Particulate polycyclic aromatic hydrocarbons and *n*-alkanes in recycled paper processing operations

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Abstract

The aliphatic and polycyclic aromatic fractions of dust collected in the vicinity of recycled paper processing operations were analyzed using gas chromatography/mass spectrometry. Total measured dust concentration (up to 8.73 ± 2.02 mg/m^3) fluctuated substantially in the different steps of paper manufacture. This was attributed to the type of the operation such as, the release of fibers and particles during paper cutting and the use of reactive chemicals and excessive water under high temperature and pressure during the bleaching and the water rinsing/drying step. Particulate polycyclic aromatic hydrocarbons (PAHs) (from fluorene to benzo[*ghi*]perylene with mean concentrations from 3.8 ± 0.5 to 41.4 ± 0.4 ng/m^3) and the unresolved mixture of branched, cyclic and unsaturated hydrocarbons (UCM) were measured in all samples while, *n*-alkanes from *n*-C$_{20}$ to *n*-C$_{27}$, were only observed in cutting and packaging areas (from 180.6 ± 18.9 to 4297.9 ± 794.9 ng/m^3). The profile of occupational PAHs in bleaching and treatment of contaminated recycled raw paper was comparable to that observed for anthropogenic activities. The values of molecular diagnostic ratios indicated the contribution of oil residues and emissions from worklifts and other equipment used for pulp and paper handling. Total benzo[*a*]pyrene-equivalent (BaP) concentrations of particulate PAHs (varied from 323 up to 1104 pg/m^3), provided evidence that workers were exposed to high quantities of PAHs as compared with exposures to urban air and other indoor settings, posing long-term threat to their health.

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1. Introduction

Exposure to chemical agents in the paper industry is associated with various health outcomes such as lung injuries and eventually mortality and morbidity [1–6]. Occupational exposure and epidemiological studies showed that inhalation of dust (paper and soft-paper) and chlorine compounds seriously affect lung function, exacerbate allergic asthma [7] and reactive airways dysfunction syndrome [1,2,8]. Increased mortality rates due to ischaemic heart diseases are also found to be associated with exposures to sulfur compounds [5]. This is caused by the penetration of chemical species and dust into the pulmonary alveoli to induce inflammatory responses or deteriorate organism's immune system [9,10]. Pulp and paper mill workers are exposed to a mixture of irritant gases and dust including organic solvents (e.g. isopropanol) and compounds (e.g. formaldehyde, biphenyl and polychlorinated biphenyls), minerals (e.g. asbestos) and fibers, inorganic gases (e.g. ammonia and chlorine), heavy metals (e.g. copper and chromium) and bioaerosols (e.g. fungal spores and endotoxins).

Paper production includes several steps (departments) such as pulp preparation, bleaching and refining, formation of paper sheet, coating and drying and cutting and packaging. The breaking up of contaminated recycled material containing cellulose fibers utilizes several chemicals (e.g. caustic soda, ammonia and lime), high temperatures and pressures to form the pulp. Bleaching and refining using chlorine, chlorine oxide, hydrogen peroxide and other chemicals are also critical steps to remove residues from the pulp and produce high-quality white paper. The material is then rinsed with water and chemical additives (e.g. clay), spread on a porous surface and dried using a hydraulic press to form the sheet of paper. Afterwards, sheet goes through a section of heated cylinders to dry and polish

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paper, which subsequently is collected in rolls. Further treatment of the paper rolls include supplementary smoothing and polishing, decorating with patterns, cutting into smaller pieces and preparation of the household products. The use of excessive heat, pressure and reactive chemicals during paper production results in the formation/emissions of inorganic and organic by-products (e.g. PAHs, dioxins and polychlorinated biphenyls) that can pose significant threat to employees' health. In addition, the use of large quantities of water eventually increases the aerosol-bound water content into the occupational settings [11,12].

The findings of the International Agency for Research in Cancer (IARC) epidemiological study of pulp and paper industry on workers showed that exceedances of the threshold limit values (TLV) of the American Conference of Governmental Industrial Hygienist (ACGIH) [13] were frequently measured for a wide variety of chemical agents used [14]. For instance, carbon monoxide highest concentrations measured in fine, coated paper and on-machine coating departments were up to 14 orders of magnitude higher than the corresponding TLV. The highest dust concentration, a common pollutant in all paper making departments, was measured in winding and paper cutting sections and the concentrations were regularly higher than the TLV (10 mg/m^3 for total dust and 5 mg/m^3 for respirable dust) [13,14]. Up-to-date, most of studies focused in the characterization of non-solvent organic compounds including a limited number of studies on organochlorine and polychlorinated dibenzo-dioxins and furans (PCDD/Fs). On the contrary, there are insufficient data on organic by-products such as PAHs that have been associated with significant cancer risk to humans even at very low concentration levels (in the order of pg/m^3) [15,16].

The objectives of this study were: (i) the determination of the chemical pattern of particulate PAHs and aliphatic hydrocarbons in paper processing departments; (ii) the use of molecular concentration ratios such as carbon preference index (CPI) [17], wax *n*-alkanes (%WNA) content [18], "*unresolved complex mixture*" content to *n*-alkanes content (UCM/NA) [18], *odd-to-even* predominance (OEP) [19,20] and PAHs concentration diagnostic ratios [21] to reconcile the presence of *n*-alkanes and PAHs in occupational aerosols and to compare them with those from other possible sources; (iii) the investigation of the variation of their concentrations in different paper processing departments; (iv) the evaluation of health-related risk by estimating the benzo[*a*]pyrene-equivalents (BaP) for PAHs [16,22]. For the needs of this study, area samples were collected in order to monitor the levels and identify the sources of dust and PAHs in specific departments. They do not represent the actual personal exposures because workers are interacting with different indoor (e.g. office and smoking areas) and outdoor microenvironments during their shifts. The results of this study, can be eventually used by the scientific community, industries and regulatory authorities and agencies to identify the sources of contaminants, design and apply operative and targeted exposure studies, evaluate the impact of occupational dust and PAHs in different departments on personal exposures and thus, utilize effective control measures.
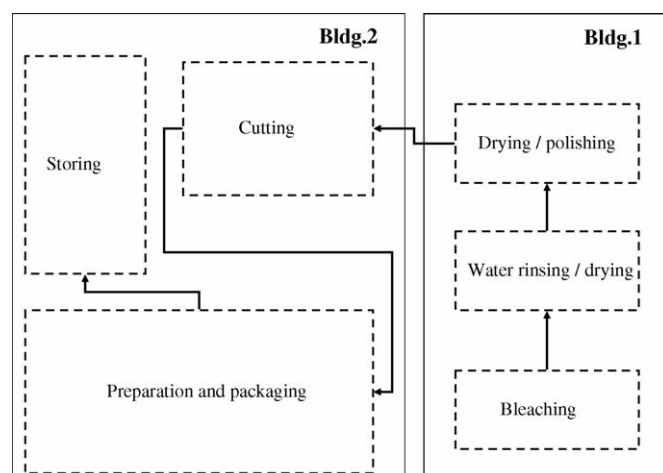

Fig. 1. The layout and process diagram of the paper processing departments.

2. Materials and methods

2.1. Site description and sampling

Aerosol sampling was conducted in all departments of a paper processing facility, located in Athens, Greece. A layout of the operations and departments of the facility including the production flow is depicted in Fig. 1. A total of (30) 24-h samples were collected in bleaching (*n* = 4), water rinsing/drying (*n* = 4), drying/polishing (*n* = 4), cutting (*n* = 4), preparation and packaging (*n* = 10) and storing (*n* = 4). A central air circulation system is used to maintain constant microenvironmental (e.g. temperature) conditions during working hours. Samplers were installed in the vicinity of (no more than 3 m) the aforementioned operations, approximately at 1.5 m height and at least 2.0 m away from long vertical surfaces (e.g. walls) and air conditioning inlets and outlets (Fig. 2). Total dust was collected on 37-mm Whatman Teflon (PTFE) filters with porous size of 2 μm, having collection efficiency higher than 99.999% for particles with radius larger than 0.3 μm (Fig. 2). Each filter was attached to a single elutriator (5.00 cm [L] × 0.37 cm [i.d.]) to minimize the effect of wind (due to the air circulation system) and the entrainment

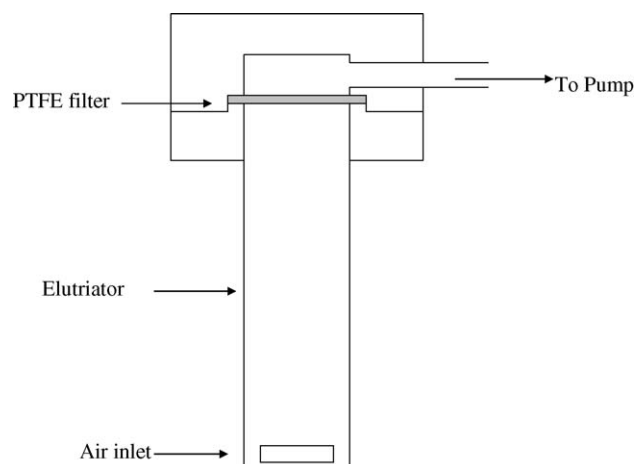Fig. 2. The schematic of the sampler.

of large (with radius higher than 150 μm) airborne material (Fig. 2). Flow rate was measured at the beginning and at the end of the sampling using pre-calibrated rotameters. After collection, filters were placed in dedicated petridishes and wrapped with aluminium foil to avoid contamination and photochemical transformations.

2.2. Mass measurements and chemical analysis

Particle mass was determined by gravimetric analysis (Mettler MX-5, Switzerland). Pre- and post-sampling weighing of Teflon filters has been done after 48-h conditioning at controlled temperature ($20 \pm 1\,^{\circ}C$) and relative humidity ($40 \pm 5\%$). Laboratory and field blank filters were used to evaluate possible contamination during handling and weighing. Each filter was weighed at least three times.

For the determination of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs), Teflon filters (TFs) were extracted by sonication with 10 ml of methylene chloride for 1 h. The organic extract was concentrated under rotary evaporation transferred to a 1.8 ml vial and dried under a gentle stream of nitrogen. Disposable Pasteur pipettes were packed with glass wool and 0.250 g of pre-cleaned silica gel and activated at 120 °C overnight. Prior use, the activated silica gel was washed with 5.0 ml of *n*-hexane. The organic extract was diluted in 300 μl of hexane and placed on the top of the silica gel. Aliphatic and PAHs were co-eluted with 1.2 ml *n*-hexane (fraction F1, aliphatics) and 1.5 ml of *n*-hexane/toluene (50:50, v/v) (fraction F2, PAHs and alkyl-PAHs), respectively. The fractions were concentrated using gentle nitrogen flow and transferred to GC–MS insert containing vials with 250 μl *n*-hexane. The individual fractions were spiked with internal standards: 1-chlorohexadecane for F1 and chloro-triphenyl methane for F2, before analysis for the quantification of the compounds.

All samples were analyzed on a Varian STAR 3400 gas chromatography (GC) coupled with Varian SATURN 2000 ion trap mass spectrometer in electron mode and 8200 autosampler. The GC system was equipped with a VF-5MS capillary column (Varian, Factor Four; 50 m × 0.21 mm i.d. × 0.25 μm film thickness) and split/splitless 1078 injector. The carrier gas was helium with a flow rate of 1 ml/min. The temperature ramp was splitless injection at 290 °C, oven temperature held at 70 °C for 1 min, temperature increased to 160 °C at a rate of 7.5 °C/min with holding time of 1 min, increased to 290 °C at a rate of 10 °C/min and column held at 290 °C for 30 min. Full scan mode and ion preparation method using the selected ion storage (SIS) mode were applied to detect *n*-alkanes and PAHs, respectively. The ion trap was kept at 150 °C and operated under electron ionization mode using automatic gain control (AGC), with a TIC target of 20.000 for full scan and 5.000 for SIS mode, the filament emission current being set at 20 μA and electron multiplier voltage at 1750 V. The SIS mode parameters were optimized with ionization storage level of 48 *m/z* and maximum ionization time of 55.000 μs.

High-purity solvents (hexane, toluene and methylene chloride) (SupraSolv grade) and silica gel (70–230 mesh) were purchased from Merck (Darmstadt, Germany). *n*-Alkanes and PAHs standards were obtained from ChemService (USA). Thirty-seven millimeter Teflon filters from Whatman were used. Silica gel and glass wool were pre-extracted in a Soxhlet apparatus overnight and kept dry until use. Glassware was baked for 12 h at 550 °C and kept in dessicators until use. Reference *n*-alkanes (39.1–196.7 ng/μl) and PAHs solutions (8–35 ng/μl) were prepared to evaluate the detection limits and linearity of the method. Filter background and possible contamination during handling and transport from/to the sampling sites were negligible for PAHs and *n*-alkanes. Analysis of spiked filters showed that recoveries varied from 70.2 up to 93.7% for the identified compounds.

2.3. Molecular diagnostic ratios

The molecular diagnostic ratios were calculated to obtain more information about the characteristics of aliphatic hydrocarbons and PAHs, since the distribution of homologues is strongly associated with formation mechanisms of carbonaceous aerosol. In particular, the following diagnostic ratios were estimated:

- The carbon preference index for *n*-alkanes (ratio *odd-to-even*) was calculated as follows [17]:

$$CPI = \frac{\sum(C_{21} - C_{27})}{\sum(C_{22} - C_{28})}$$

n-Alkanes with biogenic (natural) and environmental tobacco smoke (ETS) origin exhibit a strong odd-to-even predominance and thus, high values of CPI (CPI $\gg$ 1). On the other hand, *n*-alkanes originated from high-temperature combustion of fossil fuels and other anthropogenic activities are close to unit (CPI $\sim$ 1).

- The percentage biogenic "*wax*" content of *n*-alkanes (%WNA-C_n) was calculated as follows [18]:

$$\%WNA\text{-}C_n = \left(1 - \frac{0.5(C_{n-1} + C_{n+1})}{C_n}\right) \times 100$$

Based on the differences in *n*-alkanes profiles from biogenic and anthropogenic sources, the contribution of biogenic sources on *n*-alkane concentration was calculated and therefore, the input of possible biogenic sources is evaluated. Negative values of %WNA-C_n were taken as zero.

- Running *odd-to-even* predominance ratios were computed using the following equation [19]:

$$OEP\,\text{running-ratio for}\,C_n = \left(\frac{C_{n-2} + 6C_n + C_{n+2}}{4(C_{n-1} + C_{n+1})}\right)^{(-1)^{n-1}}$$

OEP values were plotted against the carbon chain length to construct the OEP curves. The pattern of OEP curve depends upon the origin of *n*-alkanes (e.g. ETS, higher terrestrial plant epicuticular waxes and gasoline combustion) and thus provides evidence about the source of alkanes [19–23].

- The ratio of total concentration of nine combustion PAH (CPAH) (fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzofluoranthenes, benzo[a]pyrene, benzo[e]pyrene, indeno[123-cd]pyrene and benzo[ghi]perylene) to the total PAHs concentration (TPAHs) (CPAHs/TPAHs) was determined. Rogge et al. [24] calculated the value of CPAHs/TPAHs ratio for non-catalyst (0.41) and catalyst-equipped (0.51) automobiles and for heavy duty diesel trucks (0.30). Other PAHs concentration diagnostic ratios included:

- methyl-phenanthrenes to phenanthrene: (MP/P);
- benzo[a]anthracene to (benzo[a]anthracene and chrysene/triphenylene): [BaA/(BaA + CT);
- benzo[e]pyrene to (benzo[e]pyrene and benzo[a]pyrene): [BeP/(BeP + BaP)];
- fluoranthene to (fluoranthene and pyrene): [Fl/(Fl + Py)];
- indeno[123-cd]pyreneto to (indeno[123-cd]pyrene and benzo[ghi]perylene): [IP/(IP + BgP)].

In addition, the ratio of the sum of eight carcinogenic PAHs: (benzo[a]anthracene, chrysene, benzo[b/k]fluoranthenes, benzo[a]pyrene, dibenzo[ah]anthracene, benzo[ghi]perylene and indeno[123-cd]pyrene) concentrations to the TPAHs concentrations to evaluate the carcinogenic content of occupational PAHs [25].

3. Results and discussion

3.1. Concentration levels and homologues distribution

Mean concentrations for total dust, PAHs and n-alkanes, the abundant PAH and the molecular diagnostic ratios of specific compounds are reported in Table 1. For aliphatic hydrocarbons, the homologues range (C_m–C_n), the homologue with the highest concentration ($C_{n, max}$), the molecular diagnostic ratios such as carbon preference index, the ratio of unresolved complex mixture to total n-alkanes and the percentage "wax" n-alkane contribution are also presented in Table 1.

Total dust concentrations were 1.79 ± 0.80 mg/m^3 in bleaching, 4.24 ± 2.53 mg/m^3 in spraying/drying, 0.51 ± 0.06 mg/m^3 in drying, 8.73 ± 2.02 mg/m^3 in paper cutting, 0.57 ± 0.12 and 0.59 ± 0.04 mg/m^3 in preparation and packaging and finally, 0.64 ± 0.11 mg/m^3 in packaging and storing departments (Table 1). Although the dust concentration levels varied significantly for different departments, they were lower than the 2003-TLV concentration of 10 mg/m^3 [13]. The TLV for total dust set by the ACGIH has been adopted by European Union and National legislations which reported also enforceable occupational exposure limits (OEL) for nearly 600 chemicals including a limited number of PAHs [26,27]. Although, there are no 24-h and annual limits for total dust in ambient air, total dust concentrations were substantially higher than the PM$_{10}$ (particles with aerodynamic diameter less than 10 μm) standards set by the European Union (EU) (50 μg/m^3 for daily average) and the U.S. Environmental Protection Agency (EPA) (150 μg/m^3 for daily average) [28,29]. Up-to-date, there are no limits for ambient concentrations of PAHs and other organic compounds. Based on previous studies, personal exposure during the working hours accounted for about 15–70% of the total dust collected on a 24-h basis, thus, workers in paper processing departments were exposed to approximately up to 6.45 mg/m^3.

The observed concentrations were comparable to those previously obtained in 75 pulp and paper mills at 15 countries (pulp-

Table 1

Mean (±standard error) dust concentrations, PAH concentrations and diagnostic molecular ratios and n-alkanes concentrations, homologue ranges (C_m–C_n), homologues with the maximum concentration ($C_{n, max}$) and molecular diagnostic ratios

	Bleaching	Spraying/drying	Drying/polishing	Cutting	Packaging	Packaging	Packaging/storage
Dust (in μg/m^3)	1793.5 ± 801.5	4243.6 ± 2529.5	508.6 ± 65.6	8731.0 ± 2026.0	568.6 ± 1	591.2 ± 41.5	645.8 ± 115.2
(i) Polycyclic aromatic hydrocarbons							
Abundant PAH	Benzo[b/k]-fluoranthene	Benzo[b/k]-fluoranthene	Benzo[b/k]-fluoranthene	Dimethyl-phenanthrenes	Benzo[b/k]-fluoranthene	Benzo[b/k]-fluoranthene	Benzo[b/k]-fluoranthene
Concentration (in ng/m^3)	5.1 ± 1.1	6.4 ± 1.6	3.8 ± 0.5	41.4 ± 0.4	9.5 ± 1.6	10.8 ± 0.4	18.3 ± 0.9
CPAHs/TPAHs[a]	0.64 ± 0.05	0.70 ± 0.07	0.79 ± 0.04	0.47 ± 0.02	0.81 ± 0.04	0.73 ± 0.02	0.78 ± 0.01
MP/P[a]	1.56 ± 0.16	1.11 ± 0.12	0.98 ± 0.03	1.50 ± 0.08	0.89 ± 0.10	1.49 ± 0.19	0.88 ± 0.15
BaA/(BaA + CT)[a]	0.21 ± 0.03	0.32 ± 0.08	0.27 ± 0.01	0.31 ± 0.01	0.33 ± 0.04	0.34 ± 0.03	0.25 ± 0.01
BeP/(BaP + BeP)[a]	0.67 ± 0.06	0.65 ± 0.03	0.73 ± 0.08	0.75 ± 0.01	0.83 ± 0.04	0.79 ± 0.02	0.75 ± 0.01
Fl/(Fl + Py)[a]	0.48 ± 0.01	0.51 ± 0.01	0.53 ± 0.05	0.42 ± 0.01	0.42 ± 0.03	0.37 ± 0.01	0.50 ± 0.01
IP/(IP + BgP)[a]	0.28 ± 0.05	0.30 ± 0.05	0.36 ± 0.10	0.42 ± 0.01	0.52 ± 0.01	0.51 ± 0.03	0.48 ± 0.06
(ii) Aliphatic hydrocarbons							
C_m–C_n	–	–	–	C_{20}–C_{27}	C_{20}–C_{27}	C_{20}–C_{27}	C_{20}–C_{27}
$C_{n, max}$	–	–	–	C_{22}	C_{23}	C_{24}	C_{22}
Concentration (in ng/m^3)	–	–	–	4297.9 ± 794.9	286.8 ± 65.3	180.6 ± 18.9	688.6 ± 141.4
UCM (in μg/m^3)	5.2 ± 0.9	5.7 ± 1.8	2.8 ± 1.2	229.7 ± 38.3	14.2 ± 3.7	7.1 ± 0.3	36.6 ± 9.0
CPI[b]	–	–	–	1.05 ± 0.01	0.96 ± 0.06	1.51 ± 0.64	1.13 ± 0.08
UCM/NA[b]	–	–	–	57.1 ± 19.5	49.6 ± 4.9	40.9 ± 4.6	55.2 ± 9.9
%WNA[b]	–	–	–	14.48	12.52	19.12	9.84

[a] MP/P, methyl-phenanthrenes to phenanthrene; BaA/(BaA + CT), benzo[a]anthracene to (benzo[a]anthracene and chrysene/triphenylene); BeP/(BaP + BeP), benzo[e]pyrene to (benzo[e]pyrene and benzo[a]pyrene); Fl/(Fl + Py), fluoranthene to (fluoranthene and pyrene); IP/(IP + BgP), indeno[123-cd]pyrene to (indeno[123-cd]pyrene and benzo[ghi]perylene).

[b] CPI, carbon preference index; %WNA content, leaf wax n-alkanes; UCM, unresolved complex mixture; NA, total n-alkanes concentration.

ing and refining, 0.37 mg/m^3; fine and coated paper machines, 1.7 mg/m^3; soft and tissue paper machines, 8.6 mg/m^3; winding, cutting and grading, 4.3 mg/m^3) [14]. The highest concentration was measured in the paper cutting department followed by spraying/drying and bleaching areas (Table 1) compared to those measured in other departments. This variation reflected differences in emission sources and processes [14], such as the generation of large amounts of paper dust and fibers at cutting machines and increased paper fibers and aerosol-bound water content during bleaching and spraying. For example, based on model calculations [30] aerosol-bound water at 50% RH can vary between 20 and 35% of fine particulate matter. Occupational dust concentrations were comparable to those measured in indoor smoking environments [23] but substantially lower than those determined in indoor non-smoking public buildings and outdoors [23,31,32].

Parent and methyl-PAHs from fluorene (MW 166) to benzo[*ghi*]perylene (MW 276) were detected in all samples. A typical gas chromatogram of the aromatic fraction is illustrated in Fig. 3a while details of methyl- and dimethyl-phenanthrene
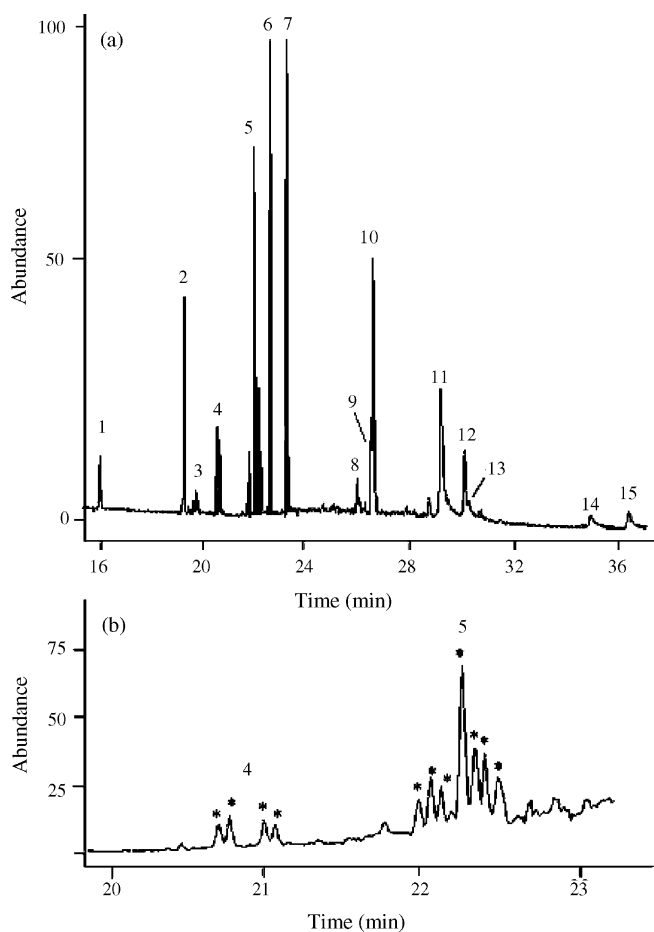

Fig. 3. Characteristic gas chromatograms of (a) PAHs: (1) fluorene, (2) phenanthrane, (3) anthracene, (4) methylphenanthrane, (5) dimethylphenanthrane, (6) fluoranthene, (7) pyrene, (8) 4-H-cyclopenta[*cd*]pyrene, (9) benzo[*a*]anthracene, (10) chrysene/triphenylene, (11) benzo[*b*/*j*/*k*]fluoranthene, (12) benzo[*e*]pyrene, (13) benzo[*a*]pyrene, (14) indeno[123-*cd*]pyrene and (15) benzo[*ghi*]perylene) and (b) substituted phenanthranes: (4) methylphenanthranes and (5) dimethylphenanthranes.

(DMP) isomers are shown in Fig. 3b. The most abundant PAHs in all samples was benzo[*b/k*]fluoranthene, with the exception of paper cutting department where DMPs accounted for almost 35% of total PAHs. Fig. 5a shows the percentage distribution of parent PAHs. For paper bleaching, spraying and drying departments, five-ring PAHs (benzofluoranthenes and benzopyrenes) were the predominant species (~50%) followed by low molecular weight (pyrene/fluoranthene, ~20% and fluorine, ~10%); heavy PAHs (benzo[*ghi*]perylene and indeno[123-*cd*]pyrene > 10%) (Fig. 5a). A similar profile was also observed for packaging and storing departments, which suggested the contribution of similar sources. On the contrary, for paper cutting department, four-ring PAHs (fluoranthene/pyrene) constituted almost 30% of non-substituted PAHs, while the contribution of five-ring PAHs was approximately 10% (Fig. 5a). As mentioned, the possible impact of petrogenic PAHs sources in this departments was also supported by the elevated levels of dimethylphenanthranes, a indicator of unburned fossil fuel contamination [33].

Total PAHs concentrations were 5.1 ± 1.1 ng/m^3 in bleaching, 6.4 ± 1.6 ng/m^3 in spraying/drying, 3.8 ± 0.5 ng/m^3 in drying, 41.4 ± 0.4 ng/m^3 in paper cutting, 9.5 ± 1.0 and 10.8 ± 0.4 ng/m^3 in preparation and packaging and finally, 18.3 ± 0.9 ng/m^3 in packaging and storing departments (Table 1). Despite the limited use of high-temperature combustion processes (e.g. furnaces) and hazardous chemicals (e.g. diesel, gasoline and tobacco smoke), total particulate PAHs concentration levels measured in this study were comparable to those measured in other working environments (e.g. carbon black manufacturing plants, 4.24–612.00 ng/m^3) [34]. Urban and background PAHs concentrations in the region [32] were lower than those measured in the paper processing departments. Furthermore, occupational PAHs concentrations were substantially higher than those measured in indoor non-smoking areas but lower that those estimated for indoor environments where smoking is allowed [23]. In all cases, concentration of individual particulate PAHs (e.g. naphthalene and benzo[*a*]pyrene) were lower than the existing OEL values (50 mg/m^3 for naphthalene and 0.005 mg/m^3 for benzo[*a*]pyrene) [26,27]. PAHs concentrations in paper production processes (bleaching, spraying, drying and polishing), suggested the release of small quantities of PAHs in comparison with the other departments (cutting and packaging) (Table 1). The use of worklifts, brake lining and oil residues may be the cause of high concentrations in paper cutting and packaging and storing departments.

The aliphatic fraction of occupational aerosol was comprised of *n*-alkanes and the unresolved complex mixture of cyclic, branched and unsaturated hydrocarbons (Fig. 4a and b). The latter is presented as a broad envelope of the baseline in the chromatograms (Fig. 4a) and it is a strong indication of oil residues and incomplete combustion by-products [35]. *n*-Alkanes were only detected in paper cutting packaging and storing areas (Fig. 5b), while UCM was determined in all departments providing evidence of minimal *n*-alkane formation and/or oil residue contamination during paper production. Particle-associated *n*-alkanes ranged from *n*-eicosane (C$_{20}$) to *n*-heptacosane (C$_{27}$) with maxima at *n*-C$_{22}$, *n*-C$_{23}$ and *n*-C$_{24}$
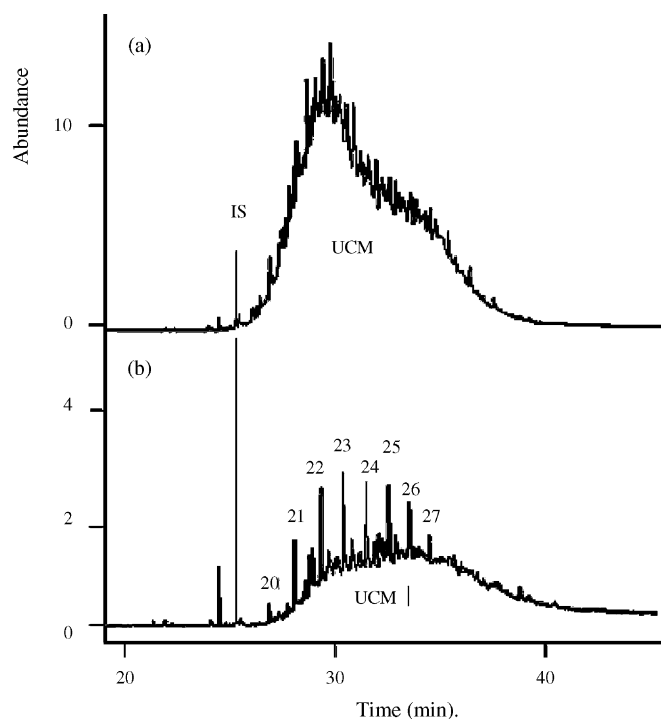
Fig. 4. (a and b) Characteristic gas chromatograms of the aliphatic fraction (IS, internal standard; UCM, unresolved complex mixture; 20–27, number of carbon atoms).

(Fig. 5b and Table 1) were detected in occupational aerosol. Total particulate *n*-alkane concentrations were $4297.9 \pm 794.9\,\text{ng/m}^3$ in cutting, 286.8 ± 65.3 and $286.8 \pm 18.9\,\text{ng/m}^3$ in packaging and $688.8 \pm 141.4\,\text{ng/m}^3$ in storing departments (Table 1). With the exception of paper cutting department, measured levels of particulate alkanes were somewhat lower than those measured in smoking environments [23,31], but noticeably higher compared to those determined in outdoor and indoor non-smoking areas [23,31,32]. The predominance of low molecular weight alkanes ($<C_{28}$) indicated the possible absence of biogenic sources, including environmental tobacco smoke (in compliance with safety regulations) [32,33] in all departments. High alkanes concentrations in the paper cutting area may be associated with emissions/contamination from worklifts and other machineries operated to move paper rolls from the production facility [14].

3.2. Source reconciliation

The distributions of homologues are strongly associated with formation mechanisms of carbonaceous aerosol, thus, molecular diagnostic ratios (combined with similar characteristics of organic species) have been successfully used to reconcile sources of particulate PAHs and aliphatic hydrocarbons [20,21,23,36–38]. Particularly, the mean CPAHs/TPAHs ratio of 0.47 ± 0.02 in paper cutting area (Table 1), attested that petrogenic PAHs from oil residues and fugitive emission were the most abundant. On the contrary, CPAHs/TPAHs values varied from 0.64 ± 0.05 to 0.81 ± 0.04 in other departments (Table 1) which pointed out the impact of high temperature combustion sources (e.g. worklifts, penetration of vehicle and truck
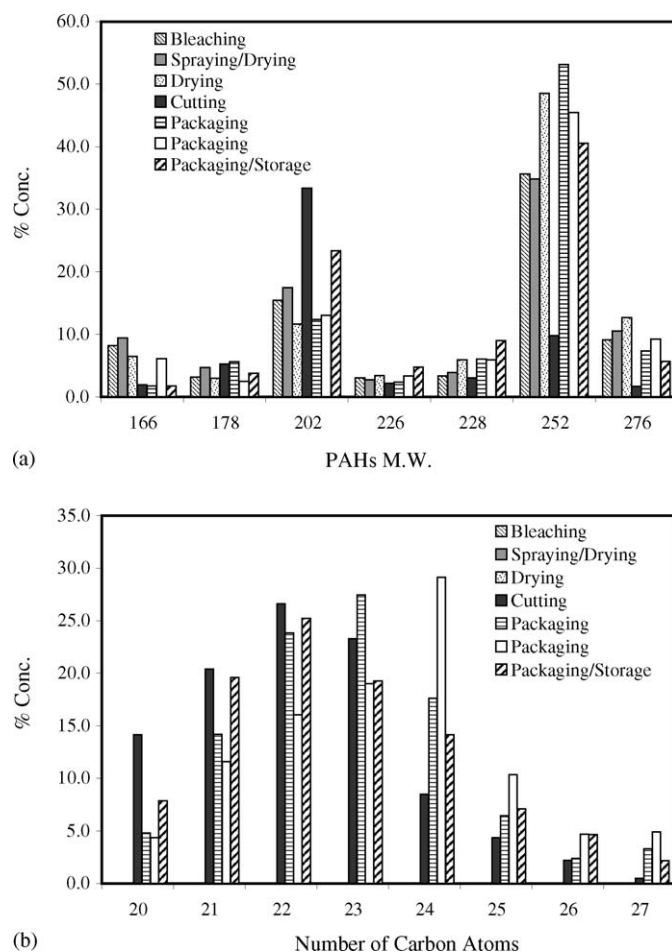

Fig. 5. Relative distributions of particulate PAH (a) and *n*-alkane (b) collected in different paper processing departments.

emissions). The chromatographic profiles of substituted phenanthranes provided also valuable information for the sources of PAHs [36–38]. Particularly, the ratio of 1-, 2-, 3- and 4/9-methylphenanthranes to the parent phenanthrene had mean values close to one (Fig. 3b and Table 1) which were indicative of the mixed origin from vehicular emissions (from worklifts and to a lesser extent from automobiles and heavy trucks) and unburned fossil fuels [38]. DMP profiles at all occupational samples demonstrated also an obvious contribution from anthropogenic sources with maxima at 2,6- and 1,3-, 2,10-, 3,9- and 3,10-dimethyl isomers (Fig. 3b) [36].

Other molecular diagnostic ratios were also considered to assess the characteristics of PAHs in the paper processing facilities. BaA/(BaA + Chr) mean ratio values (from 0.21 ± 0.03 to 0.34 ± 0.03) highlighted oil residues as a potential source of PAHs (Table 1) [23,39]. In addition [BeP/(BeP + BaP)] mean ratio values varied from 0.65 ± 0.03 to 0.83 ± 0.04 (Table 1) which noted the important contribution of PAHs from oil residues (Table 1). Mean Fl/(Fl + Py) ratio values ranged from 0.37 ± 0.01 to 0.53 ± 0.05 (Table 1) and [IP/(IP + BgP)] ratio values from 0.28 ± 0.05 to 0.52 ± 0.02 (Table 1) were comparable to those reported for traffic (gasoline combustion) emissions [23,38–40] (Table 1). Overall, a combined contribution of oil/diesel residues and combustion-related emissions were iden-

tified. Although PAHs are mostly by-products of the incomplete combustion of organic material (e.g. fossil fuels and tobacco), the emission of PAHs during the bleaching, spraying and drying processes is still possible due to the pooled use of highly reactive chemicals at high temperature and pressure. In paper cutting, packaging and storing departments, contamination from work-lifts and other gas- and diesel-powered machineries operated in the departments was the major source of PAHs.

No *odd-to-even* predominance was showed for the whole range of particulate *n*-alkanes in all departments (Fig. 5b) as it is expressed by the carbon preference index. Indeed, mean CPI values were close to unit (from 0.96 ± 0.06 to 1.51 ± 0.54) which underscored the contribution of manmade sources such as oil/diesel residues and gasoline emissions (Table 1). The strong anthropogenic input was further supported by high UCM/NA ratios (from 40.6 ± 4.6 to 55.2 ± 9.9; Table 1) and low (<20%) "*WNA*" percentages (from 9.84 to 19.12%; Table 1) [23,33]. The *odd-to-even* curves (Fig. 6) calculated for *n*-alkane concentrations associated with occupational aerosol were comparable to those previously obtained for urban aerosol [23]. It was previously observed that the curve of OEP versus *n*-alkane carbon atoms number is characteristic for samples of common origin [31]. This observation, in accordance with the aforementioned molecular diagnostic ratios, demonstrated the predominant input of *n*-alkanes, from oil residues, emissions from worklifts and other machineries and possible contributions from vehicle and trucks emissions.

3.3. Carcinogenicity

The use of potency-equivalent factors (PEFs) to evaluate PAHs lung cancer risk, assuming unit risk for benzo[a]pyrene was suggested [16,22,41–43]. For the needs of this study, BaP-equivalent concentrations were estimated as the product of PEFs from Nisbet and Lagoy and CARB/OEHHA studies and the con-
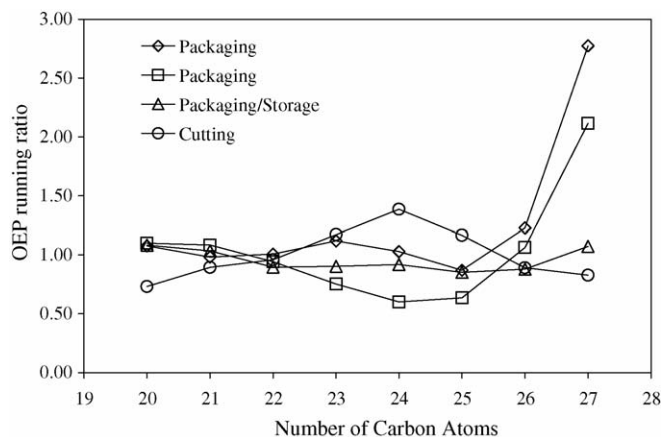

Fig. 6. *n*-Alkane *odd-to-even* predominance (OEP) plots for aerosol collected in paper cutting, packaging and storing departments.

centrations for each individual PAH [16,22,41–43]. In addition, the ratio of the sum of the concentrations of the eight carcinogenic PAHs, to the TPAHs was calculated [25]. Table 2 shows the BaP-equivalent concentrations of particulate PAHs and the mean of the carcinogenic PAHs/TPAHs ratio for the seven departments.

The carcinogenic PAHs/TPAHs ratio values of 0.11 in cutting, 0.38 in bleaching, 0.40 in spraying/drying, 0.49 in drying/polishing, 0.50 and 0.45 in packaging and 0.44 in storing departments (Table 2), demonstrated that except for the paper cutting department where the highest total particulate PAHs concentrations were determined, the carcinogenic PAHs were the most abundant components in the other departments These findings were in line with the spatial variation of the total BaP-equivalent concentrations for particulate PAHs. In fact, they were: 324 pg/m³ in bleaching, 535 and 323 pg/m³ in spraying, drying and polishing, 665 pg/m³ in cutting and 649, 752 and 1104 pg/m³ in packaging and storing areas (Table 2). More than

Table 2
Mean carcinogenic PAHs/TPAHs ratio values and mean BaP-equivalent concentrations estimated using cancer potency-equivalent factor (PEF) for individual PAHs in each paper processing departments

PAH	PE	Bleaching	Spraying/drying	Drying/polishing	Cutting	Packaging	Packaging	Packaging/storage
CarcinogenicPAHs/TPAHs		0.38	0.40	0.49	0.11	0.50	0.45	0.44
BaP-equivalent concentrations (in pg/m³)								
Fluorene	0.001	–	1	–	2	–	–	–
Phenanthrene	0.001	–	–	–	2	–	–	1
Methylphenanthrane	0.001	–	–	–	3	–	–	–
Dimethylphenanthrane	0.001	1	1	1	14	1	1	2
Anthracene	0.01	–	–	–	1	–	–	–
Fluoranthene	0.00	–	–	–	5	1	1	2
Pyrene	0.001	1	–	–	8	1	1	2
4(H)cyclopenta[cd]pyrene		–	–	–	–	–	–	–
Benzo[a]anthracene	0.1	–	–	–	30	20	20	40
Chrysene	0.01	1	1	1	8	3	4	12
Benzo[b/k]fluoranthene	0.1	90	90	90	260	290	280	490
Benzo[e]pyrene		–	–	–	–	–	–	–
Benzo[a]pyrene	1	200	400	200	300	300	400	500
Indeno[123-cd]pyrene	0.1	30	40	30	30	30	40	50
Benzo[ghi]perylene	0.01	1	2	1	2	3	5	5
Total		324	535	323	665	649	752	1104

80% of BaP-equivalent concentrations were due to five-ring PAHs (both benzofluoranthenes and benzopyrenes). This suggested that people working in these departments were exposed to higher inhalation cancer risk as compared to urban air exposures [44,45].

BaP-equivalent concentrations accounted for less than 10% of total PAHs concentration, thus, the total inhalation risk associated with this PAH mixture was approximately 10% assuming that the carcinogenic potency for each individual PAH is similar to BaP PEF. The difference between the actual and BaP-equivalent concentrations was primarily due to variations in the concentrations of low molecular weight and substituted PAHs that did not contribute significantly to the overall carcinogenicity. On the other hand, volatile PAHs can react with nitrogen oxides (that are emitted from worklifts) to form mutagenic nitrated polycyclic aromatic compounds (N-PACs) [25]. Studies showed that the estimated inhalation risk estimated using PEF values can actually account for up to 15% of actual total risk because of PAHs multipathway carcinogenicity [16,25]. In addition, the possible contribution of gas-phase PAHs was not considered. Gas-phase PAHs concentrations tend to be higher for volatile homologues (such as naphthalene and fluorene; with low PEFs values) and lower for heavier (with high PEFs values) PAHs as compared to those measured in particulate phases [23,29,34,45], but they constitute an important component of cancer risk [34,45] especially in indoor environments and workplaces.

Considering the acute toxic and chronic mutagenic properties of PAHs in low concentrations [41–43], exposure to occupational organics can have a deleterious effect on health, although their concentrations are lower than the corresponding OEL values [26,27]. For this reason, controls of occupational exposures should take into consideration the coexistence of a wide variety of chemical components (e.g. PAHs and nitrated PAHs) with synergetic roles. According to U.S. National Institute for Occupational Safety and Health [46], engineering control strategies including methods to prevent hazardous emissions at their source, techniques to diminish occupational levels of hazardous pollutants and policies to manage the exposure time of workers at the hazardous environments are suggested. Substitution for hazardous materials contributed to significant reductions of occupational exposures in other sectors [47], while wetting a ground surface may be the most appropriate method for low dust emissions, especially in operations which changes are not possible [48]. The use of local exhaust ventilation (LEV) techniques in other industrial operations resulted in low occupational exposures [48]. The details of controls may differ for occupational areas due to variations in location (type of building), type of operation (e.g. chemicals, heating and office buildings), local climatology (e.g. ambient temperature) and existing controls (e.g. filtration and air-exchange rates); however, the use of engineering control strategies is found to be more effective, compared to personal protective equipment (the most common practice in most of occupational settings) [46]. In addition to benefits in occupational health, engineering control strategies exhibited *cost-to-effectiveness* ratios of about US$ 105.00 per healthy year in U.S. and Canada only for silicosis patients, in contrast to con-

ventional dust masks and respirators that exhibited values higher than US$ 191.38/year [49].

4. Conclusions

The chemical profiles of particulate PAHs and *n*-alkanes in different departments of paper processing were determined. Aerosol samples were collected and analyzed by gas chromatography/mass spectrometry techniques. Total measured dust concentrations varied substantially for different departments; however, they were lower than the 2003-TLV and European and National OEL. These discrepancies were attributed to the type of the operation, the use of worklifts and the excessive water spraying/drying during paper production. Concentration levels of PAHs and aliphatic hydrocarbons were comparable and/or lower than those measured in other occupational areas and in indoor smoking environments, but considerably higher than outdoor urban levels. The molecular markers approach was used to reconcile the sources of particulate PAHs and aliphatic hydrocarbons in paper processing departments. The mean values of the CPAH/TPAH and MPh/Ph ratios were indicative of a mixed origin from oil residues, unburned fossil fuels and high-temperature combustion of organic material. With respect to the chemical composition, these conclusions were further supported by the values of Fl/(Fl + Py). BaA/(BaA + CT), BeP/(BeP + BaP) and IP/(IP + BgP) diagnostic ratios that were comparable to those calculated for anthropogenic activities such as motor oil and car emissions.

The distribution of *n*-alkanes indicated also sources with strong anthropogenic characteristics. This was in agreement with high UCM/NA ratio and the minor contribution of biogenic alkanes (%WNA). As a result, alkanes were attributed to emissions from worklifts and other gas- and diesel-powered equipment used for transport and handling of paper rolls. Because of the intensive chemical treatment of dirty recycled paper with chemicals under high temperature and pressure to remove contaminants during paper bleaching, spraying and polishing, PAHs and *n*-alkanes can be released into the department. However, their profiles do not differ from those observed for other anthropogenic sources. The minor contribution of emissions from vehicles and heavy duty trucks that penetrated into the occupational setting was also possible.

BaP-equivalent concentrations were estimated in order to evaluate the inhalation cancer risk. Non-volatile five-ring PAHs were the most abundant species exhibiting significant long-term cancer risk for workers. The estimated total inhalation cancer risk of particulate PAHs was higher that those estimated for urban exposures in previous studies. The inhalation risk can substantially increase by considering other factors such as the gas phase of PAHs and the chemical transformation of PAHs to highly carcinogenic nitrated-PACs. A critical observation of this study is that although dust concentrations are overall significantly lower than the 2003-TLV and European and National OEL, providing an indication of well-maintained dust control techniques based on existing regulations, workers were exposed to elevated concentrations of carcinogenic PAHs. This finding suggest that PAHs (and their oxygenated

and nitrated-derivatives) along with other organic species and criteria pollutants (CO, SO$_2$ and dust) should be considered for future exposure assessment studies and regulatory purposes in order to reduce occupational exposures and related diseases.

Acknowledgements

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