Contribution of wood combustion to PAH and PCDD/F concentrations in two urban sites in

Northern Italy

Andrea Piazzalunga[a], Manuela Anzano[a], Elena Collina[a], Marina Lasagni[a], Francesco

Lollobrigida[b], Antonella Pannocchia[b], Paola Fermo[c], Demetrio Pitea[a]

[a] Dept. Environmental Sciences, Milano-Bicocca University, piazza della Scienza 1, 20126

Milan, Italy

[b] ARPA Piemonte, Dipartimento di Torino, Via Pio VII 9, 10135 Torino, Italy

[c] Dept. Inorganic and Analytical Chemistry, Milano University, via Venezian 21, 20133 Milan,

Italy

Corresponding author: Elena Collina; e-mail elena.collina@unimib.it; ph. +390264482841;

fax +390264482839

Abstract

The use of residential wood combustion represents an important renewable energy source, but it contributes in a considerable way to atmospheric particulate matter (PM) concentration in urban as well as in rural sites. Moreover, recent studies pointed out wood burning as an important source of PAH.

In the present work, the influence of wood combustion on PM was studied, investigating its contribution to the carbonaceous PM fraction and to benzo(a)pyrene (B[a]P) and polychlorodibenzo-p-dioxins and polychlorodibenzofurans (PCDD/F) concentrations, using levoglucosan as a marker. PM10 samples were collected daily for six months in two sites located in Piemonte (Northern Italy): Torino and Susa. Composite monthly samples were chemically characterized, analyzing the concentrations of levoglucosan, B[a]P, PCDD/Fs, organic carbon (OC), elemental carbon, major anions and cations, and metals.

PM and OC concentrations were almost twice in Torino with respect to Susa, while levoglucosan and B[a]P concentrations were almost comparable at the two sites. Therefore, wood combustion affects more Susa than Torino. Concentrations of B[a]P and levoglucosan were highly correlated in both sites. Using the macro tracer method and the emission factors reported in literature, the wood combustion percentage contribution to B[a]P concentration was estimated and resulted as the main source in both sites. The levoglucosan to soluble potassium ratio was higher in Torino with respect to Susa, indicating that combustion plants with different efficiency are used at the two sites. PCDD/F concentrations were higher in Torino than in Susa.

Keywords

wood burning, particulate matter, source apportionment, benzo[a]pyrene,

polychlorodibenzo-p-dioxins and polychlorodibenzofurans, levoglucosan

1. Introduction

In an effort towards reduction of greenhouse emissions, following targets are being pursued

in EU within 2020: 20% reduction in CO_2 emissions; 20% share of renewable energies in

energy consumptions; increase in energy efficiency to achieve 20% saving in energy

consumptions (European Commission, 2007).

There are several alternative renewable energy sources which can be used instead of fossil

and conventional fuels. The decision as to what types of energy source should be utilized

must, in each case, be made on the basis of economic, social, environmental and safety

considerations.

In this perspective, the extensive use of biomass, both in the residential sector and for

electricity production in power plants, is considered as an alternative option.

As far as Italy is concerned, preliminary results of a study carried out by ENEA (Italian

National Agency for new Technologies, Energy and Sustainable Economic Development) and

APAT (Italian Environment Protection and Technical Services Agency) show that the

expansion of domestic burning of wood logs, briquettes, chips and pellet will contribute for a

significant quote to the renewable share of the energy budget (Pignatelli et al., 2008).

However, it is well known that biomass combustion in domestic appliances is a significant

emission source for air pollutants (Kocbach Bølling et al., 2009). Several studies were carried

out in North America (e.g., Rogge et al., 1998, Purvis et al., 2000, Fine et al., 2004) and -

more recently - in Europe (e.g., Boman et al., 2003, Saarikoski et al., 2008, Hellen et al.,

2008, Caseiro et al., 2009). Together with NO_x and CO, wood smoke consistently produces

particulate matter (PM), contributing for a relevant share to the total PM2.5 and PM10 emitted.

The effluents from these sources contain numerous toxic/carcinogenic components, such as formaldehyde and benzene (Gustafson et al., 2007), polycyclic aromatic hydrocarbons, PAHs (Cooper, 1980), and free radicals (Leonard et al., 2000).

Estimates and scenario assessed for the European Commission point out that the domestic biomass combustion is the main source of PAHs emitted into the atmosphere. The exposure to this kind of pollutants can cause serious health impairments (Kim et al., 2011).

Being formed in combustion and thermal processes (Everaert and Baeyens, 2002, Pitea et al., 2008, Hites, 2011), also polychlorodibenzo-p-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) are present in the emissions from biomass combustion (Lavric et al., 2004). It has been highlighted also that the relative contribution of diffuse and small scale sources to the national/regional profile is increasing. Among these contributions, domestic biomass burning is estimated to be the third one for relevance, after waste treatment and steel industry, in Lombardia region, the largest region of Northern Italy and next to the Piemonte region (Caserini and Monguzzi, 2002). In countries with state of the art incinerators and steel works, the relevance is even higher.

In the present work, the influence of wood combustion on PM was studied, investigating its contribution to the carbonaceous PM fraction and to benzo(a)pyrene (B[a]P) and polychlorodibenzo-p-dioxins and polychlorodibenzofurans (PCDD/F) concentrations, using levoglucosan as a marker. Levoglucosan is formed in pyrolysis process of cellulose and hemicellulose containing materials, and thus is an unambiguous tracer for biomass burning emission (Shafizadeh, 1968). B(a)P is used as an indicator for toxic PAHs (Belis et al., 2011).

In Italy, PCDD/F concentrations were determined in atmospheric particulate samples just

4

few times (Caserini et al., 2004, Turrio-Baldassarri et al., 2005, Menichini et al., 2007, Colombo et al., 2009, Onofrio et al., 2011).

PM was sampled in two sites situated in the Po Valley, the most industrialized and trafficked area in Italy. Strong atmospheric stability affects this area especially during wintertime, causing prolonged periods with high pollution levels (PM10 often higher than 100 µg m^{-3}).

2. Sampling and analyses

PM10 was sampled according to UNI EN 12341 by the environmental protection agency of Piemonte region (Agenzia Regionale di Protezione Ambientale Piemonte) with a medium volume sampling device (TCR Tecora; 2.3 m³ h^{-1}) on quartz fiber filters (47 mm diameter), one filter was collected every day. Sampling was carried out for six months in the period October, 1st, 2006 – March, 31st, 2007 and was performed in two towns: Torino (45'3"N / 7'40"E), capital of Piemonte region, with 908 853 inhabitants the fourth Italian city by population, and Susa (45' 8''N / 7' 3''E), with 6 743 inhabitants, situated near the Alps and therefore visited by many tourists during holidays and week-ends. In Torino, the sampling site was in a road where about 12 000 vehicles drove by every day; in Susa it was located in a residential area (Figure 1).

Before and after the samplings, the filters were exposed for 48 hours on open but dust-protected sieve-trays in an air-conditioned weighing room (T = 20 ± 1 °C and relative humidity R.H. = 50 ± 5%), where they were weighed using an analytical microbalance (precision 1 µg).

In order to quantify also organic micropollutants present at low concentrations as PCDD/Fs, the chemical characterization was performed on monthly composite samples. From each filter (daily sample) one portion (for the determination of ions and anhydrosugars, total

carbon (TC), and elemental carbon (EC)) or two portions (for the determination of B[a]P, and metals) of 5 mm diameter were cut out and combined to obtain the monthly composite samples.

To quantify the inorganic constituents (chloride, nitrate, sulfate, sodium, ammonium, potassium, magnesium, calcium ions), the monthly composite samples were extracted with 20 mL Milliq water; the aqueous solutions obtained were analyzed by ionic chromatography. Extraction and analytical procedure were described in detail in Fermo et al. (2006a). On the same solutions the concentration of anhydrosugars levoglucosan (LG) and mannosan (MN) was determined with high pressure anion exchange chromatography coupled with pulsed amperometric detector (HPAEC-PAD) (Piazzalunga et al., 2010).

The determination of total carbon (TC) was done measuring the CO_2 evolved from the combustion, in oxygen and at 950 °C, of all the material on the monthly composite sample. Non-dispersive IR photometry (NDIR, Tekmar, Dohrmann Apollo 9000) was used for this determination. The same apparatus was used to determine elemental carbon (EC), but the filters were previously heated in pure oxygen at 435°C so that they were free of all the organic matter (Fermo et al., 2006b). Organic carbon (OC) was computed as the difference between TC and EC.

For B[a]P determination the monthly composite samples were extracted with cyclohexane and the extracts were analyzed by GC-MS according to Annex VII of Italian Ministerial Decree 25th November 1994.

For metal determination the monthly composite samples were digested and the content of arsenic (As), cadmium (Cd), nickel (Ni) and lead (Pb) was determined by ICP-OES / AAS according to UNI EN 14902:2005.

The remaining filter portions (about 10 cm^2 for each day) were put together according to the sampling month; in this way, monthly composite samples of about 39 mg PM for Susa and 100 mg PM for Torino were obtained. For the determination of 2,3,7,8-substituted PCDD/F concentration, the composite samples were extracted according to EPA 1613 method (EPA 1994); the extracts were analyzed by a gas – chromatograph (Varian CP3800) coupled to a triple quadrupole mass spectrometer (Varian 320MS).

3. Results

3.1 Annual trends

Figures 2 and 3 report the monthly trends for concentrations of PM10 and B[a]P for the years 2006 and 2007. The samples were analyzed by the local environmental protection agency using the same analytical techniques reported in Materials and Methods section (personal communication). In particular, the boxes in Figure 2 and 3 show the months that underwent full chemical characterization. As in other cities of the Po Valley, we observed a marked seasonal pattern, with a significant increase during the cold season due to the different dispersion conditions; furthermore in winter also additional sources of PM are to be considered (e.g. residential heating).

PM10 concentrations are higher in Torino than in Susa whereas B[a]P concentrations at the two sites are comparable. In Torino, as in many other cities of the Po Valley, during the winter months PM10 concentrations are often above EU daily limit of 50 µg m^{-3}. In Torino the threshold limits have been exceeded for more than 150 days year^{-1} both in 2006 and 2007.

Both in Torino and Susa, the B[a]P annual limit value of 1 ng m^{-3} was exceeded in 2006, whereas both stations fulfilled the same limit in 2007. The B[a]P winter average was higher

than 1 ng m^{-3} both in 2006 and in 2007. B[a]P showed lowest concentrations in the warm period (from April to September), with average concentrations of about 0.08 ng m^{-3} and 0.05 ng m^{-3} at Susa and Torino respectively. The monthly average concentrations in the cold period ranged from 0.18 to 3.83 ng m^{-3} in Susa and from 0.12 to 4.22 ng m^{-3} in Torino. B[a]P concentrations in the warm and cold period were comparable to those detected in other sites in Northern Italy (Van Drooge and Ballesta, 2009; Belis et al., 2011).

The presence of higher PAH concentrations in colder periods in comparison to those measured in warmer periods was in agreement with other studies and was explained by the combination of factors related to the physicochemical properties, such as volatility related to the gas/particle partitioning, and reactivity with oxidants, but also with meteorological conditions, such as atmospheric stability, and the strength of the potential emission sources. According to the equation proposed by Yamasakl et al. (1982) it is possible to calculate the gas/particle distribution of B[a]P as a function of temperature. In the investigated period, in October the average monthly temperature was the highest and equal to 14 °C and 16 °C in Susa and Torino, respectively. In October, the percentage of B[a]P present in the gas phase is less than 5% compared to that present in the PM. This percentage decreases (< 1%) for both sites during the coldest months (December to February). So, the different gas/particle distribution is not sufficient to justify the increased concentrations of B[a]P during the colder months.

3.2 Chemical composition

As for the concentration of PM, also the concentrations of the main chemical constituents (TC, OC, EC, nitrate, sulfate, ammonium, and potassium) in Torino are about twice as Susa (Table 1). Indeed, the percentage chemical composition at the two sites does not show

8

major differences and carbonaceous particles represent about 30% by mass (Figure S1 in Supporting Information). The ionic compounds, usually of secondary origin (nitrate, sulfate and ammonium) represent approximately 30% of the mass. The unexplained mass, due to the presence of metal oxides, water and any errors, is about 40%.

Apart from major constituents, other compounds have been analyzed, in order to characterize the PM with respect to possible sources and to evaluate its impact on human health. For this reason, B[a]P and the 2,3,7,8-chlorinated PCDD/F congeners were determined (Table S1 in Supporting Information).

Figure 4 shows the concentration trends for LG and organic micropollutants. The concentrations measured in Torino are comparable to those of Susa. We observed an increase in concentrations during the colder months (December to February); the B[a]P and PCDD/Fs have a maximum concentration during the month of December at both sites.

PCDD/F concentrations (Figure 4) were higher in Torino (1.2 pg m^{-3} - 2.5 pg m^{-3}) than in Susa (0.6 pg m^{-3} - 2.1 pg m^{-3}) and were consistent with those outlined by other national studies (Turrio-Baldassarri et al., 2005, Menichini et al., 2007) carried out in urban and rural areas.

Until now, the studies carried out in Italy were mainly related to the role of municipal solid waste incinerators (MSWI) to the local PCDD/F air concentration (Caserini et al., 2004, Colombo et al., 2009); a recent study investigated the potential role of a steel plant on the PCDD/F air concentration in Piemonte region (Onofrio et al., 2011).

Figure 5 shows the congener profiles of the seventeen 2,3,7,8-chlorinated substituted PCDD/Fs detected in the six samples collected at the two monitoring stations.

The samples showed different profiles in terms of abundance of single congener. Overall, the homologue profile of each monitoring station, according to Lohmann and Jones (1998) showed an increasing concentration of PCDD with increasing chlorination levels, while a

decreasing concentration of PCDF congeners with increasing chlorination levels was not observed (Figure 5).

Regarding the metals (As, Cd, Ni, Pb), the concentrations measured in Torino were higher than those in Susa, the metal present in higher concentration was Ni (18 ng m^{-3} and 13 ng m^{-3} in Torino and Susa, respectively), while the concentration of As, Cd and Pb were below 1 ng m^{-3} at both sites.

Considering the PM-mass-normalized concentrations, an increase of metal content during the colder months was not observed, in contrast to organic micropollutants. The only exception was the Ni content in the PM sampled in Susa, which showed a maximum in December (1500 ppm). The average Ni content determined for the other months was 200 ppm; while in Torino the mean concentration of this metal was about 230 ppm.

3.3 Wood burning contribution to sample composition

The data collected were compared to examine similarities and associations between samples using Principal Components Analysis, PCA (12 observations - 6 samples in 2 locations - and 12 variables). Principal component analysis (PCA) is a multivariate eigenvalue/eigenvector method designed to extract information in a data set. It reduces the number of variables to fewer ones which summarize the information and highlight the dominant patterns or major trends in the data. The new variables, called PC or principal components, are linear combinations of the original ones. For each component, the absolute value of the "loading" indicates how much the variable contributes to that PC. The "score" projection in the PC plane indicates the presence of natural grouping among objects. To investigate the influence of the original variables on the samples and to interpret relationships between experimental

groups and variables, "biplots" are used. In a biplot, samples are displayed as points while variables are displayed as vectors.

PM-mass-normalized concentrations determined for EC, OC, LG, sulfate, nitrate, potassium, lead, nickel, PCDD/F, B[a]P, cadmium, arsenic were autoscaled prior to modeling and then the data were processed using the STATISTICA 9.0 software.

Figure 6 shows the biplot in the space of the first component, PC1, accounting for 53.51% of the dataset variability, and the second component, PC2, which accounts for 16.73% of the dataset variability. PCA analysis makes a clear distinction between the samples collected in Susa (clustered along the positive direction of PC1) and those collected in Torino (clustered along the negative direction of PC1); exceptions are the samples collected in Susa in the months of February and March, which seem more similar to the samples collected in Torino. Moreover, the biplot (Figure 6) points out that PC1 was mainly influenced by nitrate (one of the parameters characteristic of secondary formation processes) in the negative direction and EC, OC, LG, potassium, PCDD/F, B[a]P (related to biomass burning) in the positive direction.

So it can be hypothesized that Torino samples are mainly determined by secondary processes while wood burning contributes most to the characteristics of Susa samples.

In the following, the wood combustion contributions to PM, OC, EC, B[a]P and PCDD/F is evaluated.

3.3.1 Wood burning contribution to PM, OC and EC

The ratio between LG-C (LG carbon content) and OC is a useful indicator for estimating the relative contribution of wood combustion to OC (Puxbaum et al., 2007). At the two sites this ratio is between 0.018 and 0.074 (Figure S2 in Supporting Information), and is comparable to

11

those measured at other sites in Lombardia region (Piazzalunga et al., 2011, Belis et al., 2011), the largest region of Northern Italy and next to the Piemonte region.

In Susa this ratio is about twice than in Torino (Table 1), showing a larger contribution of the wood combustion. In Torino, the ratio was similar to that measured in Milano (0.021) (Piazzalunga et al., 2011), the second largest Italian city by population located about 140 km from Torino.

Both in Torino and Susa the LG-C/OC ratio increases during the colder months (Figure S2 in Supporting Information).

According to the inventory of atmospheric emissions (IREA 2007), in Torino only 0.3 % of the residential surface is heated with wood; yet LG-C/OC ratio is about half of that recorded in Susa where about 11 % of the residential surface is heated with wood. However, in absolute value, in the main city more than 110 000 m² of residential spaces are heated with wood, while this value drops to only 28 000 m² in Susa. It can also be hypothesized that part of the particulate sampled at Torino was not locally produced but came from the surrounding territories; in fact the city is located in a plain surrounded by densely populated areas and in the province of Torino about 7 % of the residential surface (over 6 million m²) is heated by wood. On the other hand Susa, being an alpine site, is less influenced by the transport of pollutants from the surrounding territories.

According to Schmidl et al. (2008), the ratio between LG and mannosan (MN) is an indicator of the type of wood used (hardwood vs. softwood): for hardwood the ratio is about 13 while for softwood it is about 4. On this basis, from the calculated LG/MN values (Table 1) it can be estimated that, in Torino, about 80 % of the wood used is of hardwood type while in Susa this percentage decreases to about 70 %.

The ratio K^+/LG (Table 1) confirms the differences between the two sites being higher in Torino than in Susa. The presence of an additional non combustion source in Torino was ruled out on the basis of the similar trends observed for the monthly concentrations of K^+ and LG (Figure S3 in Supporting Information). A higher ratio may indicate that, in Torino and surroundings, combustion systems are used that operate at higher temperatures, with improved combustion efficiency and resulting in emissions with a lower amount of organic compounds (Caseiro et al., 2009 and references therein; Sandradewi et al., 2008).

In literature many methods have been proposed to estimate the contribution of wood combustion to concentrations of PM, OC and EC (Szidat et al., 2006, Caserio et al., 2009, Favez et al., 2010): macro-tracer method; Positive Matrix Factorization, PMF; Chemical Mass Balance, CMB; radiocarbon method. These methods have recently been applied in Northern Italy (Bernardoni et al., 2011, Gilardoni et al., 2011, Perrone et al., 2012, Piazzalunga et al., 2011) and a good homogeneity in the results has been obtained; at present these are the only Italian studies published in the literature.

In this study, because of the limited number of samples, the most useful method for the quantification of the contribution of wood combustion to PM and to the carbonaceous fraction is the macro-tracer method. The main problem in applying this method is the choice of suitable emission factors. The ratio LG/PM, LG-C/OC and OC/EC measured at the source, in fact, depend on many factors: type of wood, type of facility (new or old stove, fireplace, ...), type of combustion (flaming vs. smoldering) and at present burning tests conducted on plants and types of wood in Europe are still scarce. Furthermore, as to our knowledge, information on the types of plants present in Piemonte region is lacking. To calculate the percentage contribution of wood combustion to PM and CO, Szidat et al. (2006) proposes to use as emission factor the average value of the data present in the literature. According to

13

Piazzalunga et al. (2011), emission factors derived from the PMF profiles of the sources are more robust and these profiles can indeed be considered to be representative of the different types of plants on the territory and of the different types of wood used. Given the previously discussed similarities between Piemonte and Lombardia regions, we propose to use the profiles obtained for wood burning source by Bernardoni et al. (2011) and reported in Table S2 in Supporting Information.

Table 2 shows the contribution of wood combustion to PM and the carbonaceous component at the two sites in this study.

Wood combustion is confirmed to be an important source of PM and its contribution is high as concerns the carbonaceous fraction, in particular in the alpine town and in the coldest months (December to February).

3.3.2 Wood burning contribution to B[a]P

The ratio between the B[a]P carbon content (B[a]P-C) and LG-C is a useful tool to determine the biomass combustion contribution to PAH concentrations; in both sites the trend observed (Figure S4 in Supporting Information) is very similar with an average value of 3.4 ‰ in Torino and 3.3 ‰ in Susa.

In December, in particular, the ratio significantly increases in both sites by a factor three (Torino 9.6 ‰, Susa 7.9 ‰), thus indicating the contribution of an additional source to PAH concentration.

According to Chen et al. (2001), hydrocarbon (HC) and carbon monoxide (CO) emissions from vehicle exhaust increase gradually with the decrease of atmospheric temperature. As high concentrations of CO and HCs in the exhaust of vehicles are indicative of incomplete combustion, also an increase of aromatic compound emission can be hypothesized. In fact

Deng et al. (2011) pointed out that, during the winter season, PCDD/F emission factors from vehicles increase by a factor 3 to 6 with respect to the warmer season. So, the increase in B[a]P concentration observed, especially in December, can be related to the traffic source. Moreover, in Susa, the B[a]P-C to LG-C ratio is higher in the colder months of January and February than in October, November and March (Figure S4 in Supporting Information). This observation can be explained considering that diesel oil residential combustion can be an important source of aromatic compounds (Ravindra et al., 2008). In fact, in Susa 12% of housing surface is diesel heated (IREA 2007).

A recent paper by Belis et al. (2011) compares four methods for the quantification of wood combustion contribution to B[a]P concentration: CMB, Multi Linear Regression (MLR), PMF, and Levoglucosan tracer method. However, CMB and MLR require a detailed knowledge of the sources (Viana et al., 2008) and, as already discussed, there is a lack of emission profiles for combustion of different wood typologies in heating devices widespread in Italy. On the other hand, application of PMF requires a broad number of samples (Vecchi et al., 2008). So, the Levoglucosan tracer method is the most appropriate for our data set. This method assumes a single source for LG and requires, for its application, the knowledge of the ratio LG to B[a]P deriving from biomass burning. Belis et al. (2011), on the basis of data published with information on both LG and PAHs emitted from biomass burning, established a correlation between B[a]P and LG (B[a]P = 0.0011 ($\pm$ 0.0001) $\times$ LG, N = 48, r^2 = 0.54). This correlation can be used to estimate the contribution of wood combustion to the measured B[a]P concentration; the calculated contributions are 65% $\pm$ 29% for Torino and 60% $\pm$ 24% for Susa. These results are consistent with those determined for Lombardia region (Belis et al., 2011) and confirm that, during the cold season, residential wood combustion, at the

actual technology level, is the main source of atmospheric PAHs, with the exception of December month, as already mentioned.

3.3.3 Wood burning contribution to PCDD/F

To evaluate the contribution of wood combustion to the measured PCDD/F concentrations, the application of usual methodologies as the macro tracer approach (Caseiro et al., 2009) is not possible. In fact, as to our knowledge, PCDD/Fs were never included in the determination of emission profile for the source wood combustion, with few exceptions (Gullett et al., 2003). So, accurate determination of emission profile is still needed, with quantification of both PCDD/Fs and a marker characterizing the source as LG.

To overcome this difficulty, the congener profiles of the 2,3,7,8-substituted PCDD/Fs were selected as the signatures of possible PCDD/F emission sources (Lee et al., 2004).

The profile for each PM sample was calculated summing up the concentrations of the congeners with the same chlorination degree and normalizing to the total weight of the 2,3,7,8-congeners. Subsequently, the mean profiles for Torino and Susa were calculated (2,3,7,8-fingerprints) (Figure S5 in Supporting Information).

To identify the possible PCDD/F sources for ambient air concentrations measured in Torino and Susa, the 2,3,7,8-fingerprints determined for the two sampling sites together with those reported in literature for different sources (Thoma, 1988, Miyabara et al., 1999, Everaert and Baeyens, 2002, Onofrio et al., 2011) were analyzed by PCA (10 variables and 10 observations). Figure 7 presents the score plot from PCA, where PC1 explains 54.64% of the total variance, while PC2 explains 23.68% of the total variance.

In Figure 7, the observations with similar congener profiles are closely located, while those which have divergent patterns are located further apart.

It can be noticed that the composition of PM sampled in Torino is mostly influenced by the traffic source, as the data point falls next to a PM sample collected in a tunnel (Miyabara et al., 1999). On the other hand, the composition of the sample collected in Susa presents similarities with that of soot from wood combustion (Thoma, 1988). In fact, the PM of Susa as well as the other two data points relative to wood combustion are the only ones clustered along the negative direction of PC2.

Moreover, the 2,3,7,8-fingerprints of both Susa and Torino samples are very different from those characteristic of a steel plant located in Piemonte region at half way between the two sampling sites, confirming the limited influence of this source in the local PCDD/F air concentrations (Onofrio et al., 2011).

4. Conclusions

The influence of wood combustion on PM was investigated. PM10 samples were collected daily for six months in two sites located in Piemonte (Northern Italy): Torino and Susa. Composite monthly samples were chemically characterized, analyzing the concentrations of LG, B[a]P, PCDD/Fs, OC, EC, major anions and cations, and metals. These concentrations were in agreement with those determined in other studies for the main cities of the Po Valley.

Concerning PM, OC and EC, on the basis of the LG content, it can be concluded that wood combustion affects more Susa than Torino. On the other hand, the wood burning contribution to B[a]P was similar in both sites and about 60 %.

With respect to wood burning contribution to PCDD/Fs, the 2,3,7,8-fingerprints of PM sampled in Torino were mostly influenced by the traffic source, whereas those of the samples collected in Susa were similar to those of soot from wood combustion.

5. References

Belis, C.A., Cancelinha, J., Duane, M., Forcina, V., Pedroni, V., Passarella, R., Tanet, G.,

Douglas, K., Piazzalunga, A., Bolzacchini, E., Sangiorgi, G., Perrone, M.G., Ferrero, L.,

Fermo, P., Larsen, B.R. (2011). Sources for PM air pollution in the Po Plain, Italy: I. Critical

comparison of methods for estimating biomass burning contributions to benzo(a)pyrene.

Atmos. Environ., *45*, 7266-7275.

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., Fermo, P. (2011). PM10 source

apportionment in Milan (Italy) using time- and size-resolved data. *Sci. Total Environ.*, *409*,

4788–4795.

Boman, B.C., Forsberg, A.B., Jarvholm, B.G. (2003). Adverse health effects from ambient air

pollution in relation to residential wood combustion in modern society. *Scand. J. Work

Environ. Health*, *29*, 251-260.

Caseiro, A., Bauer, H., Schmidl, C., Pio, C., Puxbaum, H. (2009). Wood burning impact on

PM10 in three Austrian regions. *Atmos. Environ.*, *43*, 2186-2195.

Caserini, S., Monguzzi, A.M. (2002). PCDD/Fs emissions inventory in the Lombardy Region:

results and uncertainties. *Chemosphere*, *48*, 779-786.

Caserini, S., Cernuschi, S., Giugliano, M., Grosso, M., Lonati, G., Mattaini, P. (2004). Air and

soil dioxin levels at three sites in Italy in proximity to MSW incineration plants.

Chemosphere, *54*, 1279–1287.

Chen, L.W.A., Doddridge, B.G., Dickerson, R.R., Chow, J.C., Mueller, P.K., Quinn, J., Butler,
W.A. (2001). Seasonal variations in elemental carbon aerosol, carbon monoxide and sulfur
dioxide: Implications for sources. *Geophys. Res. Lett., 28*, 1711-1714.

Colombo, A., Benfenati, E., Mariani, G., Lodi, M., Marras, R., Rotella, G., Senese, V., Fattore,
E., Fanelli, R. (2009). PCDD/Fs in ambient air in north–east Italy: the role of a MSWI inside
an industrial area. *Chemosphere*, *77*, 1224–1229.

Cooper, J.A. (1980). Environmental impact of residential wood combustion emissions and its
implications. *JAPCA*, *30*, 855-861.

Deng, Y., Peng P., Ren, M., Song, J., Huang, W. (2011). The winter effect on formation of
PCDD/Fs in Guangzhou by vehicles: A tunnel study. *Atmos. Environ.*, *45*, 2541-2548.

EPA (1994). Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution
HRGC/HRMS. Method 1613 U.S. Environmental Protection Agency.

European Commission (2007). An Energy Policy for Europe. COM(2007)1

Everaert, K., Baeyens, J. (2002). The formation of dioxins in large scale thermal processes.
Chemosphere, *46*, 439-448.

Favez, O., El Haddad, I., Piot, C., Boréave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L.,
Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C., D'Anna, B. (2010).
Inter-comparison of source apportionment models for the estimation of wood burning
aerosols during wintertime in an Alpine city, Grenoble (France). Atmos. Chem. Phys., *10*,
5295-5314.

Fermo, P., Piazzalunga, A., Vecchi, R., Valli, G. (2006a). Set-up of Extraction Procedures for
Ions Quantification in Aerosol Samples. *Chemical Engineering Transaction*, *10*, 203-208.

Fermo, P., Piazzalunga, A., Vecchi, R., Valli, G., Ceriani, M. (2006b). A TGA/FT-IR study for
measuring OC and EC in aerosol samples. *Atmos. Chem. Phys.*, *6*, 255-266.

Fine, P.M., Cass, G.R., Simoneit, B.R.T. (2004). Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. *Environ. Eng. Sci.*, *21*, 387-409.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J.P., Larsen, B.R., Karl, M., Stenstrom, K., Genberg, J., Henne, S., Dentener, F. (2011). Better constraints on sources of carbonaceous aerosols using a combined (14)C - macro tracer analysis in a European rural background site. *Atmos. Chem. Phys., 11*, 5685–5700.

Gullett, B.K., Touati, A., Hays, M.D. (2003). PCDD/F, PCB, HxCBz, PAH, and PM Emission Factors for Fireplace and Woodstove Combustion in the San Francisco Bay Region. *Environ. Sci. Technol.*, *37*, 1758-1765.

Hellen, H., Hakola, H., Haaparanta, S. (2008). Influence of residential wood combustion on local air quality. *Sci. Total Environ.*, *393*, 283-290.

Hites, R.A. (2011). Dioxins: An Overview and History. *Environ. Sci. Technol.*, *45*, 16-20.

IREA (2007). Inventario Regionale delle Emissioni in Atmosfera. www.sistemapiemonte.it/irea/

Kim, K.H., Jahan, S.A., Kabir, E. (2011). A review of diseases associated with household air pollution due to the use of biomass fuels. *J. Haz. Mat.*, *192*, 425-431.

Lavric, E.D., Konnov, A.A., De Ruyck, J. (2004). Dioxin levels in wood combustion – a review. *Biomass Bioenergy*, *26*, 115-145.

Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Tsai, P.J., Wu, K.Y., Lin., C. (2004). Source Identification of PCDD/Fs for Various Atmospheric Environments in a Highly Industrialized City. *Environ. Sci. Technol.*, *38*, 4937-4944.

Leonard, S.S., Wang, S., Shi, X., Jordan, B.S., Castranova, V., Dubick, M.A. (2000). Wood

smoke particles generate free radicals and cause lipid peroxidation, DNA damage,

NFkappaB activation and TNFalpha release in macrophages. *Toxicol.*, *150*, 147-157.

Lohmann, R., Jones, K.C. (1998). Dioxins and furans in air and deposition: A review of levels,

behaviour and processes. *Science Tot. Environ.*, *219*, 53-81.

Menichini, E., Iacovella, N., Monfredini, F., Turrio-Baldassarri, L. (2007). Atmospheric

pollution by PAHs, PCDD/Fs and PCBs simultaneously collected at a regional background

site in central Italy and at an urban site in Rome. *Chemosphere*, *69*, 422–434.

Miyabara, Y., Hashimoto, S., Sagai, M., Morita, M. (1999). PCDDs and PCDFs in vehicle

exhaust particles in Japan. *Chemosphere*, *39*, 143-150.

Onofrio, M., Spataro, R., Botta, S. (2011). The role of a steel plant in north-west Italy to the

local air concentrations of PCDD/Fs. *Chemosphere*, *82*, 708–717.

Perrone, M.G., Larsen, B.R., Ferrero, L., Sangiorgi, G., De Gennaro, G., Udisti, R. , Zangrando,

R., Gambaro, A., Bolzacchini, E. (2012). Sources of high PM2.5 concentrations in Milan,

Northern Italy. Molecular marker data and CMB modelling. *Sci. Total Environ., 414*, 343-

355.

Piazzalunga, A., Fermo, P., Bernardoni, V., Vecchi, R., Valli, G., de Gregorio, M.A. (2010). A

simplified method for levoglucosan quantification in wintertime atmospheric particulate

matter by high performance anion-exchange chromatography coupled with pulsed

amperometric detection. *Intern. J. Environ. Anal. Chem.*, *90*, 934-947.

Piazzalunga, A., Belis, C., Bernardoni, V., Cazzuli, O., Fermo, P., Valli, G., Vecchi, R. (2011).

Estimates of wood burning contribution to PM10 in Lombardy (Po Valley, Italy) using

different approaches, *Atmos. Environ., 45*, 6642-6649.

Pignatelli, T., D'Elia, I., Vialetto, G., Bencardino, M., Contaldi, M. (2008). The use of bio-mass: synergies and trade-offs between Climate Change and Air Pollution, in Italy. *17th Annual International Emission Inventory Conference, Portland*, OR, US Environmental Protection Agency.

Pitea, D., Bortolami, M., Franzoni, F., Collina, E., Cortili, G., Lasagni, M., Piccinelli, E. (2008). Prevention of PCDD/F formation and minimization of their emission at the stack of a secondary aluminium casting plant, *Environ. Sci. Technol.*, *42*, 7476-7481.

Purvis, C.R., McCrillis, R.C., Kariher, P.H. (2000). Fine particulate matter (PM) and organic speciation of fireplace emissions. *Environ. Sci. Technol.*, *34*, 1653-1658.

Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., Pio, C. (2007). Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. *J. Geophys. Res.*, *112*, D23S05.

Ravindra, K., Sokhia, R., Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ., 42*, 2895–2921.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T. (1998). Sources of Fine Organic Aerosol. 9. Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces. *Environ. Sci. Technol.*, *32*, 13-22.

Saarikoski, S.K., Sillanpää, M.K., Saarnio, K.M., Hillamo, R.E., Pennanen, A.S., Salonen, R.O. (2008). Impact of biomass combustion on urban fine particulate matter in Central and Northern Europe. *Water, Air and Soil Pollution*, *191*, 265-277.

Sandradewi, J., Prévôt, A. S. H., Alfarra, M. R., Szidat, S., Wehrli, M. N., Ruff, M., Weimer, S., Lanz, V. A., Weingartner, E., Perron, N., Caseiro, A., Kasper-Giebl, A., Puxbaum, H.,

Wacker, L., Baltensperger, U. (2008). Comparison of several wood smoke markers and source apportionment methods for wood burning particulate mass. *Atmos. Chem. Phys. Discuss., 8*, 8091-8118.

Schmidl, C., Marr, L.L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H. (2008). Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmos. Environ., 42,* 126–141.

Shafizadeh, F. (1968). Pyrolysis and combustion of cellulosic materials. *Adv. Carbohyd. Chem.*, *23*, 419-474.

Szidat, S., Jenk T.M., Synal, H.-A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., Baltensperger, U. (2006). Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by 14C. *J. Geophys. Res. D: Atmos.***,** *111*, D07206.

Thoma, H. (1998). PCDD/F-concentrations in chimney soot from house heating systems. *Chemosphere*, *17*, 1369-1379.

Turrio-Baldassarri, L., Abate, V., Iacovella, N., Monfredini, F., Menichini, E. (2005). Occurrence of PCDD/Fs in urban air before and after the ban of leaded gasoline. *Chemosphere*, *59*, 1517–1524.

Van Drooge, B.L., Ballesta, P.P. (2009). Seasonal and Daily Source Apportionment of Polycyclic Aromatic Hydrocarbon Concentrations in PM10 in a Semirural European Area. *Environ. Sci. Technol.*, *43*, 7310–7316.

Vecchi, R., Chiari, M., D'Alessandro, A., Fermo, P., Lucarelli, F., Mazzei, F., Nava, S., Piazzalunga, A., Prati, P., Silvani, F., Valli, G. (2008). A mass closure and PMF source

apportionment study on the sub-micron sized aerosol fraction at urban sites in Italy. *Atmos. Environ., 42*, 2240-2253.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, A., Szidat, S., Prevot, A.S.H., Hueglin, C., Bloemen, H., Wahlin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W., Hitzenberger, R. (2008). Source apportionment of particulate matter in Europe: A review of methods and results. *J. Aerosol Sci., 39*, 827-849.

Yamasaki, H., Kuwata, K., Miyamoto H. (1982). Effects of Ambient Temperature on Aspects of Airborne Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.*, *16*, 189-194.

Table 1: mean concentrations and standard deviation (s.d.) of PM and chemical constituents as well as significant ratios in the October 2006 – March 2007 period.

	Susa	s.d.	Torino	s.d.
PM ($\mu g\ m^{-3}$)	31.7	7.5	82.8	18.1
TC ($\mu g\ m^{-3}$)	7.4	1.8	15.7	3.4
OC ($\mu g\ m^{-3}$)	5.4	1.3	11.9	3.0
EC ($\mu g\ m^{-3}$)	2.02	0.64	3.72	0.61
Nitrate ($\mu g\ m^{-3}$)	5.0	2.3	13.8	4.1
Sulfate ($\mu g\ m^{-3}$)	1.89	0.22	4.37	0.86
Ammonium ($\mu g\ m^{-3}$)	1.89	0.73	5.21	1.81
Potassium ($\mu g\ m^{-3}$)	0.30	0.12	0.49	0.23
Levoglucosan ($\mu g\ m^{-3}$)	0.75	0.34	0.68	0.29
Mannosan ($\mu g\ m^{-3}$)	0.087	0.036	0.066	0.033
BaP ($ng\ m^{-3}$)	1.33	1.33	1.27	1.51
PCDD/F ($fg\ m^{-3}$)	1157	515	1747	523
PCDD/F ($fg_{TEQ}\ m^{-3}$)	81	45	61	44
LG-C/OC	0.058	0.017	0.024	0.005
LG/MN	8.7	1.8	10.3	3.5
K^+/LG	0.42	0.07	0.74	0.17

Table 2: wood burning contribution to PM, OC and EC in the October 2006 – March 2007
period.

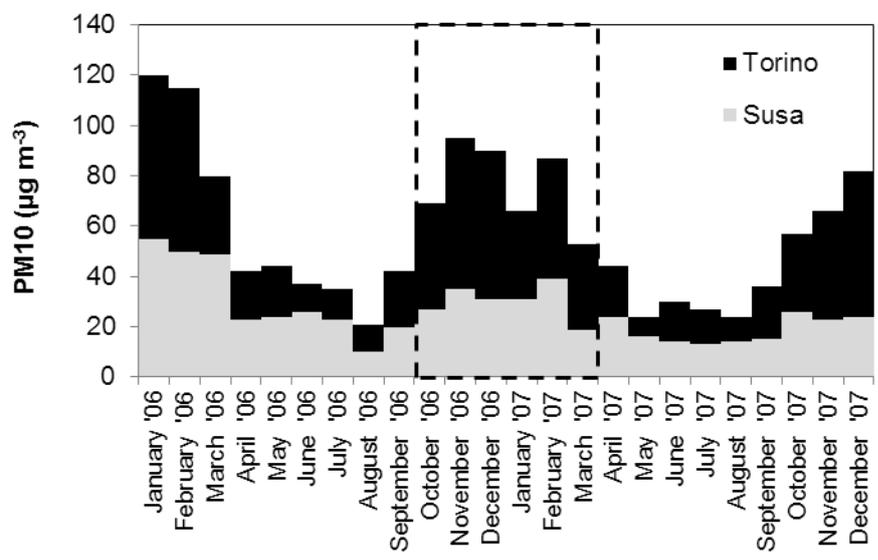|	PM$_{wb}$	OC$_{wb}$	EC$_{wb}$
	min - max	min - max	min - max
Torino	9% - 19%	22% - 37%	10% - 29%
Susa	20% - 55%	41% - 90%	20% - 49%

Figure captions

Figure 1: Sampling sites.

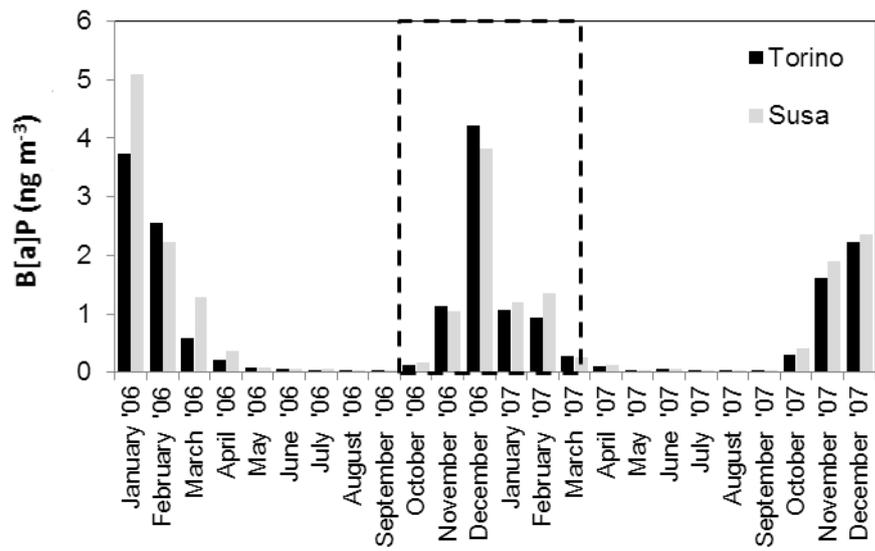Figure 2: Monthly trends for concentrations of PM10.

Figure 3: Monthly trends for concentrations of B[a]P.
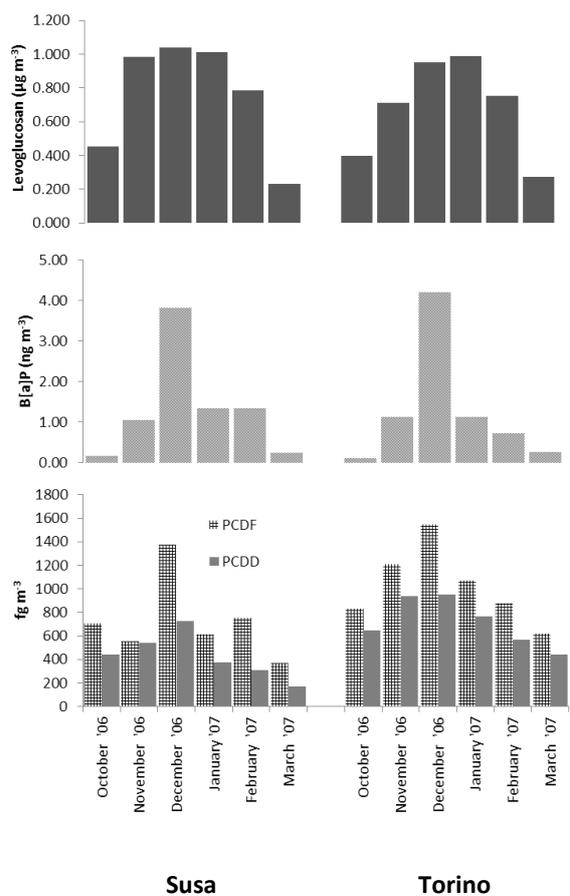
Figure 4: Monthly concentrations of LG, B[a]P and PCDDs/Fs.

Figure 5: <mark>Monthly concentrations</mark> of the 2,3,7,8-chlorinated PCDD/Fs in Susa (S) and Torino

(T).

Figure 6: Biplot in PC1 – PC2 space (S: Susa PM sample - T: Torino PM sample).

Figure 7: Score plot for the comparison of the 2,3,7,8-fingerprints.

Supporting Information

Table S1: Mean monthly concentrations of B[a]P, PCDDs and PCDFs in Susa (S) and Torino (T) ambient air in the October 2006 – March 2007 period.

Table S2: Emission ratio for wood burning source obtained by PMF (Bernardoni et al., 2011).

Figure S1: Mean percentage chemical composition of PM in the October 2006 – March 2007 period.

Figure S2: Monthly concentrations of K^+ and LG together with their ratio.

Figure S3: Monthly trends for LG-C/OC ratio.

Figure S4: Monthly trends for B[a]P-C to LG-C ratio.

Figure S5: Mean 2,3,7,8-fingerprints determined for Torino and Susa.

Figure captions

Figure 1: Sampling sites.

Figure 2: Monthly trends for concentrations of PM10.

Figure 3: Monthly trends for concentrations of B[a]P.

Figure 4: Monthly concentrations of LG, B[a]P and PCDDs/Fs.
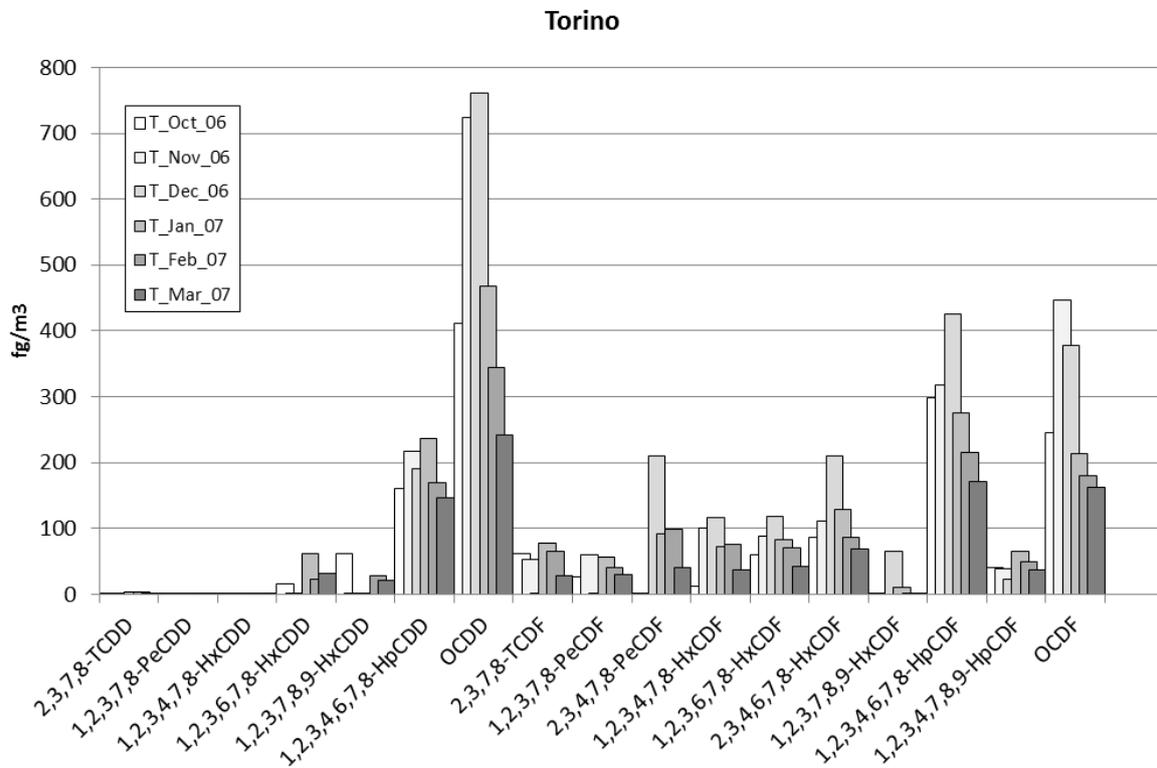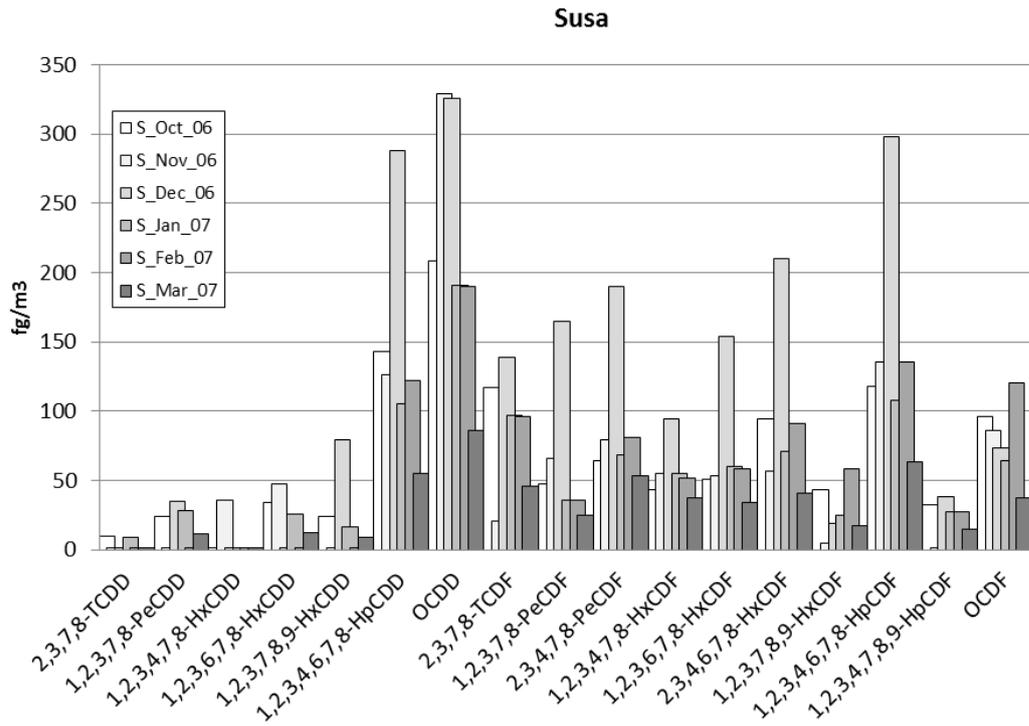
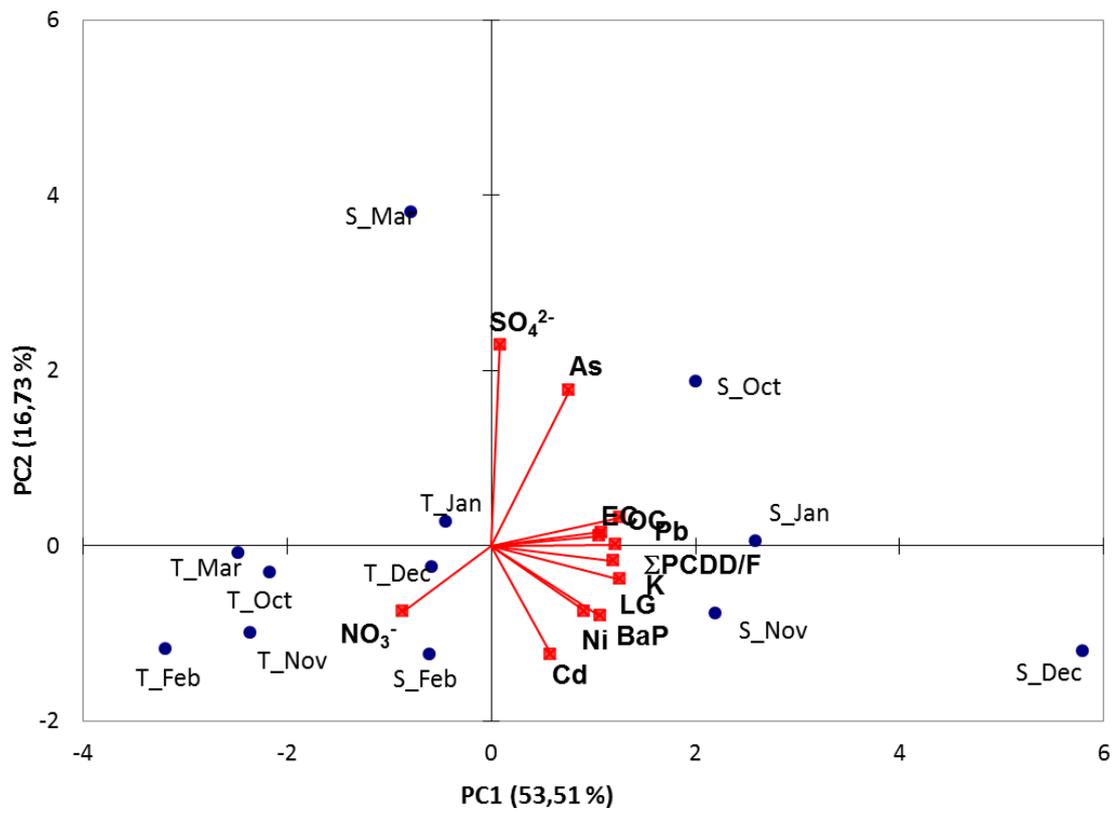Figure 5: Monthly concentrations of the 2,3,7,8-chlorinated PCDD/Fs in Susa (S) and Torino

(T).

Figure 6: Biplot in PC1 – PC2 space (S: Susa PM sample - T: Torino PM sample).

Figure 7: Score plot for the comparison of the 2,3,7,8-fingerprints.

Figure 1: Sampling sites.

Figure 2: Monthly trends for concentrations of PM10.

Figure 3: Monthly trends for concentrations of B[a]P.

Figure 4: Monthly concentrations of LG, B[a]P and PCDDs/Fs.

Figure 5: Monthly concentrations of the 2,3,7,8-chlorinated PCDD/Fs in Susa (S) and Torino (T).

Figure 6: Biplot in PC1 – PC2 space (S: Susa PM sample - T: Torino PM sample).
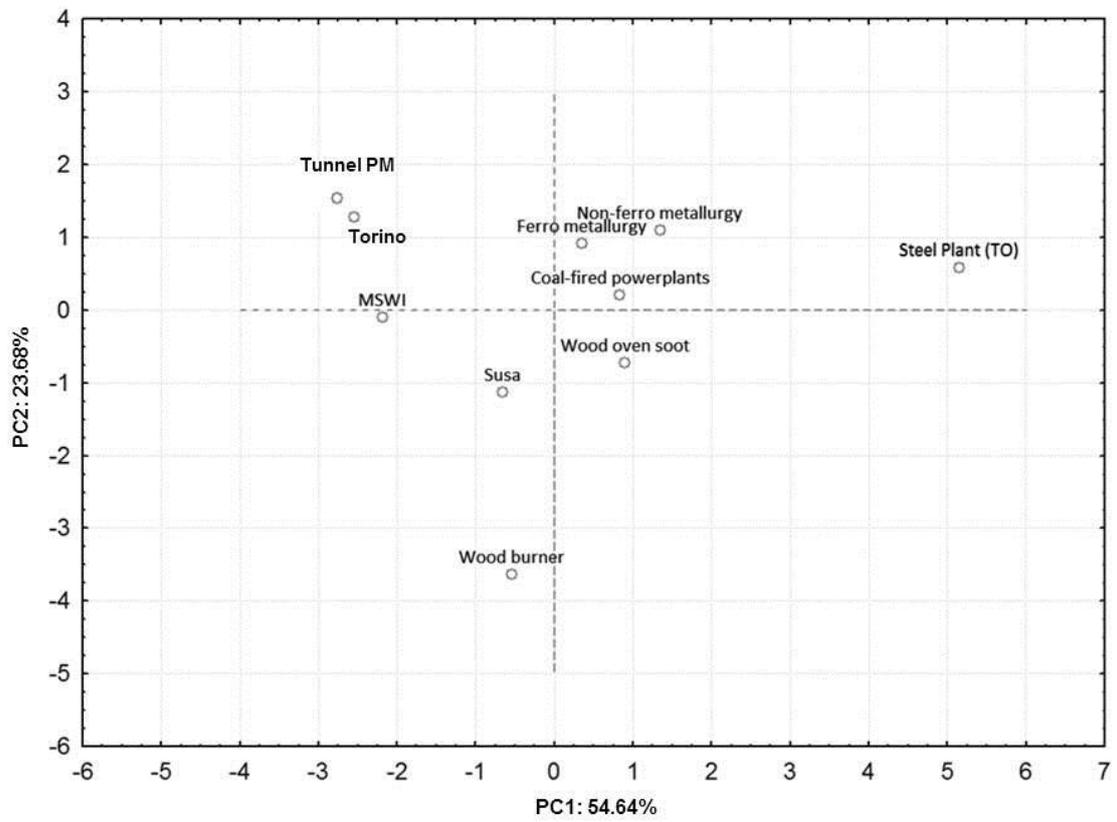
Figure 7: Score plot for the comparison of the 2,3,7,8-fingerprints.

Supporting Information:

Table S1: Mean monthly concentrations of B[a]P, PCDDs and PCDFs in Susa (S) and Torino (T) ambient air in the October 2006 – March 2007 period.

Table S2: Emission ratio for wood burning source obtained by PMF (Bernardoni et al., 2011).

Figure S1: Mean percentage chemical composition of PM in the October 2006 – March 2007 period.

Figure S2: Monthly trends for LG-C/OC ratio.

Figure S3: Monthly concentrations of K^+ and LG together with their ratio.

Figure S4: Monthly trends for B[a]P-C to LG-C ratio.

Figure S5: Mean 2,3,7,8-fingerprints determined for Torino and Susa.

Table S1: Mean monthly concentrations of B[a]P, PCDDs and PCDFs in Susa (S) and Torino (T) ambient air in the October 2006 – March 2007 period.

	Benzo(a)pyrene
Sample	ng/m^3
S_Oct 06	0.18
S_Nov 06	1.05
S_Dec 06	3.83
S_Jan 07	1.35
S_Feb 07	1.34
S_Mar 07	0.25
T_Oct 06	0.12
T_Nov 06	1.13
T_Dec 06	4.22
T_Jan 07	1.13
T_Feb 07	0.74
T_Mar 07	0.27

	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD
Sample	fg/m³	fg/m³	fg/m³	fg/m³	fg/m³	fg/m³	fg/m³
S_Oct 06	10	24	< LOD	34	24	143	208
S_Nov 06	< LOD	< LOD	36	47	< LOD	126	329
S_Dec 06	< LOD	35	< LOD	< LOD	79	288	326
S_Jan 07	9	28	< LOD	26	16	105	191
S_Feb 07	< LOD	< LOD	< LOD	< LOD	0	122	190
S_Mar 07	< LOD	11	< LOD	12	9	55	86
T_Oct 06	< LOD	< LOD	< LOD	16	62	160	411
T_Nov 06	< LOD	< LOD	< LOD	< LOD	< LOD	217	724
T_Dec 06	< LOD	< LOD	< LOD	< LOD	< LOD	190	761
T_Jan 07	3	< LOD	< LOD	61	0	237	467
T_Feb 07	4	< LOD	< LOD	23	28	170	345
T_Mar 07	< LOD	< LOD	< LOD	31	21	147	242

Sample	2,3,7,8-TCDF fg/m³	1,2,3,7,8-PeCDF fg/m³	2,3,4,7,8-PeCDF fg/m³	1,2,3,4,7,8-HxCDF fg/m³	1,2,3,6,7,8-HxCDF fg/m³	2,3,4,6,7,8-HxCDF fg/m³	1,2,3,7,8,9-HxCDF fg/m³	1,2,3,4,6,7,8-HpCDF fg/m³	1,2,3,4,7,8,9-HpCDF fg/m³	OCDF fg/m³
S_Oct 06	117	47	64	43	51	94	43	118	32	96
S_Nov 06	21	66	79	55	53	57	5	135	< LOD	86
S_Dec 06	139	165	190	94	154	210	19	298	38	73
S_Jan 07	97	36	68	55	60	71	25	108	27	64
S_Feb 07	95	36	81	52	58	91	58	135	27	120
S_Mar 07	46	25	53	37	34	41	17	63	15	37
T_Oct 06	61	26	< LOD	12	59	87	< LOD	299	41	245
T_Nov 06	53	59	< LOD	101	89	111	< LOD	317	38	446
T_Dec 06	< LOD	< LOD	210	117	118	210	65	425	23	377
T_Jan 07	78	57	91	72	83	128	11	275	66	213
T_Feb 07	65	41	99	75	70	87	< LOD	216	49	180
T_Mar 07	28	30	40	37	42	69	< LOD	172	37	163

1   Table S2: Emission ratio for wood burning source obtained by PMF (Bernardoni et al., 2011).

2

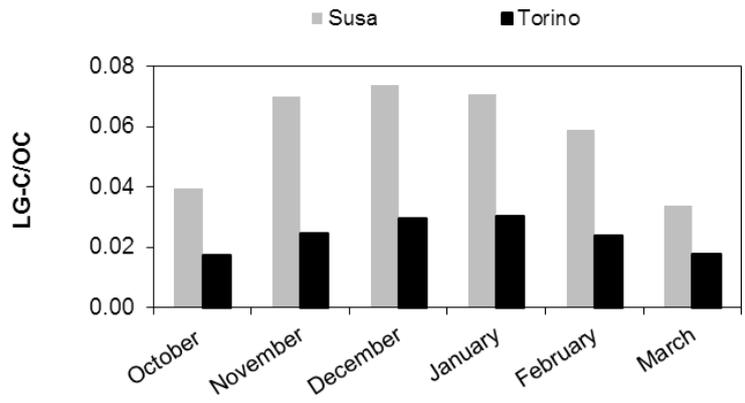|	**Emission ratio**
Site	Milano
Number of samples	180
LG/PM	0.059
LG-C/OC	0.082
LG/MN	10.2
OC/EC	5.5

3

1
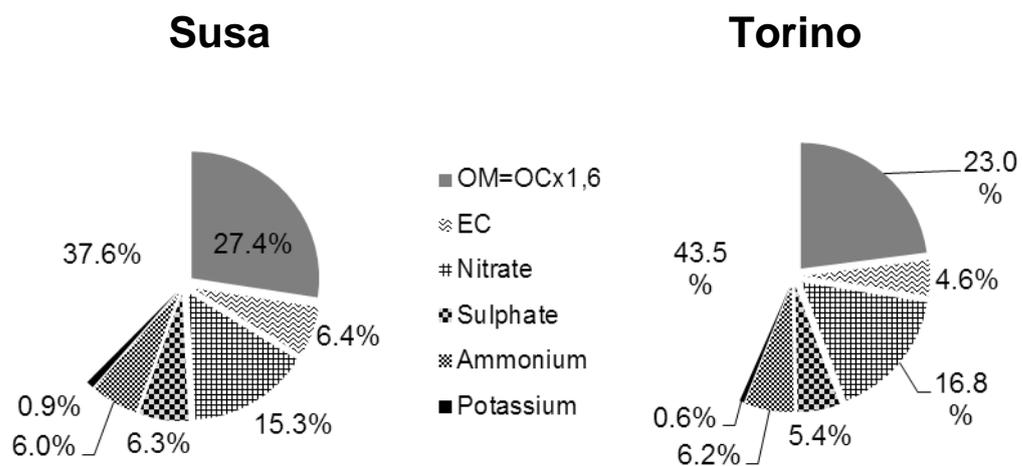
2

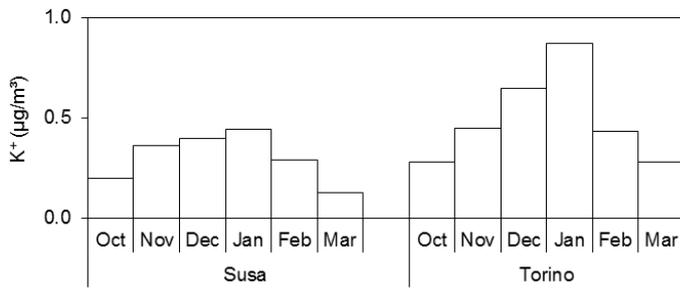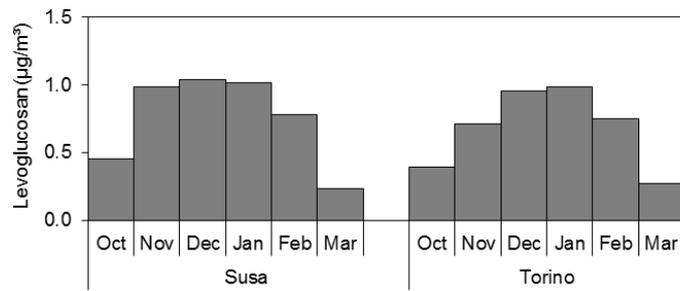3   Figure S1: Percentage chemical composition of PM.

4

1

2

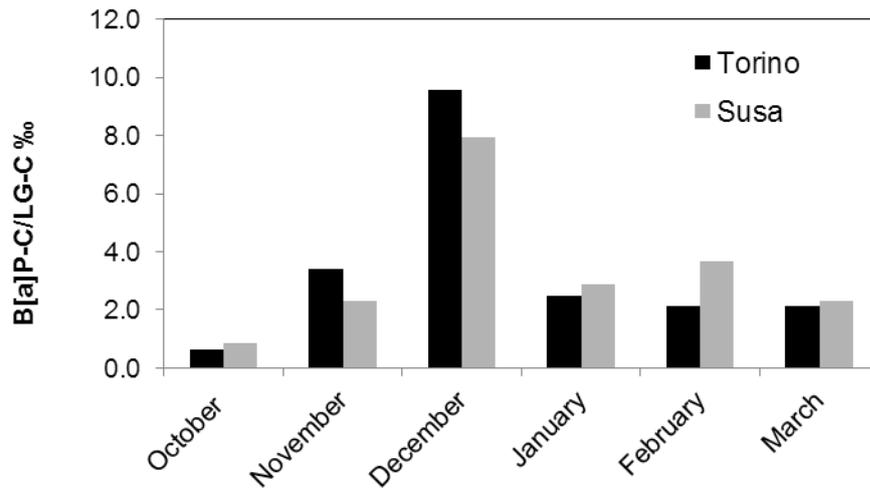3   Figure S2: Monthly trends for LG-C/OC ratio.

4

1

2

3
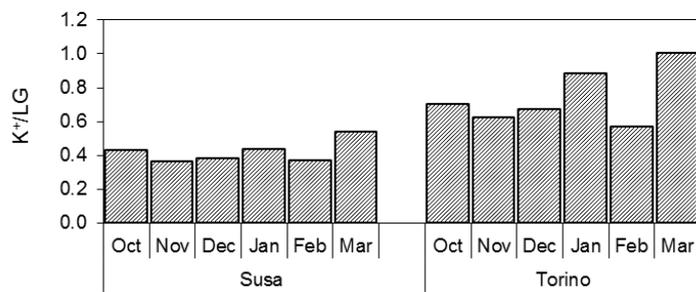
4

5

6   Figure S3: Monthly concentrations of K$^+$ and LG together with their ratio.
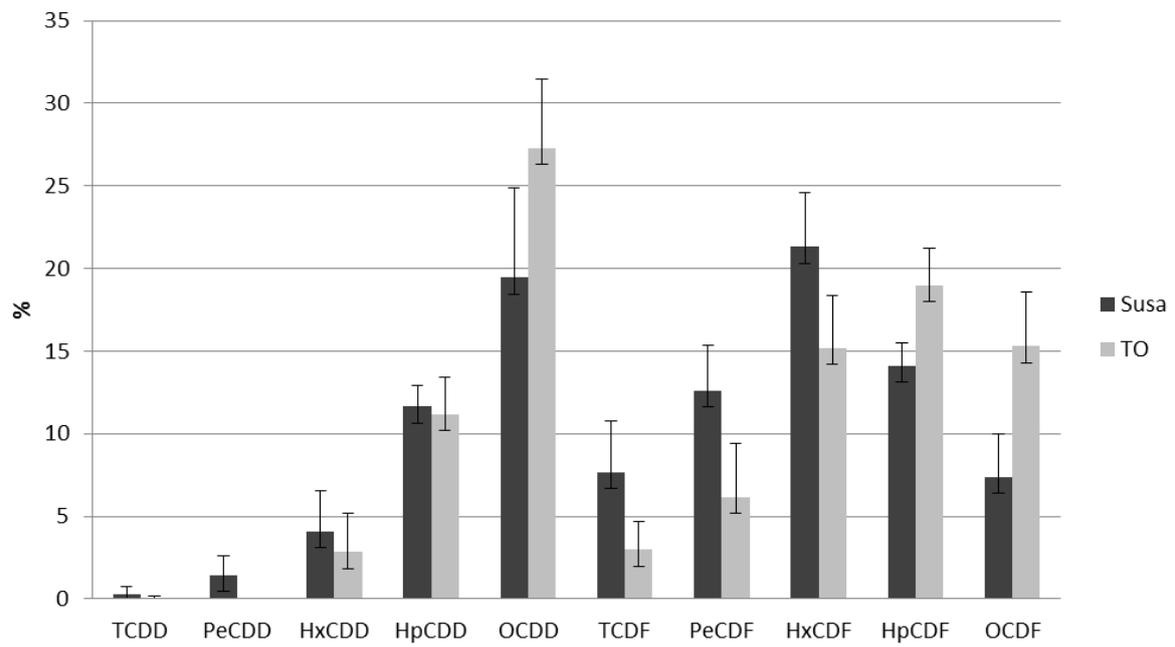
7

1

2

3   Figure S4: Monthly trends for B[a]P-C to LG-C ratio.

4

1

2

3 Figure S5: Mean 2,3,7,8-fingerprints determined for Torino and Susa.

4