

## Cancer and cardiovascular effects from exposure to combustion products

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### BACKGROUND

The key indoor air exposures leading to cancer and severe cardiovascular consequences are radon, certain volatile organic compounds (VOCs) and incomplete combustion generated particulate matter (PM and PAHs) and carbon monoxide. Of these radon [1] and carbon monoxide [2] are dealt with in focused presentations, PM and VOCs are covered in the current presentation.

Complete oxidation of a hydrocarbon fuel would result in only water and carbon dioxide as combustion products. Combustion of even the simplest fuel, methane (over 90 % of natural gas), however, is a complicated chemical process, let alone combustion of the infinitely more complex solid fuels, coal and wood. Complete oxidation is never achieved even in the most advanced industrial scale boiler plants, which are built upon generations of engineering sciences, are equipped with advanced flue gas cleaning technologies, and employ professional operating teams using a network of sensors and automated feedback control systems.

In comparison, the domestic combustion devices to heat, cook and entertain (fireplaces, incense, candles) represent much simpler technologies, use more heterogeneous fuels, are operated by untrained lay persons, and are hardly ever equipped with any feedback control or flue gas cleaning. Consequently the harmful emissions per generated heat unit of small scale combustion devices are orders of magnitude higher than those of industrial and power generating stations (NO<sub>x</sub> is an exception). A fact that highlights the consequences of this difference is that per unit operating time the emissions of particle phase polycyclic aromatic hydrocarbons (PAH<sup>1</sup>) are equally large for a residential woodstove and a coal fired generating station with 10.000 times larger heat output.

The total emissions of combustion particles to outdoor air are orders of magnitude higher than into indoor air, but the intake fraction (*iF*) of the particles emitted into indoor air that is inhaled by people, and could thus harm their health is in the order of 10<sup>-2</sup>..10<sup>-3</sup>, i.e. 100 – 10.000 times the intake fraction of particles emitted into outdoor air [3, 4]. Therefore by far the highest exposures to combustion particles (also vapours and gases) occur in indoor air, and originate from indoor sources.

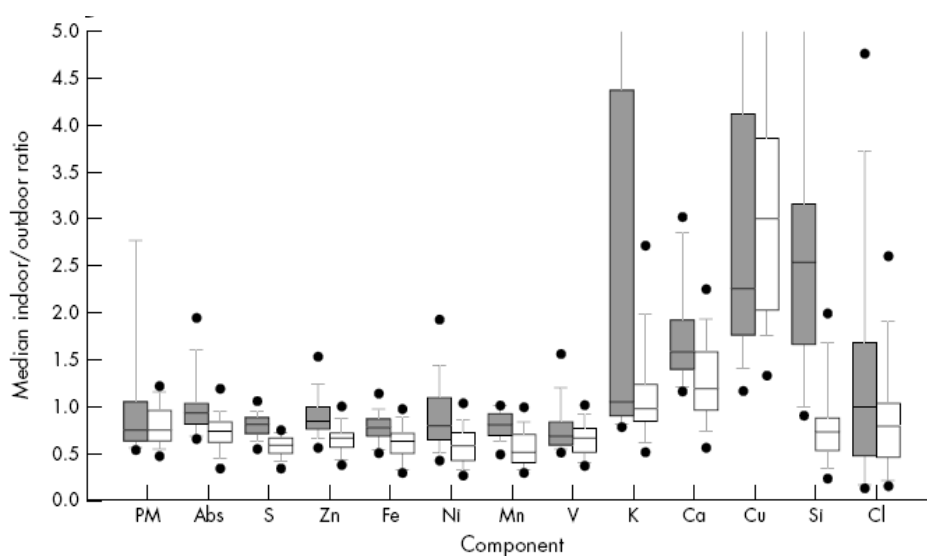
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<sup>1</sup> ) PAH:s are characteristic for visible smoke particles from incomplete combustion and contain most of the combustion generated carcinogens which make e.g. tobacco smoke carcinogenic. Polyaromatic organic matter (POM) is an often used broader definition that includes PAH.

## COMBUSTION PARTICLES

Combustion processes generate both fine particles (aerodynamic diameter  $\leq 2.5 \mu\text{m}$ ,  $\text{PM}_{2.5}$ , measured as mass of the particulate matter per  $1 \text{ m}^3$  of air) and ultrafine particles (UFP#, usually measured as the number count of particles  $< 0.1 \mu\text{m}$  per  $1 \text{ cm}^3$  of air. The count is insensitive to the upper but very sensitive to the lower size limit of the particles counted, typically  $0.02 - 0.03 \mu\text{m}$ ).

The compounds that characterise the combustion generated PM are elemental carbon (EC, also black smoke, BS, black carbon, BC), organic carbon (OC, including the previously mentioned PAH and POM). In an indoor and outdoor, urban and rural  $\text{PM}_{2.5}$  in Hong Kong, the indoor and outdoor concentrations of  $\text{PM}_{2.5}$  mass and EC were highly correlated but the correlation was much lower for OC. All concentrations were higher in indoor than outdoor air, but the difference was highest ( $\text{I/O} = 1.8$ ) for OC, indicating significant contributions from indoor sources, most likely combustion [5] and cooking.



**Figure 1.** I/O ratios of several elemental constituents of  $\text{PM}_{2.5}$  in Helsinki and Amsterdam. ULTRA-study [6]

In the ULTRA study in Helsinki and Amsterdam I/O ratios were analysed for a number of  $\text{PM}_{2.5}$  constituents inside and outside of non-ETS residents. Only Cu was consistently dominated by indoor sources. I would speculate that its apparently omnipresent, yet highly variable indoor source is electric machinery: vacuum cleaners, kitchen blenders, etc. In addition, K, indicating wood combustion, was dominated by indoor sources in many residences in Amsterdam and some in Helsinki. Indoor source contributions were also often significant for the indoor concentrations of Ca and Si, which indicate soil dust [6]. In the Western European context and in the absence of smoking, the average contribution of indoor sources to combustion particles is minimal. Instead the main indoor source contributions are mineral dusts and – surprisingly – phosphate particles, probably originating from detergent residues in clothing [7,8].

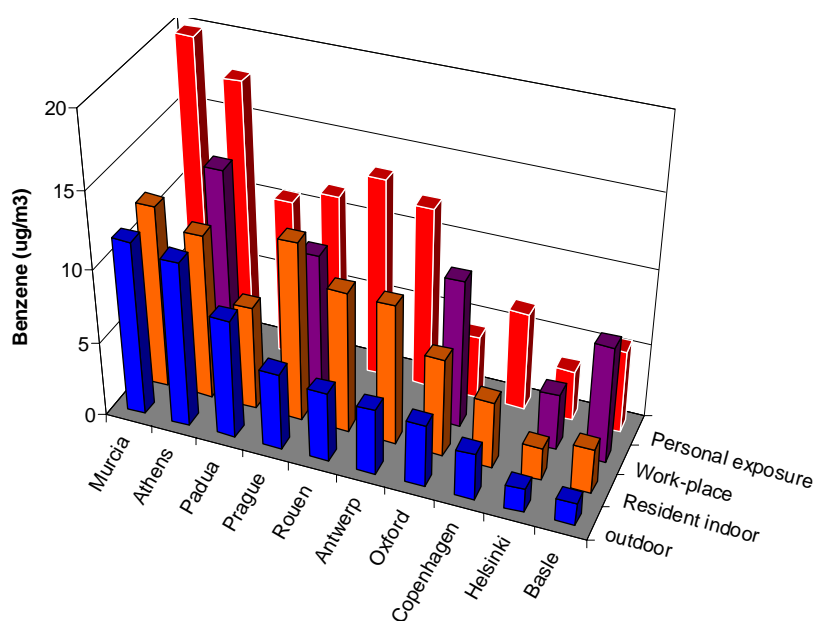
In a regression modelling study, using *EXPOLIS* data from six European cities, the presence of indoor combustion sources explained 16 % (smoking) and 14 % (gas stove) of the variation of the 48 h indoor concentrations of PM<sub>2.5</sub> [9]. In a French regression modelling study indoor combustion processes explained 36 % (smoking) of the variation of the PM<sub>2.5</sub> exposures [10].

In a study focused on the short-term indoor PM concentrations, peak concentrations of 30 - 60 µg/m<sup>3</sup> for PM<sub>0.02-0.5</sub> and 10 - 300 µg/m<sup>3</sup> for PM<sub>0.7-10</sub> were observed in kitchen during oven cooking, while cleaning activities (8 µg/m<sup>3</sup> for PM<sub>0.02-0.5</sub> and 30 µg/m<sup>3</sup> for PM<sub>0.7-10</sub>) and mobility of the occupants (4 µg/m<sup>3</sup> for PM<sub>0.02-0.5</sub> and 20 µg/m<sup>3</sup> for PM<sub>0.7-10</sub>) contributed much less [11]. In the US PM<sub>2.5</sub> exposure study, RIOPA, meat cooking in particular was speculated to be a source of high indoor concentrations of particulate amides, but also other particulate aliphatics and amines were found in high indoor vs. outdoor concentrations [12].

Combustion particles may form a large fraction of indoor air particulate matter – e.g. 1/3 in the *EXPOLIS* sample in Helsinki, but in the absence of significant indoor combustion sources this PM originates from ambient air [8], and exposure to it can be best prevented by modern building structures and ventilation systems [13]. The highest exposures to combustion particles by far, however, occur indoors in the most primitive conditions [14]. Indoor combustion processes may increase the levels of indoor air ultrafine particles by 2, 3 orders of magnitude in comparison to a situation without the source.

## **VOCs AND CARBONYLS**

After CO, VOCs are found in *highest indoor air concentrations*, and are consequently also responsible for the highest long-term population exposures. VOCs are no doubt the most studied indoor air contaminants. In a review of 68 American and European indoor air studies, Brown [15] lists ethanol, 1,1,1-trichloroethane, toluene, limonene, acetone and xylenes as the indoor air VOCs with the highest average concentrations. In Helsinki, Finland, indoor concentrations of acetone, formaldehyde, toluene, xylenes and limonene were the highest [16]. In a study of 3 German cities, the highest average indoor air concentrations were observed for limonene, toluene and pinene [17]. The top rank lists in these different studies are similar, acknowledging that ethanol was only considered by Brown and formaldehyde - not a VOC - was only considered in the Helsinki list.



**Figure 2.** Average personal, indoor (work and home) and outdoor air benzene concentrations in 10 European cities measured in the EXPOLIS [16] and MACBETH [20] studies.

In the German Environmental Survey (GerES II) [18] 74 VOCs were analysed in the personal air (7 days) in a sub-sample of 108 participants representing 36 study locations. The mean exposure to total VOCs was  $901 \mu\text{g}/\text{m}^3$ , with 95<sup>th</sup> percentile as high as  $2810 \mu\text{g}/\text{m}^3$ . Mean personal exposure concentrations for the different VOC classes were highest for oxygenated VOCs ( $308 \mu\text{g}/\text{m}^3$ ), followed by aromatics ( $286 \mu\text{g}/\text{m}^3$ ), alkanes ( $187 \mu\text{g}/\text{m}^3$ ), terpenes ( $98 \mu\text{g}/\text{m}^3$ ) and aliphatics ( $21 \mu\text{g}/\text{m}^3$ ) [19].

Some of these VOCs are readily produced in and emitted from incomplete combustion processes (e.g. aromatics, notably benzene, and oxygenated VOCs), others have combustion as one of the sources (e.g. aliphatics, alkanes, aldehydes), and the sources of yet others are clearly non-combustion (terpenes, halogenated). With the exception of the last category and outside of the most obvious cases, it is in practice difficult to define the proportion of the different VOCs that originate from combustion sources. E.g. aromatic VOCs are the main components in many solvents used in household products, although benzene – because it is an IARC classified human carcinogen – is currently found in the solvents only as a low level impurity. Benzene can, therefore be regarded as a useful indicator for the VOCs from combustion sources, and the indoor / outdoor ratio of benzene as an indicator of the contribution of indoor combustion sources.

Comparison of the average indoor and outdoor benzene concentrations in 10 European cities [16, 20], see Figure 2, reveals that the average indoor source contribution is quite small, in the order of 10% or less in Murcia, Athens, Padua, Copenhagen and Helsinki. On the other hand the average residential indoor contribution is in the order of 50% or more in Antwerp, Prague and Antwerp, with particularly high workplace contributions in Basle and Oxford. While the lowest indoor source contributions indicate also low combustion source contribution, it is

unclear how much of the high indoor source contributions originate from combustion processes.

### Contributions of indoor sources to indoor exposures

The highest personal exposures to VOCs are often due to high residential indoor concentrations. In the *EXPOLIS* study, e.g., in Helsinki, workplace and home indoor concentrations were the leading factors for 1/3 of the higher than average benzene exposures. [21]

According to Brown [15] the indoor sources contribute of all VOCs the least (1/2 or less) to benzene, butanal and carbon tetrachloride. In Helsinki the contributions of residential and occupational indoor sources to total personal exposures were highest for aldehydes, terpenes and xylenes, lowest for benzene, toluene and nonane [16].

In the GerES II -study multivariate analysis was carried out to determine and quantify the major sources of personal exposure to various VOCs, with main focus on aromatics. The only significant indoor source for benzene was tobacco smoke, i.e. biomass combustion. [19]

### Differences between regions

*Between cities:* According to the *EXPOLIS* study differences between the average residential indoor air VOC concentrations in 7 European cities were remarkable, and in the non-smoking indoor spaces with hardly any combustion heating or cooking devices in Helsinki, the indoor source contribution to benzene exposure was marginal, and to the other aromatics also small (22, 23)

**Table 1.** Average VOC concentration differences between 6 European cities, note the high proportion and variation of aromatics, which have the highest contribution from combustion processes (*EXPOLIS*) ( $\mu\text{g}/\text{m}^3$ ) [16]

VOC Group	Lowest avg.	Avg	Highest avg.
Alcohols	2 (Basel)	25	60 (Milan)
Aldehydes	10 (Basel)	25	63 (Milan)
Alkanes	18 (Helsinki)	48	127 (Milan)
<b>Aromatics</b>	<b>43 (Helsinki)</b>	<b>163</b>	<b>463 (Milan)</b>
Esters	3 (Bas.&Hel.)	16	70 (Milan)
Halogens	2 (Bas.&Hel.)	28	130 (Milan)
Miscell.	21 (Basel)	59	98 (Mil.& Ath.)

The high average indoor concentrations in Milan in particular were due to a small number of very high levels. The indoor levels reflected the respective outdoor air VOC levels, but were in average 50 % (alkanes, aromatics, esters) ... 150 % (alcohols, halogenated VOCs) higher.

*Urban - rural:* In a German study outdoor and indoor concentration differences for BTEX-concentrations between urban (High traffic area in the city of Hannover) and rural (in Wedemark, no major traffic nearby) areas were assessed [24, 25]. Although the average outdoor air concentration were about 10 times higher in the urban vs. rural

area, the respective indoor air concentrations of benzene were only about 50% higher in the city. For the other aromatics the average indoor concentrations in the urban and rural areas were even closer. I.e. for BTEX compounds indoor sources all but eliminated the urban-rural indoor exposure differences. The high indoor vs outdoor benzene concentrations in the rural area indicate that combustion is probably the most important source.

Unlike the particulate matter in general, and combustion generated PM<sub>2.5</sub> in particular, the indoor concentrations of VOCs are typically far higher in indoor than outdoor air. For combustion generated VOCs, benzene as a marker, this difference is, however, the smallest. The presence of indoor sources and inappropriate ventilation may still result in indoor concentrations that are one or two orders of magnitude higher than those in outdoor air.

## CONCLUSIONS

- Compared to outdoor sources, benzene and fine PM from indoor sources cause 100 ... 10 000 times more exposure per unit mass released.
- Most exposure to benzene and fine PM from combustion sources occurs in indoor environments but – in the absence of smoking - has outdoor origins.
- The contribution of indoor combustion sources to exposure varies greatly, not only between buildings and residences, but also between the European cities.
- The highest and sometimes acutely dangerous exposures to combustion products, however, have indoor origins and occur indoors.

## REFERENCES

1. McLaughlin J, Bochicchio F. Radon and Lung Cancer. (Draft) Proceedings: 1st EnVIE Conference on Indoor Air Quality and Health for EU Policy. Finlandia Hall, Helsinki, 12-13.6.2007.
2. Carrer P. Carbon Monoxide and Acute Intoxication. (Draft) Proceedings: 1st EnVIE Conference on Indoor Air Quality and Health for EU Policy. Finlandia Hall, Helsinki, 12-13.6.2007.
3. Smith KR. Biofuels, Air Pollution, and Health. Plenum, New York, 1987.
4. Bennett DH, McKone TE, Evans JS, Nazaroff W, Margni MD, Jolliet O, Smith KR. Defining intake fraction. *Environ. Sci. and Technol.* 2002; **36**:206A–211A.
5. Cao JJ, Lee SC, Chow JC, Cheng Y, Ho KF, Fung K, Liu SX, Watson JG. Indoor/outdoor relationships for PM<sub>2.5</sub> and associated carbonaceous pollutants at residential homes in Hong Kong – case study. *Indoor Air* 2005; **15**:197-204.
6. Janssen NAH, Lanki T, Hoek G, Vallius M, de Hartog JJ, Van Grieken R, Pekkanen J, Brunekreef B. Associations between ambient, personal, and indoor exposure to fine particulate matter constituents in Dutch and Finnish panels of cardiovascular patients. *Occup. Environ. Med.* 2005; **62**:868–877.
7. Hänninen OO, Lebret E, Ilacqua V, Katsouyanni K, Künzli N, Srám RJ, Jantunen

MJ. Infiltration of ambient PM<sub>2.5</sub> and levels of indoor generated non-ETS PM<sub>2.5</sub> in residences of four European cities. *Atmos. Environ.* 2004;**38**:6411-6423.

8. Koistinen KJ, Edwards RD, Mathys P, Ruuskanen J, Künzli N and Jantunen MJ. Sources of fine particulate matter in personal exposures and residential indoor, residential outdoor and workplace microenvironments in the Helsinki phase of the EXPOLIS study. *Scand. J. Work Environ. Health* 2004; **30 suppl 2**:36-46.

9. Lai HK, ApSimon H, Bayer-Oglesby L, Götschi T, Jantunen MJ, Künzli N, Kulinskaya E, Nieuwenhuijsen MJ, Schweizer C, Colvile R. Determinants of indoor air concentrations of PM<sub>2.5</sub>, black smoke and NO<sub>2</sub> in six European cities (EXPOLIS study). *Atmos. Environ.* 2006; **40**:1299-1313.

10. Gauvin S, Reungoat P, Cassadou S, Déchenaux J, Momas I, Just J, Zmirou D. Contribution of indoor and outdoor environments to PM<sub>2.5</sub> personal exposure of children - VESTA study. *Sci. Tot. Environ.* 2002; **279**:175-181.

11. Abt E, Suh HH, Allen G, Koutrakis P. Characterisation of indoor particle sources: A study conducted in the Metropolitan Boston Area. *Environ. Health Perspect.* 2000; **108**:35-44.

12. Reff A, Turpin B, Poreja RJ, Giovenetti R, Cui W, Weisel CP, Zhang J, Kwon J, Alimokhtari S, Morandi M, Stock T, Maberti S, Colome S, Winer A, Shendell D, Jones J. Functional group characterization of indoor, outdoor, and personal PM<sub>2.5</sub>. Results from RIOPA. *Indoor Air* 2005; **15**:53-61

13. Hänninen O, Palonen J, Tuomisto JT, Yli-Tuomi T, Seppänen O, Jantunen MJ. Reduction Potential of Urban PM<sub>2.5</sub> Mortality Risk Using Modern Ventilation Systems in Buildings. *Indoor Air* 2005; **15**:246-256.

14. Smith KR. Fuel combustion, air pollution, and health: The situation in developing countries. *Ann. Rev. Energy and Environ.* 1993;**18**:529-566.

15. Brown SK, Sim MR, Abramson MJ, Gray CN. Concentrations of Volatile Organic Compounds in Indoor Air - A Review. *Indoor Air* 1994; **4**:123-134.

16. Saarela K, Tirkkonen T, Laine-Ylijoki J, Jurvelin J, Nieuwenhuijsen MJ and Jantunen MJ. Exposure of population and microenvironmental distributions of volatile organic compound concentrations in the EXPOLIS study. *Atmos. Environ.* 2003; **37**:5563-5575.

17. Schlink U, Rehwagen M, Damm M, Richter M, Borte M, Herbarth O. Seasonal Cycle of Indoor-VOCs: comparison of apartments and cities. *Atmos. Environ.* 2004; **38**:1181-1190.

18. Seifert B, Becker K, Hoffmann K, Krause C, and Schultz C. The German Environmental Survey 1990/92 (GerES II): A representative population study. *J. Exposure Analys. Environ.Epidemiol.* 2000; **10**:103-114.

19. Hoffmann K, Krause C, Seifert B, and Ullrich B. The German Environmental Survey 1990/92 (GerES II): Sources of personal exposure to volatile organic compounds. *J. Exposure Analys. Environ. Epidemiol.* 2000; **10**:115-125.

20. Cocheo V, Sacco P, Boaretto C, De Saeger E, Pérez Ballesta P, Skov H, Goelen E, Gonzalez N, Baeza Caracena A. Urban Benzene and Population Exposure. *Nature* 2000; **404**:141.

21. Edwards RD, Schweizer C, Jantunen MJ, Lai HK, Bayer-Oglesby L, Katsouyanni K, Nieuwenhuijsen MJ, Saarela K, Srám R, Künzli N. Personal exposures to VOC in the upper end of the distribution — relationships to indoor, outdoor and workplace concentrations. *Atmos. Environ.* 2005; **39**:2299-2307.
22. Jurvelin JA, Edwards RD, Vartiainen M, Pasanen P, Jantunen MJ. Residential Indoor, Outdoor, and Workplace Concentrations of Carbonyl Compounds: Relationships with Personal Exposure Concentrations and Correlation with Sources. *J. Air & Waste Manage. Assoc.* 2003; **53**:560-573.
23. Edwards RD, Jurvelin J, Koistinen K, Saarela K, Jantunen MJ. VOC source identification from personal and residential indoor, outdoor and workplace microenvironment samples in EXPOLIS-Helsinki, Finland. *Atmos. Environ.* 2001; **35**:4829-4841.
24. Ilgen E, Karfich N, Levsen K, Angerer J, Schneider P, Heinrich J, Wichmann H-E, Dunemann L, Begerow J. Aromatic Hydrocarbons in the atmospheric environment: Part I. Indoor versus outdoor sources, the influence of traffic. *Atmos. Environ.* 2001; **35**:1235-1252.
25. Ilgen E, Levsen K, Angerer J, Schneider P, Heinrich J, Wichmann H-E. Aromatic Hydrocarbons in the atmospheric environment: Part II. Univariate and multivariate analysis and case studies of indoor concentrations. *Atmos. Environ.* 2001; **35**:1253-1264.