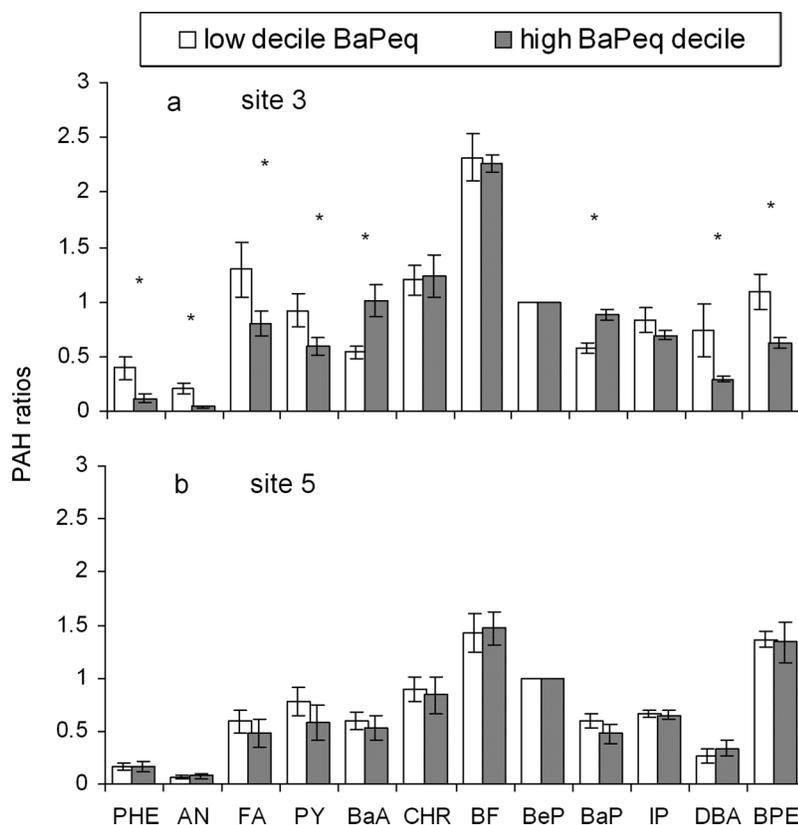


Figure 3. PAH ratios in coke oven and traffic emissions: (a) Mean PAH ratios (PAH/BeP) of the 31 heavily contaminated samples (BaPeq > P90) collected at site 3, from mid-1997 to mid-1999, during the hours downwind the coke oven (gray bars), and PAH ratios found at site 3 in samples characterized by low BaPeq concentrations (P15 < BaPeq < P25) during prevalent northern wind conditions (white bars). Asterisks indicate PAH ratios with significantly different ($p < 0.05$) relative PAH abundance. (b) PAH ratios of samples collected at street level at site 5, contemporaneously to low (white bars) and high (gray bars) contaminated samples of site 3. These two PAH profiles are not statistically different and their prevalent source is gasoline and diesel emissions in urban runs, in Mediterranean weather conditions. During the sampling period, about the 50% of vehicles circulating in Genoa were estimated to be without catalytic converters.

Table 2. Average and standard deviations of diagnostic PAH ratios, measured in vehicles and coal combustion emissions, and found in homogeneous subgroups of samples (low and high BaPeq deciles) collected in three sampling sites, near the Genoa coke oven during its full activity period (mid-1997–1999)

Sample types	N	BaPeq (ng/m ³)	FA/(FA + PY)	BaA/(BaA + CHR)	IP/(IP + BPE)
Gasoline car emissions ¹	2		0.44	0.33 – 0.38	0.09 – 0.22
Diesel car emission ¹	25		0.39 ± 0.11	0.38 ± 0.11	0.35 ± 0.10
Hard coal combustion ¹	9		0.57 ± 0.03	0.43 ± 0.04	0.52 ± 0.04
Site 3 low BaPeq deciles ²	28	0.57 ± 0.08	0.58 ± 0.05 ^c	0.31 ± 0.05	0.44 ± 0.09
Contemporaneous samples in site 4	21	1.2 ± 0.6	0.44 ± 0.16 ^{d,g}	0.38 ± 0.16 ^{d,c,g}	0.34 ± 0.04 ^d
Contemporaneous samples in site 5	24	2.2 ± 1.0	0.43 ± 0.05 ^d	0.40 ± 0.04 ^{c,d}	0.32 ± 0.03 ^d
Site 3 high BaPeq deciles ³	29	61 ± 16	0.57 ± 0.02 ^c	0.45 ± 0.02 ^c	0.53 ± 0.02 ^c
Contemporaneous samples in site 4	21	23.4 ± 11.1	0.54 ± 0.04 ^c	0.44 ± 0.06 ^c	0.52 ± 0.04 ^c
Contemporaneous samples in site 5	19	3.4 ± 3.9	0.46 ± 0.04	0.39 ± 0.05 ^d	0.35 ± 0.06 ^d

Notes: N: number of samples. Symbols: ¹Reference: Yunker et al. (2002). ²P15 < BaPeq < P25; mean temperature and standard deviation during samplings: 16.6 ± 7.0°C. ³BaPeq > P90; mean temperature and standard deviation during samplings: 21.3 ± 5.3°C. ^cNot significantly different from PAH ratios in hard coal combustion. ^dNot significantly different from PAH ratios in diesel car emissions. ^gWithin PAH ratios range in gasoline car emissions.

Several reasons support the hypothesis that the high deciles PAH profile (gray bars in Figure 3a) could be attributed to fugitive emissions of the coke oven: the occurrence of a high number of downwind hours during the samplings, their very high BaPeq concentrations, and the negligible contributions of

PAH from domestic heating plants, owing to mean temperatures (21.3 ± 5.3°C) during their samplings.

PAH profiles found at site 3 (white bars in Figure 3a) in low deciles samples, collected with colder air temperatures (16.6 ± 7.0°C) and with prevailing winds from the northeast sector,

might be representative of aged urban PAH sources, during the cold season.

The PAH profiles of site 5 samples, collected together with the high (gray bars) and low deciles (white bars) samples from site 3, are shown in Figure 3b. These two PAH profiles are statistically identical and are in agreement with PAH ratios found in traffic emissions, in particular the relative abundance of BPE, twofold higher than IP (Caricchia et al., 1999).

During this sampling period, about 50% of vehicles circulating in Genoa were estimated to be without catalytic converters.

Identification of main PAH sources by diagnostic ratios

The diagnostic PAH ratios applied to low and high BaP_{eq} deciles samples are shown in Table 2, together with reference values from the literature (Yunker et al., 2002) related to traffic (gasoline and diesel fuel emissions) and coal combustion emissions.

The agreement between the PAH ratios found in high deciles samples collected at sites 3 and 4 and the diagnostic ratios found in hard coal combustion emissions is remarkably good: All six PAH ratios were significantly not different from hard coal PAH ratios.

At site 5, near the traffic flow, five PAH ratios were significantly not different from diesel PAH ratios, while five PAH ratios were significantly different from hard coal ratios.

Among the 49 daily samples collected at site 5 during 1997–1999, only three samples had a ratio IP/(IP + BPE) \geq 0.44, values expected from coal burning, pointing again to the infrequent impact of coke oven pollution at site 5.

Discussion

The environmental impact of coke ovens has a feature that is rare in other industrial plants: The amount of pollutants emitted by its fugitive emissions is much higher than the amount of pollutants emitted, during the same time, by its stack emissions.

The fugitive emissions of a coke oven have another important characteristic: Their sources are distributed over the entire length of the plant, about 200 m, along the roof (coal charge lids) and along the two sides (coke discharge doors).

This means that the highest concentrations of PAH are located above the coke oven roof (to 7 m above sea level in Genoa coke oven) and along their lateral sides, places where coke workers operate.

Personal exposures of Genoa coke oven workers, measured during 1998, estimated a mean daily exposure to BaP of 2,930 and 1,140 ng/m³ in workers assigned to coal charging cars and to control of coal charging lids, above the top of batteries. Workers assigned to coal discharge, along the coke oven sides, were exposed to 240 ng/m³ of BaP (Bruzzone et al., 2005).

Continuously decreasing PAH concentrations are expected downwind the plant, along the directions of prevailing winds.

Another particular feature of coke ovens is that temperatures of their fugitive emissions, excluding those that are formed during pushing coke (800°C), are relatively low (50–70°C), and this limits their dispersion in height. Our measures, carried

out about 15 m above sea level in sites 1, 2, 3, and 4, confirm this peculiarity.

This means that all houses downwind from a coke oven may be heavily polluted. According to our calculation (eq 3), within a distance of 1,900 m, the annual concentration of BaP emitted by Genoa coke oven may be much greater than 1 ng/m³, the target value currently in force in the European Union countries. This result is in agreement with other studies.

Diffusion model applied to the Taranto (Italy) coke oven emissions (Liberti et al., 2006) estimated that 1,000 m away from the coke oven and at 0, 10, and 20 m above the ground, the concentrations of BaP emitted by this plant were between 2 and 25 ng/m³. Mathematical models applied to a German coke oven (Aries et al., 2007) estimated that the BaP target of 1 ng/m³ can be respected only between 1,200 and 1,770 m from this plant.

Experimental measurements made by the same authors in a coke oven with an age similar to that of the Genoa unit (35–40 years) verified that air samples collected at 250 m had annual BaP concentrations between 20 and 35 ng/m³, with a maximum BaP concentration of 130 ng/m³ measured during a sampling frequently downwind of the plant.

Our measures have largely confirmed that ordinary and extraordinary maintenances of an old coke oven are not able to significantly reduce its impact on the surrounding environment. During the best coke oven maintenance period (1998) monitored during this study (Table 1), the annual BaP concentrations were much higher than the accepted value (1 ng/m³): 9.7 ± 1.2 ng/m³ in site 3 and 4.9 ± 0.5 ng/m³ in site 4.

All these data confirm that people who live less than 1,000–2,000 m downwind of an old-design coke oven may be exposed to BaP concentrations judged potentially dangerous for their health.

All epidemiological studies aimed to verify health effects on population living near a coke oven that obtained negative or not conclusive results share the same methodological error: the use of plant distance as proxy to evaluate population exposure.

Since annual distribution of the wind directions is rarely uniform in all directions, to estimate the exposure to coke oven emissions according to only the distance of residences from the plant can greatly underestimate the actual exposure attributable to this specific source.

Table 1 shows that mean annual BaP_{eq} concentrations during 1998 measured at site 5 (2.1 ± 0.2 ng/m³) were statistically lower than values contemporary found at site 4 (6.3 ± 0.7 ng/m³), notwithstanding that both sites were at similar distances (575 m for site 4, 550 m for site 5) from the coke oven. The main reason for this difference is that site 5 was rarely downwind of the coke oven.

Our experimental measures, and those obtained by other authors (Choi et al., 2007; Weitkamp et al., 2005), have largely confirmed that the main variables for the BaP concentrations around a coke oven are the distance and the number of downwind hours (eq 1; eq 3).

Three epidemiological studies found a significant excess of health risks in populations living near a coke oven (Cara et al., 2007; Chellini et al., 2005; Marinaccio et al., 2011; Parodi et al., 2005). Only one of them evaluated the prevailing wind direction as a variable to identify and classify, according to the residence

distance along this direction, subjects exposed to coke emissions. Parodi et al. (2005), supported by information described in this paper, divided the population living near Genoa coke oven into four exposure classes, according to the downwind distance from coke oven of the census units were they lived (≤ 500 m; 500–1000 m; 1000–1500 m; >1500 m). According to eq 3, the mean daily BaP concentrations in the first three exposure classes were 9.2 ng/m^3 , 2.7 ng/m^3 , and 1.6 ng/m^3 . This approach permitted demonstration of a possible higher lung cancer risk in women living closer to the plant, inside the first exposure class (≤ 500 m downwind of the coke oven).

Our research, comparing BaPeq concentrations measured in urban sites, before and after the coke oven closure, demonstrated that at about 500 m away from this plant, contributions to air pollution of PAH emissions from a steelworks factory, heavy traffic, and domestic heating of a dense urban area were very low (2–7%).

Similar conclusions were obtained from a diffusion model applied to several industrial emissions active in Taranto (coke oven, oil refinery, cement kiln, sinter plant): At ground level, 99.5% of annual BaP concentrations was due to coke oven emissions only (Bisceglia et al., 2010).

The observed differences between the PAH profiles of traffic and coke oven emissions (Figure 3) and values of PAH ratios listed in Table 2 (high BaPeq deciles, at site 3) may be used in source apportionment methods (Ciaparra et al., 2009; Galarneau, 2008) to evaluate, with sufficient accuracy, the specific role of traffic and of coke ovens on PAH pollution measured in other places. The only limitation is that these PAH profiles and ratios can be used only with temperature ranges similar to those experienced in this study ($21.3 \pm 5.3^\circ\text{C}$).

Conclusions

Our experience demonstrated the high daily variability of coke oven fugitive emissions, caused by meteorological and plant exercise parameters. Accurate assessment of PAH pollution produced by these plants requires a specific sampling strategy. Ten to 15 daily samples each month should be collected simultaneously in several sites placed at increasing distances along the directions of prevailing winds. If, within 2 to 3 km, houses are present, sampling sites should be preferentially located on their roofs. Samplings should last a year at least, or better, 2 or 3 years; a long sampling time is essential to evaluate meteorological and seasonal variables correctly.

The present study, which followed for 13 years the activity and the closure of an old coke oven, documented that all ordinary and extraordinary maintenance actions on an old coke oven were ineffective either to guarantee the respect for target values of BaP air concentrations in the nearby residential area, or to significantly reduce its impact on the surrounding environment.

During the best coke oven maintenance period (1998) monitored during this study the annual BaP concentrations were much higher than the target value: $9.7 \pm 1.2 \text{ ng/m}^3$ in site 3 and $4.9 \pm 0.5 \text{ ng/m}^3$ in site 4.

All these data confirm that people who live less than 1–2 km downwind of an old-design coke oven may be exposed to BaP concentrations judged potentially dangerous for their health.

Although new coke ovens conceived according best available technologies have lower emission factors (one-half to one-eighth that of the old Genoa coke plant), this is counterbalanced by their greater dimensions and coke production (about six times the Genoa coke oven production). Therefore, PAH monitoring downwind of modern coke ovens is still recommended.

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