EXPOLIS-INDEX:

Work Package 3

Final Report

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Microenvironmental apportionment of VOC exposure and intake fractions for indoor sources

ABSTRACT

Although people in developed countries spend most of their time indoors, personal exposure to VOCs can result from sources located in different microenvironments (ME). The first section derives approximations that can be used to apportion personal exposure to different microenvironmental sources in population exposure studies, based on indoor and outdoor concentrations. The microenvironmental contributions of outdoor, home, workplace and other sources are then calculated for benzene, toluene, xylenes, ethylbenzene, 3 n-alkanes, benzaldehyde, and 3 terpenes (a-pinene, limonene, and 3-carene) for five EXPOLIS cities: Athens, Basel, Helsinki, Oxford, and Prague.

In general, sources in the outdoor, home and other (which includes traffic) microenvironments are all important in determining personal exposure. The workplace microenvironment, on the other hand, plays a secondary role. Exposure to total VOCs and terpenes appear dominated (>40%) by home sources. Benzene shows the smallest (<10%) home contributions in Athens, Helsinki and Oxford, though substantial (15%-20%) in Basel and Prague.

The effects of sorption and desorption by surfaces and materials indoors were found to be significant in determining indoor concentrations of VOCs, in some cases dominating emissions. Strategies to exploit these processes to reduce personal exposure are introduced as hypotheses for future research.

In the second section, the distributions of intake fraction for indoor air emissions were estimated for the same five cities in EXPOLIS. Intake fractions are an expression of the mass of a pollutant that reaches a target compared to the mass emitted by a source. They facilitate direct comparisons of the relative impact of different sources on individual or population exposure.

The computation of the distributions was obtained through Monte Carlo simulations, based on distributions of residence volume, air exchange rates and time-activity data, calculated from the EXPOLIS database, as well as on distributions from the literature. Some approximations were made that are valid for conservative pollutants and continuos sources, such as emissions from building materials, pesticides, molds, as well as for certain non-continuous sources such as cooking or cleaning products. For these categories of sources, intake fractions are approximately independent of the actual indoor concentrations and irrespective of the source.

Intake fractions in the five populations examined followed approximately lognormal distributions. The mean intake fractions computed were about 10^{-3}, with some variability across cities, ranging from 1.5×10^{-3} in Athens to 4.5×10^{-3} in Helsinki. This modest variability mostly reflects the differences in climates and consequent air-tightness of the buildings. The 95th percentile of the distributions were 2-3 times the mean values, indicating a substantial homogeneity within each population as well. These results compare well previous estimates for environmental tobacco smoke and cooking, and are 2-3 orders of magnitude larger than estimates for outdoor sources.

Part I

Microenvironmental apportionment

1.   Introduction

1.1. Rationale for microenvironmental apportionment

People in developed countries spend over 85% of their time indoors (EXPOLIS Study Group, 1999; USEPA, 1997). Much of the VOC exposure research has consequently focused on characterizing indoor exposures. This approach, however, does not address the issue of where the sources are located. Indoor exposure to VOCs is the result of a variety of different contributions from indoor and outdoor sources. Knowledge of their relative importance is an essential first step in directing regulatory, manufacturing and individual efforts to minimize risks. It is also helpful in characterizing VOC sources, whose emissions may differ in terms of risk. This section derives approximations that can be used to model the relative contributions of indoor and outdoor sources to personal exposure in the context of a population exposure study. These contributions are then calculated for selected VOCs in five European cities investigated during the EXPOLIS study: Athens, Basel, Helsinki, Oxford, and Prague.

Because indoor environments are in effect contained in the larger outdoor environment, it is possible to envisage the outdoor concentration of air contaminants as a general background to which processes in the indoor environment may add their own contribution. This basic idea can be generalized to the concept of microenvironment (ME) used in exposure assessment to indicate locations – but also activities – in which a distinct exposure to a particular agent takes place. This approach can also be described as distinguishing near- vs. far-field sources. Benzene exposure in the *traffic* microenvironment, for example, can then be thought of as resulting from the sum of a general background benzene concentration plus the specific contribution from the vehicles in the vicinity of the exposed individual. Similarly, and more clearly separated, exposure in the home will result from the amount infiltrated indoors from the outside, plus the emissions from the indoor surfaces or from activities such as cooking, smoking, spraying, etc. In principle, this separation can be carried out for every ME and it is then possible to write the personal exposure of an individual as

$$P = \sum_{i} \left(C_{oi} + C_{mi} \right) t_i \tag{1.1}$$

where P is the personal exposure, C_{oi} is the concentration attributable to the outdoor background in the i-th microenvironment, C_{mi} is the concentration attributable to sources located in the i-th microenvironment, and t_i is the time spent in that ME. In general, these two contributions to the

concentration observed in one ME cannot be measured directly, except in the trivial case of the outdoor ME itself. It is then essential to understand their relationship to measurable quantities, such as indoor and outdoor concentrations.

1.2. Approximations

The concentration of an indoor species is governed by several processes. Air exchange with the outdoor environment provides both a source and sink process. It can be assumed that there is no interception of gaseous compounds by the building envelope, except for very reactive species (Liu and Nazaroff, 2001). Emissions from materials, furniture, and selected activities are also sources. Reaction and sorption to materials provide additional sinks that can be modeled as first-order processes (Seinfeld and Pandis, 1998; Won et al., 2001). Desorption from materials, finally, contributes as a source. The combined effect of these processes can then be written in the basic mass-balance equation as

$$\frac{dC_i}{dt} = aC_o - aC_i + \frac{S_p}{V} - k_r C_i - k_s C_i + \frac{\sum k_d C_m}{V}$$

(1.2)

where C_i is the indoor concentration, C_o is the outdoor concentration, S_p is the sum of source strengths for all primary sources, V is the volume of the residence, a is the air exchange rate, and k_r is the decay rate due to reactions (indoors), k_s is the rate of sorption, and k_d and C_m are respectively the rates of desorption from, and concentration in the various materials in the indoor environment.

In practice, emissions produced by volatilization of the original components of a material (primary emissions) and emissions due to desorption are not distinguishable, nor will the concentration in all the various materials generally be known. These two source terms can then be grouped as $S_p + S_d$, with S_d referring to desorption, and expressed in units of mass per time.

To further simplify the formulation of the model, some scaling considerations can be introduced, comparing decay, air exchange and sorption rates. The decay rate varies for different compounds according to their reactivity. Indoor air chemistry is in many respects similar to nighttime tropospheric chemistry, and reaction with nitrate radical is an important pathway for many VOCs, since hydroxyl radical concentrations are low (Seinfeld and Pandis, 1998). Table 1.1 gives the approximate decay rates for some VOCs through reaction with nitrate and hydroxyl radicals indoors. The next term, air exchange rates in indoor environments are of the order of 1 h^{-1}. As for sorption rates, the process has been poorly studied in real buildings. Data from test chambers indicate specific sorption rates for various VOCs of the order of 0.1 – 1 m h^{-1} for wall materials (Popa and Haghighat, 2003) and about 10 m h^{-1} for carpets (Elkilani et al., 2003). These numbers need to be multiplied by the appropriate surface/volume ratios to obtain actual sorption rates. This value can be calculated as approximately 1 m^{-1} for a 50-150 m^2 home with empty rooms, while in inhabited homes the ratio is perhaps up to an order of magnitude larger, because of furniture and other objects. Thus, sorption rates in homes are expected to be of the order of 1 h^{-1} and upward. With the exception of terpenes, (large) alkenes, and other unsaturated compounds, then, decay due to reaction (as shown in Table 1.1) is much slower than the other two processes (air exchange and sorption). To simplify the analysis, a single rate constant $k = k_r + k_s$ can be defined, that is dominated by sorption, with the noted exceptions.

Table 1.1. Pseudo-first-order rate constants for reactions with hydroxyl and nitrate radicals. Indoor radical concentrations assumed from nighttime averages as $[NO_3]=2.4 \; 10^8$ molecules cm^{-3} (10 ppt); $[OH]=1.5 \; 10^5$ molecules cm^{-3} (Seinfeld and Pandis, 1998)

	$k_r'[NO_3]$ [a] (h^{-1})	$k_r'[OH]$ [b] (h^{-1})
benzene	$3 \; 10^{-5}$	$4 \; 10^{-4}$
toluene	$6 \; 10^{-5}$	$2 \; 10^{-3}$
m,p-xylene	$3 \; 10^{-4}$	$1 \; 10^{-2}$
nonane	$2 \; 10^{-4}$	$\sim 10^{-3}$
benzaldehyde	$2 \; 10^{-3}$	$\sim 10^{-2}$
α-pinene	5.3	$3 \; 10^{-2}$
3-carene	7.9	$5 \; 10^{-2}$

[a] k_r' from Weschler et al. (1992)
[b] adapted from Seinfeld and Pandis (1998). Reactivity estimated from n-butane for nonane, and from propanal for benzaldehyde

Over a long sampling period, only average values are measured for these variables, so that steady state can be assumed. Equation (1.1) can then be written, with the above simplifications, and neglecting the notation of average, as

$$C_i = \frac{a}{a+k} C_o + \frac{S_p + S_d}{V(a+k)} \tag{1.3}$$

The second term on the right represents the contribution to indoor concentration from all indoor emissions (both primary emissions and desorption). It will be referred to as C_e and can be written as

$$C_e = \frac{S_p + S_d}{V(a+k)} \;\; = \;\; C_i - \frac{a}{a+k} C_o \tag{1.4}$$

Indoor sorption and reaction of outdoor-generated molecules will be indicated as Cs and is responsible for the difference

$$C_s = C_o - \frac{a}{a+k} C_o \tag{1.5}$$

The relationships expressed by equations 1.3-1.5 are best understood graphically from Figure 1. Sorption and desorption always take place simultaneously, balancing each other to some extent, but with a net effect shifted towards one or the other process. When the indoor air concentration is in equilibrium with the rooms, sorption and desorption are equivalent and all emissions are primary. In the cases when primary emissions and desorption outpace sorption, a net emission to the indoor air will be observed (Figure 1). A net sorption to the indoor materials will conversely take place when the equilibrium is shifted in the direction of sorption (Figure 2) and primary sources are comparatively weak. The net effect of primary emissions and sorption/desorption equilibrium (C_n) then is simply, from equations 4 and 5

$$C_n = C_e - C_s = C_i - C_o \tag{1.6}$$

The contribution to indoor concentration from the outdoor background (C_{oi}), as defined in equation 1, can then be expressed (using eq. 1.3 and 1.5) by

$$C_{oi} = C_o \quad - \quad C_o\left(1 - \frac{a}{a+k}\right) \quad + \quad \frac{S_d}{V(a+k)} \quad = \quad \frac{C_o a + S_d/V}{a+k} \tag{1.7}$$

    Infiltration   Sorption   Desorption

It is clear from equation 1.7 that the contribution of the outdoor background to exposure in an indoor ME cannot be calculated exactly from the indoor and outdoor concentrations alone, without knowledge of the air exchange and sorption/desorption rates. The latter depend not only on the concentration during sampling, but also on the prior history of indoor concentrations, and on the molecular diffusion coefficients to and through all the sorbing materials.

Such information cannot realistically be obtained in population exposure studies. Some insight can nevertheless be gained from approximations, whose accuracy varies for different scenarios and compounds. We observe that when the indoor air is in equilibrium with the room, that is $S_d/V = C_o k$, the outdoor contribution to indoor concentration C_{oi} equals the outdoor concentration C_o. Additionally, even when conditions are far from equilibrium, the outdoor contribution to indoor concentration C_{oi} equals the indoor concentration C_i in the absence of primary sources. Based on these observations, it is possible to introduce two approximations

I) *Sorption/desorption averaging*

$$<C_{oi}> \approx < C_o>, \quad \text{if } C_n > 0$$

As departures from equilibrium are equally likely in either direction, in different homes and sampling days, the average net effect of sorption and desorption is null. A population average of the *relative* contributions of outdoor- and indoor-generated contaminants will approximate the true values in that population. No such conclusion can be applied to the individual cases, though. This approximation applies to situations where a net emission is observed (Figure 1). The indoor-source contribution is then approximated by the net emissions C_n.
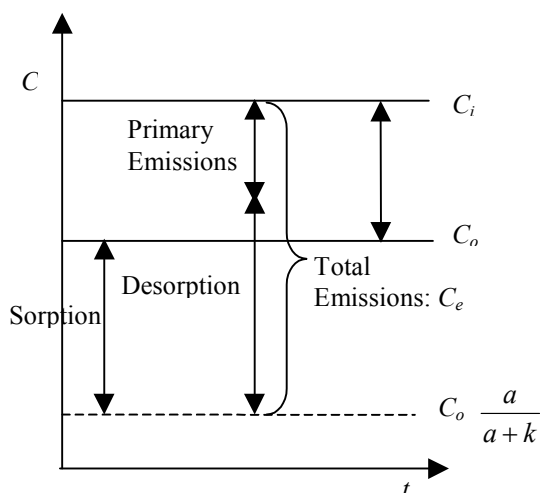
Figure 1. Relationships between indoor and outdoor concentrations in cases of net emissions taking place indoors. Ci = indoor concnetration, Co = outdoor concnetration, a = air exchange rate, k = sorption rate. The relative magnitude of primary emissions and desorption is chosen arbitrarily.

II)   *Negligible primary emissions*

$$C_{oi} \approx C_i, \quad \text{if } C_n < 0$$

In cases of net sorption on the other hand (Figure 2), conditions are clearly far from equilibrium only in one direction. The outdoor contribution, then, is most closely approximated by the indoor concentration, and the indoor-source contribution by zero. These approximations are quite reasonable, since, in practice, net sorption can be observed only when primary indoor sources are weak in the first place. A bias is introduced, however, as the outdoor contribution is always overestimated.
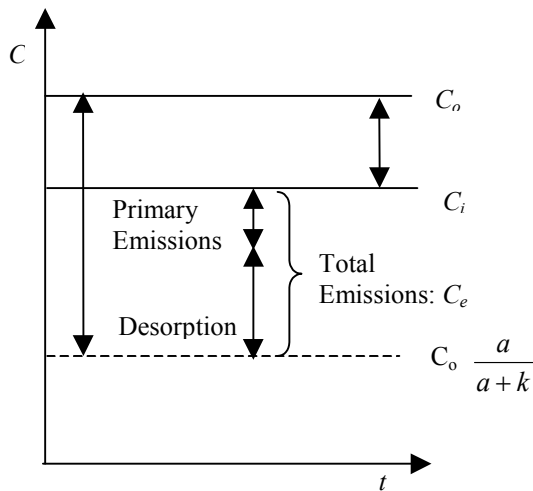
Figure 2. Relationships between indoor and outdoor concentrations in cases of net sorption taking place indoors. C_i = indoor concnetration, C_o = outdoor concnetration, a = air exchange rate, k = sorption rate The relative magnitude of primary emissions and desorption is chosen arbitrarily.

The introduction of these two approximations, however, makes it possible to express the indoor and outdoor contributions to personal exposure in indoor ME in terms of indoor and outdoor concentrations, and their difference, that are quantities directly observable in exposure studies. Their limitations to the interpretation of results, however, must be kept in mind

2.   Methodology

2.1. Description of data

During the EXPOLIS sampling campaign, personal, residential (indoor and outdoor), and indoor workplace samples were collected over 48 hours. Residential samples were obtained during the times when participants reported that they would be at home, while workplace samples were taken during working hours. Sampling took place over the course of one year, from fall 1996 to winter 1997, in the cities of Helsinki, Athens, Basel, Prague, Milan, Grenoble and Oxford (in 1998-99). A detailed description of the study design, sampling target population, and distribution of sampling locations has been published previously (EXPOLIS Study Group, 1999; Jantunen et al., 1998).

Personal exposure samples were collected using the modified Buck IH pump (A.P. Buck Inc., Orlando, FL) at 0.5-1.0 mL/min. The sampling apparatus, packed in a 5 kg aluminum briefcase, was carried by each study participant for 48 h. Microenvironmental sampling was performed using a PQ100 pump (A.P.Buck, Inc., Orlando, FL) at a 2.3 L/min flow rate.

Samples were absorbed onto Perkin Elmer Tenax TA adsorbent tubes in all cities except Basel. In Basel, samples were instead collected using Carbotrap tubes at flow rates approximately 10 times greater than in the other cities. VOC samples collected on Tenax tubes were analyzed by VTT Chemical Technology, Espoo, Finland, by thermal desorption, followed by GC separation and simultaneous detection by Mass selective Detection (MSD) and flame ionization (FID). Samples collected on Carbotrap were analyzed by Carbotech SA in Switzerland with GC/FID. Sampling technique, analysis and quality assurance are further described in other publications (Jurvelin et al., 2001).

A Time-Microenvironment-Activity diary was kept by the study participants who were asked to mark each 15 min of the day in the appropriate microenvironment category. In addition, a detailed questionnaire was compiled, describing home and workplace characteristics.

2.2. Exposure Model

Using the data available in the EXPOLIS study, it is possible to describe an individual's personal exposure as resulting from contributions of sources located in different MEs

$$P = O + H + W + B \tag{1.8}$$

where P is the personal exposure, O is the contribution from outdoor sources, H and W are the contributions of the home and workplace indoor ME respectively, and B is the balance due to exposure in other ME (such as commuting) or to activities located in the immediate vicinity of the individual (e.g. using personal care products). The latter term also carries all the effects of measurement errors in personal or microenvironmental exposure.

The various components can be written explicitly in terms of indoor and outdoor concentration with the help of the approximations described in the introduction. The outdoor and indoor contributions are then

$$O = C_o \cdot t_{ho} + \min\{C_o, C_{hi}\} \cdot t_{hi} + \min\{C_o, C_{wi}\} \cdot t_{wi} + \\ + (48 - t_{ho} - t_{hi} - t_{wi}) \cdot \min\{C_o, C_b\} \tag{1.9}$$

$$H = \max\{C_{hi} - C_o, 0\}\, t_{hi}$$
$$W = \max\{C_{wi} - C_o, 0\}\, t_{wi} \qquad\qquad\qquad\qquad (1.10a,\ 1.10b)$$

where C_o is the average home outdoor concentration, t_o is the time (in hours) spent outdoors at home during the sampling period, C_{hi} is the average concentration measured indoors at home, t_{hi} is the time spent indoors at home, C_{wi} is the average concentration measured indoors in the workplace, t_{wi} is the time spent indoors at work. The last symbol, C_b, is the equivalent concentration to which an individual would have to be exposed during the remaining time to achieve the total personal exposure observed. This level is obtained as a remainder and is defined as

$$C_b = C_p - C_{hi} \cdot f_{hi} - C_{wi} \cdot f_{wi} - C_o \cdot f_{ho} \qquad\qquad\qquad (1.11)$$

where f denotes the fraction of time (0 to 1) in each of the MEs during the sampling period.

The use of *the least of* (min) in equation 1.9 reflects Approximation II. An analogous approximation is introduced in the last term of that equation, expressing the fact that the outdoor contribution to exposure cannot be greater than the concentration to which the individual was actually exposed to, in any ME.

Only one value of outdoor concentration was available in the database, and this has been taken as representative of the outdoor background concentration in all MEs for each individual. This is, in principle, a serious limitation and its consequences will be examined in detail in section 4.3

2.3. Sample sizes

The number of individuals sampled in the different cities was 200 in Helsinki and 50 in the other cities in the project. The actual number of cases available for the present analysis was much smaller, however, only 25-30% of total population, as different selection criteria must be applied. Approximately 40% of the cases were excluded because of exposure to ETS. As that source would dominate personal exposure, results would be of little interest for the purpose of this study. Another 20% of the total population could not be used because of missing personal, outdoor or indoor measurements. These were measurements that could not be carried out or, more often, that did not meet the quality control requirements. A further 5% was excluded because personal exposure was found below the limit of detection (LOD), as any results of microenvironmental apportionment would be essentially random. Finally, approximately 5% of the total population was excluded because personal exposure was lower than the time-weighted microenvironmental exposure, that is $C_b < 0$. A 5% tolerance for measurement uncertainty was allowed, however. In practice, most cases where C_b was negative were much below a level that could be attributed to measurement uncertainty, and irrespective of the absolute magnitude of personal exposure. By and large, the same cases had a negative C_b contribution for most compounds, indicating problems at the sampling or chemical analysis stage. The nature of these problems may be varied and is not fully understood. In any event, such cases could not be used, as personal and microenvironmental exposures were not representative of each other. The percentages of excluded population given for each reason are to be interpreted as resulting uniquely from that reason, when applied in sequence, although many cases had more than one reason for exclusion (e.g. both ETS exposure and missing data). These percentages are also to be taken as a general indication, since they vary somewhat between different cities and for different compounds.

3.   Results

3.1. Results for individual compounds

The results below are given as an aggregate percentage for all samples, regardless of the city, due to sample size limitations. As these results are strongly influenced by the larger sample from Helsinki, exposure concentrations for individual cities are also provided. Comparisons between different cities are not recommended, due to small sample sizes.

Total VOCs

Figure 3. Contributions to personal exposure to TVOCs from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities.

Benzene

Figure 4. Contributions to personal exposure to benzene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities.

Toluene

Figure 5. Contributions to personal exposure to toluene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities.

o-xylene
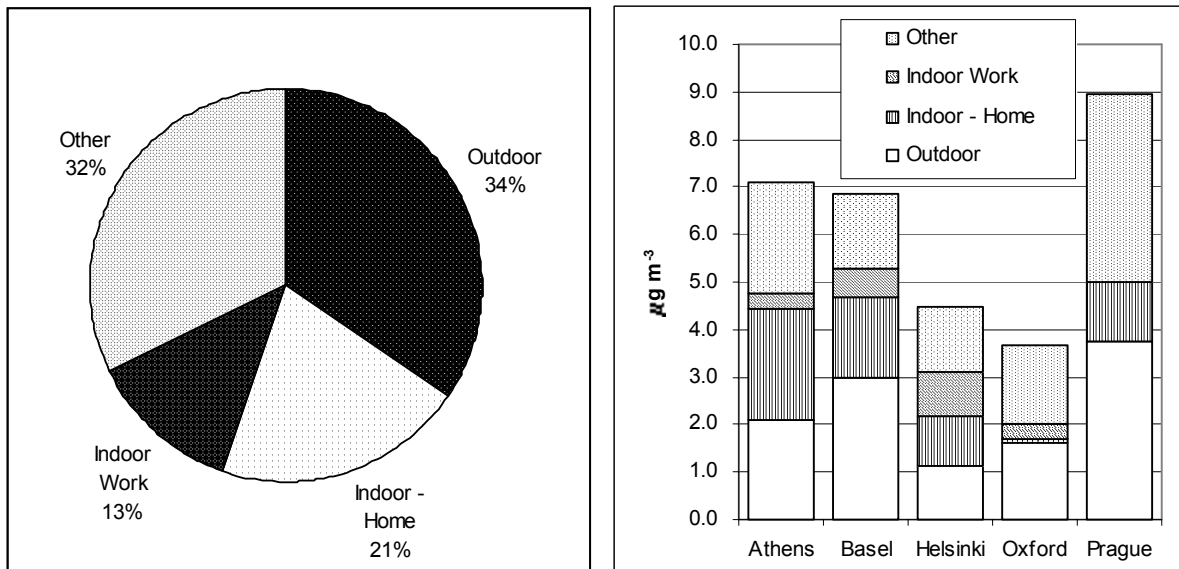
Figure 6. Contributions to personal exposure to o-xylene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities.

m,p-xylene
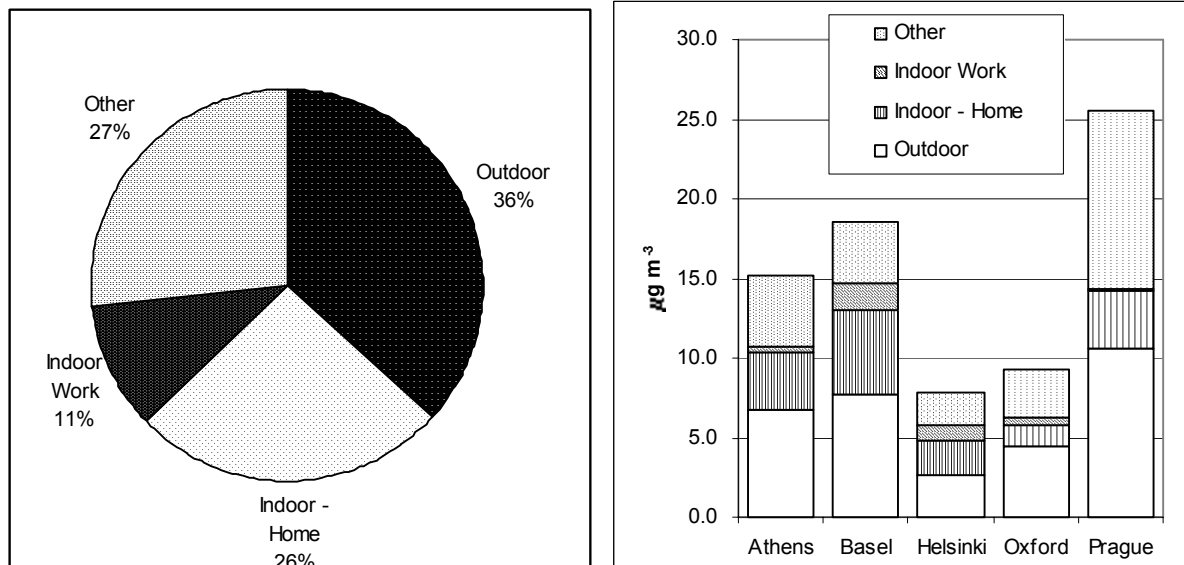
Figure 7. Contributions to personal exposure to m,p-xylene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities.

Trimethylbenzenes
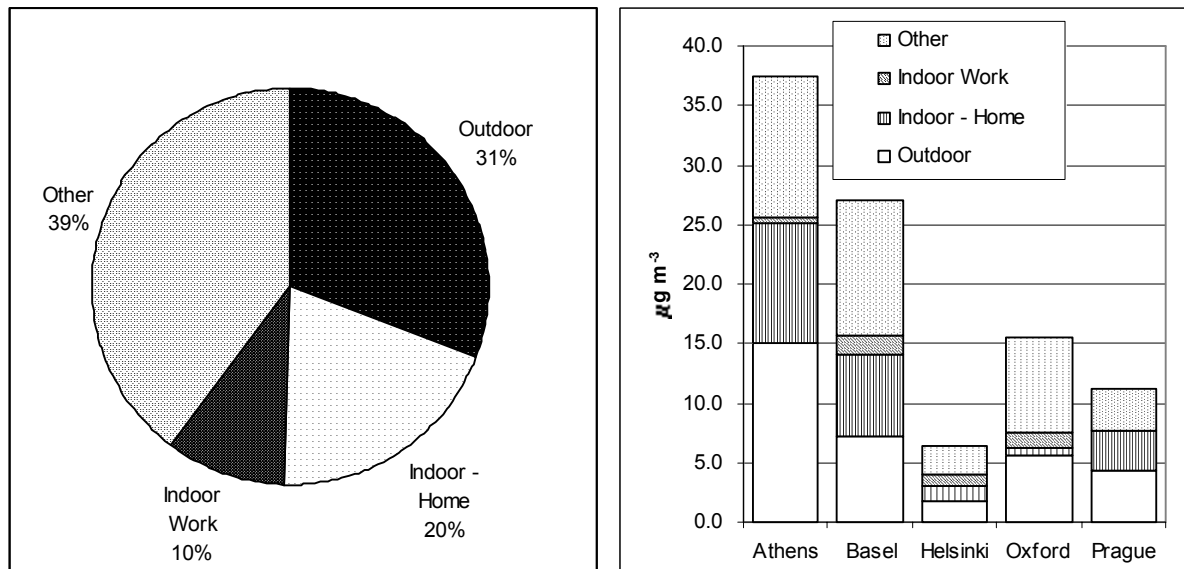
Figure 8. Contributions to personal exposure to trimethylbenzenes from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities.

ethylbenzene
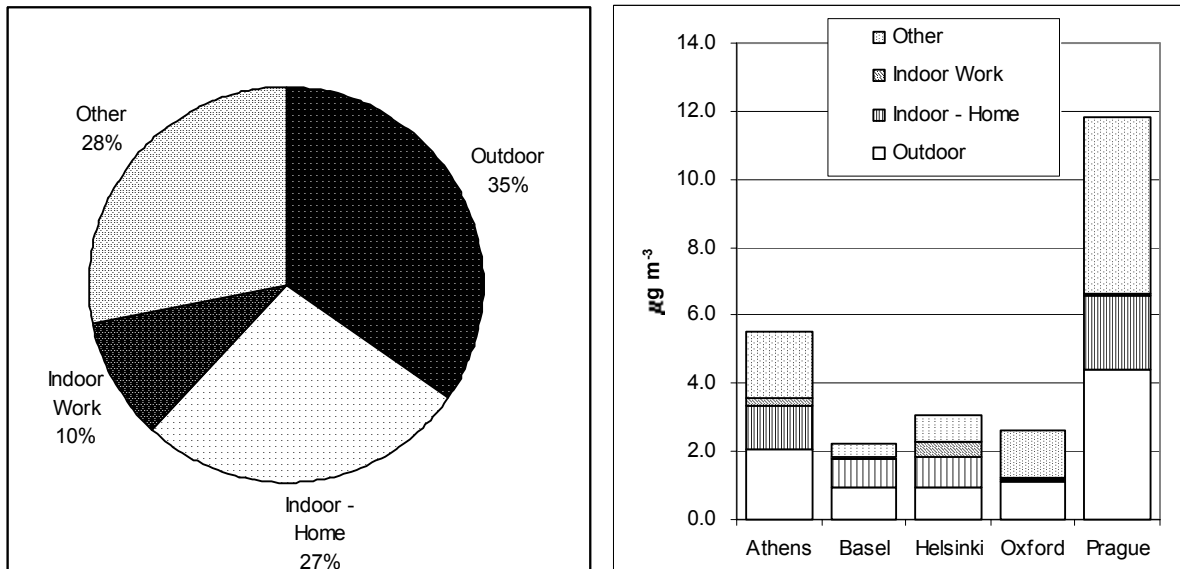
Figure 9. Contributions to personal exposure to ethylbenzene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities

nonane
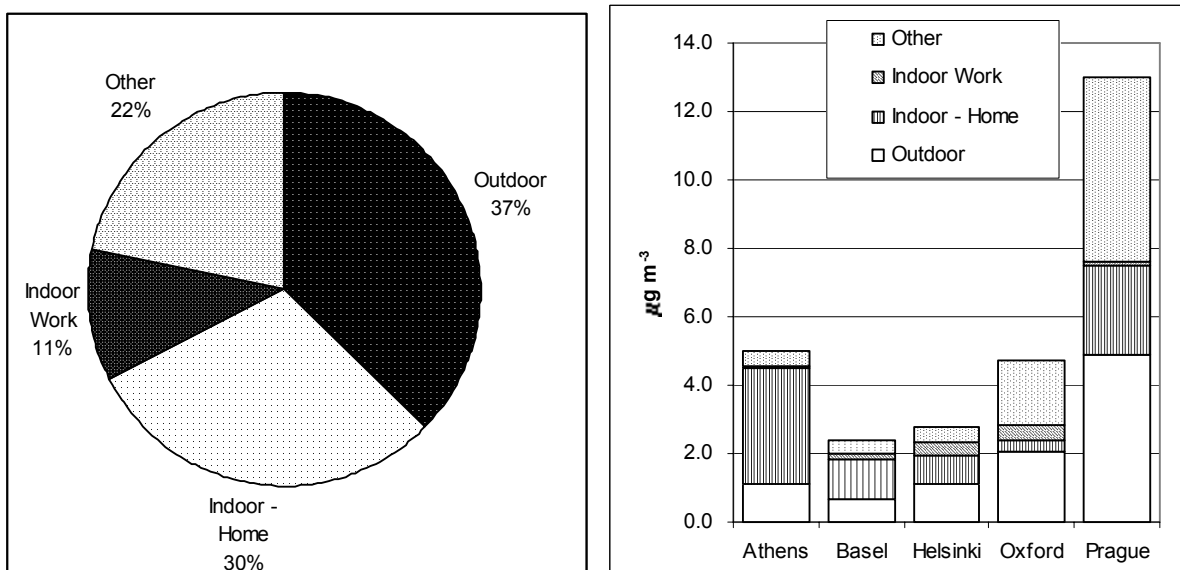
Figure 10. Contributions to personal exposure to nonane from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities

decane
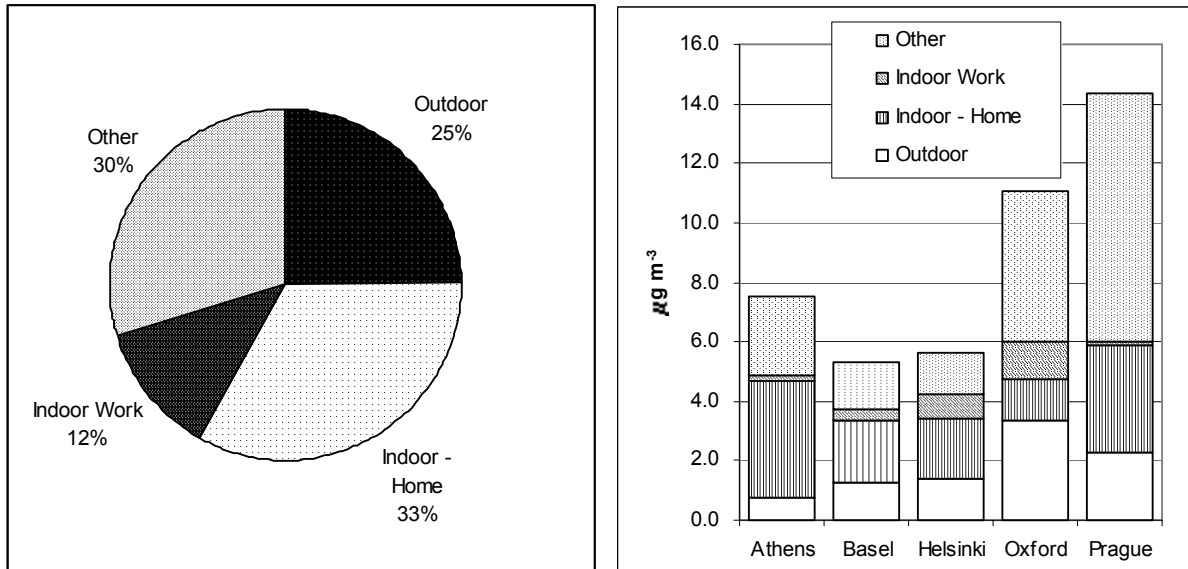
Figure 11. Contributions to personal exposure to decane from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities
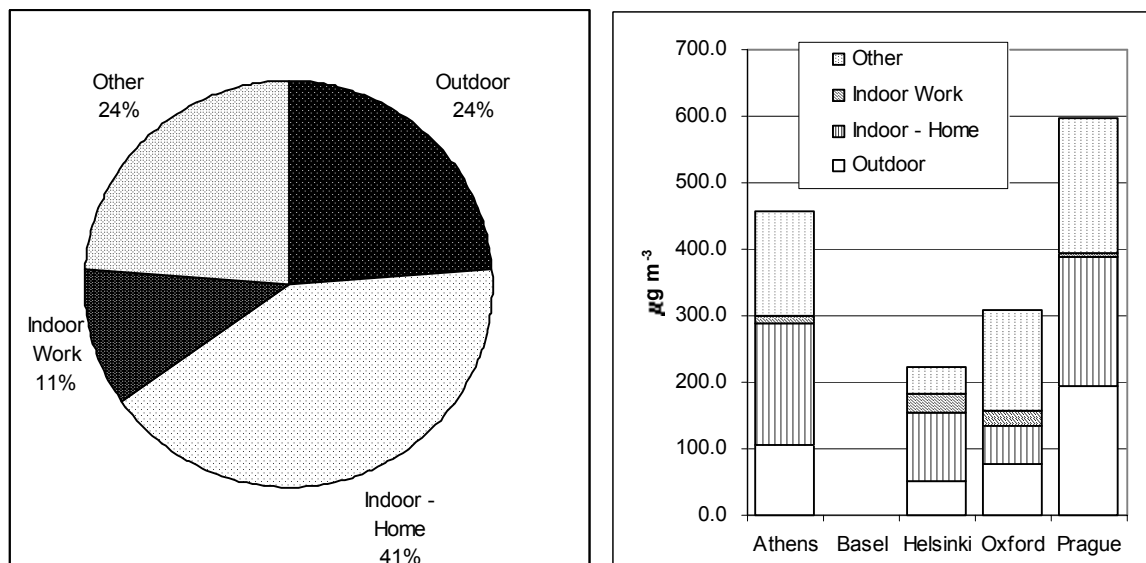
undecane
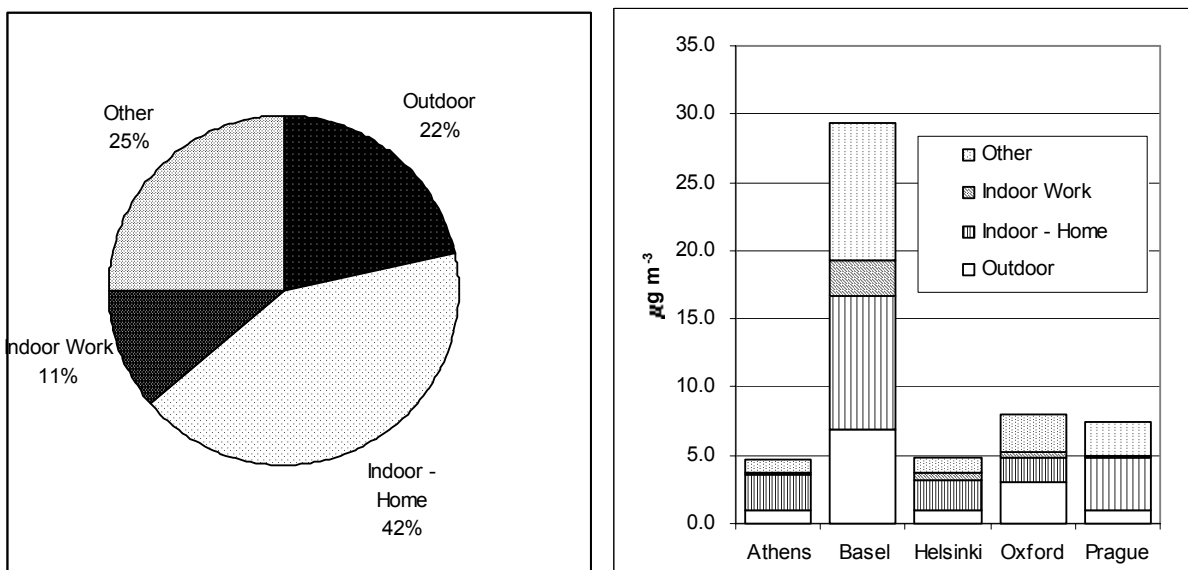
Figure 12. Contributions to personal exposure to undecane from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities

benzaldehyde
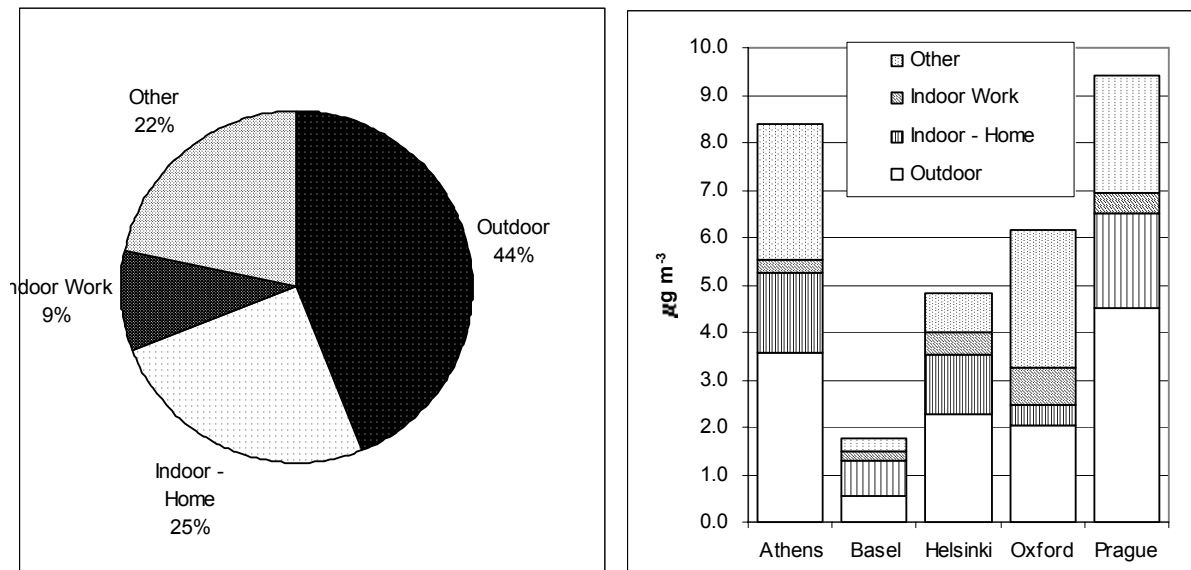
Figure 13. Contributions to personal exposure to benzaldehyde from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities
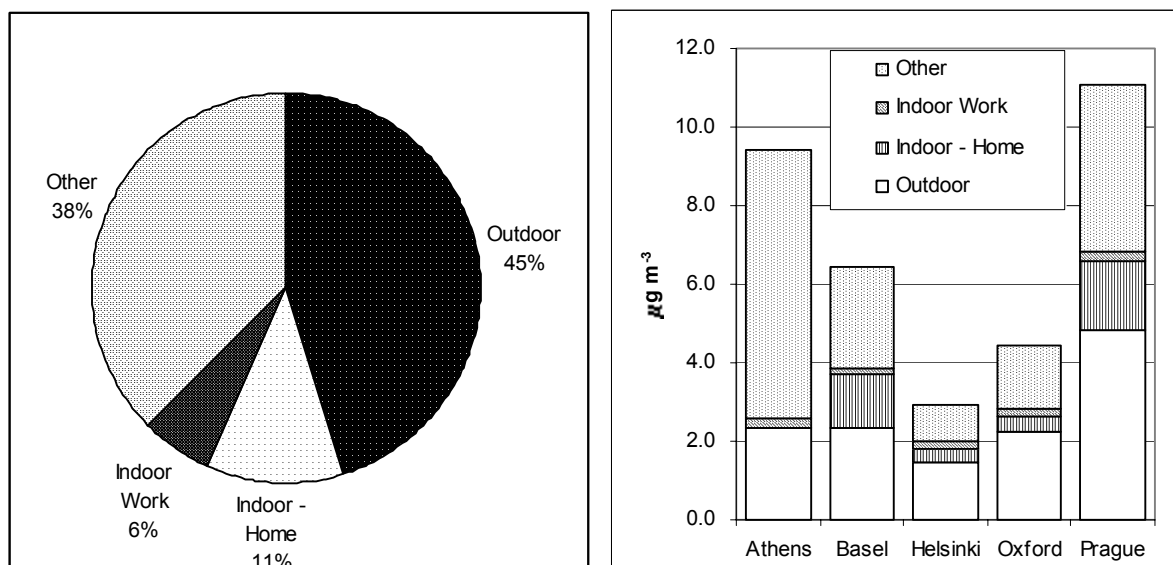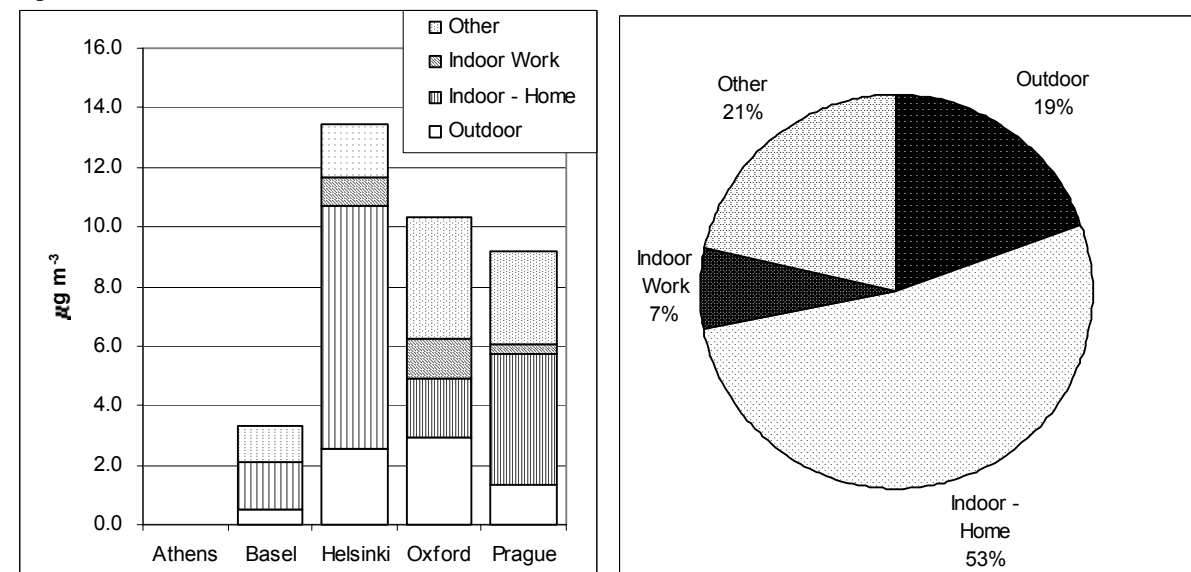
α-pinene

Figure 14. Contributions to personal exposure to α-pinene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities
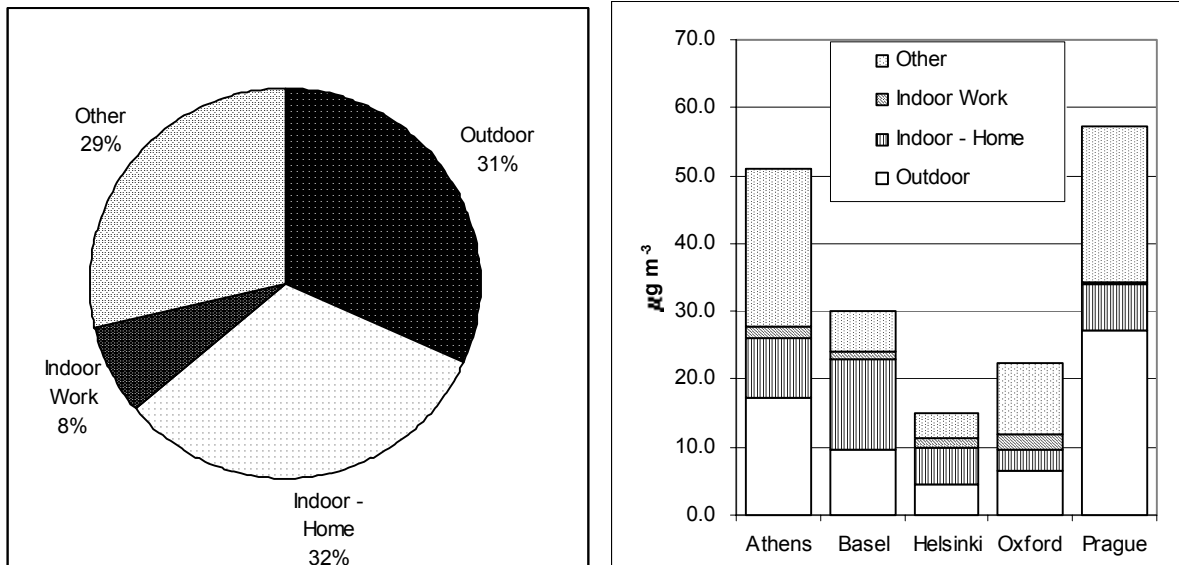
3-carene
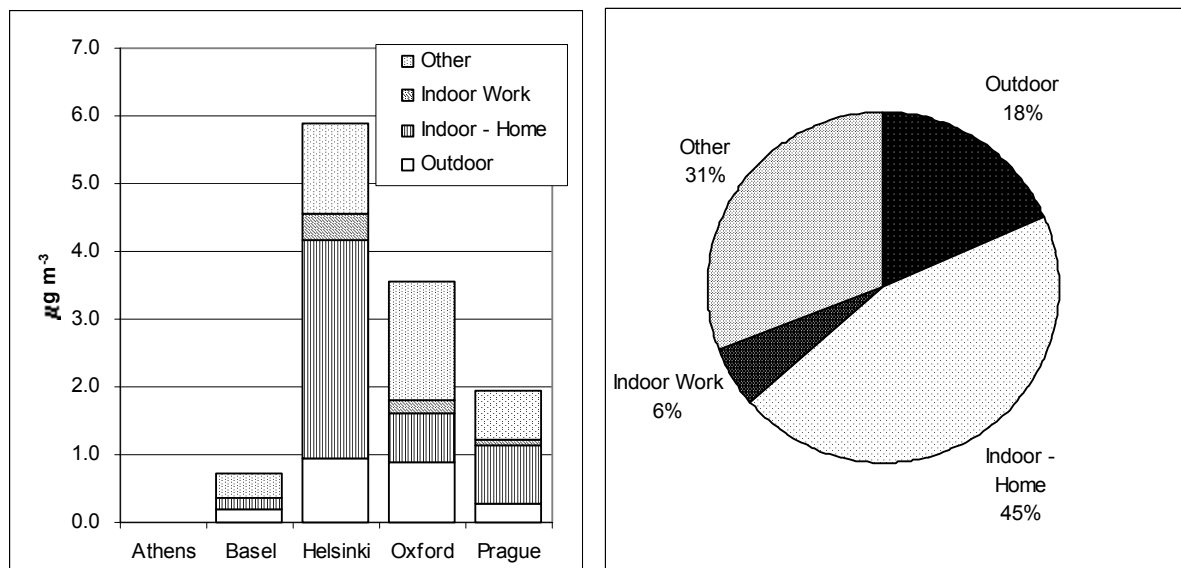
Figure 15. Contributions to personal exposure to 3-carene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities

d-limonene
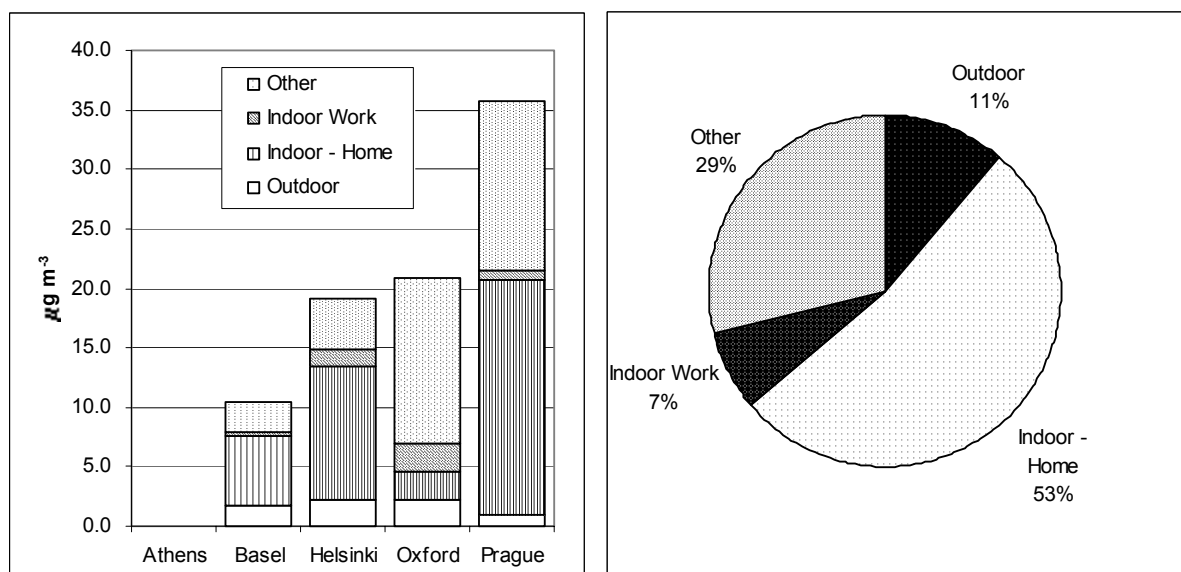
Figure 16. Contributions to personal exposure to d-limonene from different microenvironments, calculated from equations 8-11, as aggregate percentage and as exposure concentrations for individual cities

## 3.2. *Comparisons*

The contributions to personal exposure from sources in different MEs follow a common pattern (Figures 3-16), in spite of a considerable variability both across cities and compounds. In general, home, outdoor, and balance components all contribute substantially to determining personal exposure. The contribution of sources in the workplace, on the other hand, is consistently smaller (typically about 10%) in all cities and for all compounds.

Home indoor sources contribute significantly to exposure for almost all compounds, especially terpenes, about half of which appears to be generated indoors in most cities, except Oxford. A similar dominant role (40%) is apparent for TVOC. The smallest indoor contributions is seen for benzene in Athens, Helsinki, and Oxford (less than 10%), but it is nevertheless substantial for Basel (20%) and Prague (15%).

The balance of these contributions to personal exposure, representing all the other MEs (plus the error), is quite large (20-30%) in most cases, especially for aromatics. For the participants in Prague, in particular, and to a lesser extent in Athens, this component represents a major fraction of the exposure. No correlation was found between the magnitude of this component and the amount of time participants spent traveling, either by car or by all transportation means.

3.3. Sorption

The larger the proportion of cases where a net sorption is observed, the larger the possible margin of overestimation for the outdoor generated component, and conversely, for underestimation of the indoor components. As a measure of this bias, Table 2 reports the total number of cases for each compound in each city and the number of cases in which net sorption was observed. The number of cases left for the analysis is in many cases quite small, except in the case of Helsinki, where more samples were collected. A large proportion of cases indicates net sorption for some compounds such as benzene and nonane. For workplaces, it cannot be rigorously assumed that net sorption was taking place where the concentration indoors was greater than outdoors, as the home outdoor concentration gave only a general indication of the actual level. For cases of net sorption, it is possible to estimate the relative magnitude of sorption (plus decay) vs. air exchange from equation (1.3) as a lower bound, the absence of indoor sources being the limit case of equality

$$\frac{k}{a} \geq \frac{C_o - C_i}{C_i} \qquad\qquad (1.12)$$

(Cases with net emissions are not informative, since the ratio is negative; we already know the lower bound is at least zero). This value is only calculated for the home indoor environment, since it cannot be meaningfully estimated in the case of workplaces. The average lower-bound values of this ratio (Table 1.2) are typically between 1 and 10 for most compounds and cities. In the cases of terpenes, of course these values reflect both sorption and reaction; however, their lower bound estimates do not display higher values than for less reactive compounds.

In general, the number of cases where net sorption was observed is quite small. For some compounds, especially in Athens and Prague, the small numbers of total cases makes it impossible to determine whether cases with net sorption simply represent isolated outliers or a fraction of the population. For the purposes of this analysis, it is sufficient to register their existence. A pattern of correspondence between home and workplace scenarios is discernible in several cases, indicating that high outdoor concentrations, rather than low indoor ones, drive these cases.

The highest proportion of cases with net sorption is observed for benzene, consistently across cities. The homes in Oxford typically show the highest fraction of such cases, and ratios of k/a show a greater consistency. The lowest occurrence of net sorption is observed for toluene and terpenes.

The magnitude of the lower bounds estimates for k/a is consistent with estimates made in the scale analysis of equation 1.2 in the *Introduction*. Assuming values of about 1 h^{-1} for air exchange, sorption (plus reaction) rates would exceed values typically of 0.1 to 10 h^{-1}, depending on the VOCs and the city. As these are lower bound estimates that do not account for any indoor sources, actual values are in fact larger.

Table 1.2. Frequency of cases where net sorption was observed vs. total cases for each VOC and city. The bias from Approximation II is more significant where this frequency is higher. The mean lower-bound estimate of the ratio *k/a* indicates the relative magnitude of sorption (and reaction) vs. air exchange. (C_{hi} = home indoor concentration, C_o = home outdoor concentration, C_{wi} = workplace indoor concentration).

	n Tot	n $C_{hi} < C_o$	Home k/a $\geq$	n $C_{wi} < C_o$	n Tot	n $C_{hi} < C_o$	Home k/a $\geq$	n $C_{wi} < C_o$
			Benzene				Toluene	
Athens	10	3	0.29	1	6	1	0.01	0
Basel	14	4	0.64	1	15	0		0
Helsinki	62	26	1.50	20	72	2	1.70	15
Oxford	12	6	3.53	3	10	4	4.30	1
Prague	6	1	0.27	1	6	1	0.03	2
			o-xylene				m,p-xylene	
Athens	4	0		2	6	1	0.14	1
Basel	15	0		8	16	0		0
Helsinki	25	4	0.82	3	76	5	1.08	11
Oxford	7	3	1.71	5	8	3	4.40	1
Prague	6	1	0.41	4	6	1	0.33	2
			trimethylbenzenes				Ethylbenzene	
Athens	7	2	0.74	0	4	0		0
Basel	14	2	0.42	0	14	0		0
Helsinki	32	5	1.43	5	62	6	0.27	9
Oxford	14	6	1.09	3	7	3	4.53	2
Prague	6	2	0.32	2	6	1	0.21	2
			nonane				decane	
Athens	2	0		0	4	0		0
Basel	13	0		1	13	0		0
Helsinki	41	9	1.66	12	53	7	1.73	5
Oxford	11	5	3.89	1	12	2	21.33	1
Prague	6	0		2	3	0		0
			undecane				benzaldehyde	
Athens	4	0		0	6	2	0.74	0
Basel	12	0		0	9	2	0.42	0
Helsinki	64	3	0.40	7	61	5	1.43	5
Oxford	10	4	2.62	1	9	6	1.09	3
Prague	6	0		0	5	2	0.32	2
			α-pinene				3-carene	
Athens	1	0		0	1	0		0
Basel	10	1	3.58	1	5	2	5.89	0
Helsinki	47	3	0.15	2	40	3	0.23	3
Oxford	11	1	5.43	0	12	2	3.35	1
Prague	5	0		0	4	0		0
			d-limonene				TVOC	
Athens	4	0		0	6	0		0
Basel	13	1	0.11	2	n.a.			
Helsinki	64	2	0.08	5	68	2	1.30	6
Oxford	10	2	10.95	0	11	2	4.73	1
Prague	6	0	0	0	6	1	0.07	0

4.   Interpretation

The fact that sources located outdoors, in the home and in other MEs all make important, but variable, contributions means that multiple strategies could reduce personal exposure. The optimal strategy would need a discussion of the actual sources as well as economical and practical considerations. We will instead focus mainly on home indoor sources, as the most susceptible to changes by individual choices.

The outdoor contributions naturally reflect the prevailing air pollution levels in the different cities that have been previously described (Saarela et al., 2003) with respect to VOCs. These levels are highest in Athens and in Prague and lowest in Helsinki, especially for aromatics. As noted, samples from Prague are representative only of the downtown area, rather than the whole city, which may help to explain the high levels observed, particularly for traffic-related compounds.

Sources in the workplace were found to contribute much less to personal exposure. This is in spite of a bias that tends to the overestimation of this particular contribution, as discussed below (4.3). Though perhaps unexpected, this is the result of the presence in the population of individuals who do not work, work part-time, or work from home. Indeed, since the study only included adults, the effects of this ME may be even lower in the general population.

It must be stressed, however, that workplace exposure in the EXPOLIS population is not necessarily representative of that in the general population, as the high-exposure workplaces were deliberately excluded from sampling. In addition, an enrollment bias may be present, since participation in the study may have been influenced by the employers' consent, arguably less forthcoming in situations where air pollution levels may be higher. In fact, individual circumstances at work may be very different from the general findings, and some of the peak concentrations (not detailed in this paper) of alkanes and terpenes were in fact found in workplaces. Overall, in the light of these observations, it would seem that equal attention in indoor air quality research should be given to both residential and commercial buildings, at least from the standpoint of public health.

Traffic is among the sources most likely to make up the balance component of personal exposure. The study participants in all cities, in fact, reported spending in transit about 40% of the time outside home and workplace (Schweizer, 2003). The high contributions of this component for all aromatics, alkanes, and benzaldehyde would find in this source a reasonable explanation and has been previously observed (Edwards et al., 2001b; Edwards and Jantunen, 2001). The lack of correlation between this exposure component and the time spent traveling can be expected, as traveling does not necessarily imply time in intense traffic. If traffic is indeed a source for this component, the low correlation would point to exposure scenarios with high concentrations and short exposure times. For terpenes, this contribution must be explained by sources in other indoor MEs, or by use of scented products very close to the individual. These sources may also be involved for other compounds, of course, and especially benzaldehyde used in personal care products (almond oil). Caution must however be exercised in interpreting the balance of exposure, as all the measurement errors will also be grouped in this fraction.

4.1. Indoor contributions

Home indoor sources proved important for all the VOCs considered, with the notable exception of benzene, a reassuring finding in terms of potential risks. Yet, even exposure to benzene, presumably a heavily scrutinized compound in building materials and consumer products, owes a non-trivial fraction to sources in the home in Basel and Prague. A country-specific variability in exposure to compounds whose primary sources are indoors has been previously reported (Edwards et al., 2001a). The known list of possible indoor sources include attached garages, smoking guests, hobby materials, gas combustion (Ilgen et al., 2001a), charcoal combustion (Mugica et al., 2001), and wood burning

(Hedberg et al., 2002). No differences in garage presence, coal or wood use for heating between the cities were found, based on questionnaire responses. Particleboard off-gassing may be another possibility (Glass L.R. et al., 1986) and might be an explanation for Basel, that has significantly more chipboard walls than other cities. Desorption of outdoor-generated molecules from indoor surfaces and materials may also be part of the explanation, since the small number of cases, especially in Prague (*n* = 6), does not guarantee that the assumption of sorption/desorption averaging is met. This possibility is to be kept in mind for all other VOCs whenever the sample size is small (Table 2).

Similar possible indoor sources are to be found for other BTEX compounds (benzene, toluene, xylenes, and ethylbenzene). They include combustion, but also building materials, solvents, air fresheners and pesticides (Buhamra et al., 1998). Cleaning activity has also been indicated as a source of benzene and BTEX in Hong Kong homes (Guo et al., 2003). A multiplicity of small contributions from several sources seems likely in each home. In a very comprehensive study of aromatic compounds in indoor and outdoor environment, in fact, Ilgen *et al.* (2001b) could not identify specific building materials associated with elevated aromatics concentrations. A clearer understanding of these indoor sources still requires specific investigation.

Information on indoor sources of the selected alkanes is rather sparse. Cooking has been connected especially with nonane (Mugica et al., 2001) and decane (Srivastava et al., 2000), albeit in contexts that are different from typical European kitchens. Flooring materials have also been described among the sources (ECA-IAQ, 1997), particularly polypropylene fiber carpets and waxes on wood floors (Tucker, 2001). Other indoor sources may be possible, as it is clear that the residential ME is responsible for a large fraction, when not most, of the personal exposure to these compounds.

Indoor terpene sources account for the majority of personal exposure. This is in spite of the fact that reaction rates, which are very significant for these compounds, were not considered in the model. The actual ratios of indoor/outdoor contributions are in fact larger than shown in Figure 4, if the rates given in Table 1 are taken into account. Alpha-pinene and d-limonene are notorious fragrance components in a number of household products (particularly air fresheners) and 3-carene is emitted from wood (Manninen et al., 2002), among other sources. From questionnaire responses, there are no clear differences in the use of air fresheners between the cities. While high indoor concentrations of these compounds are therefore not surprising and rather harmless in themselves, terpene reactions with active species (e.g. ozone, nitric oxide) in the indoor environment result in carbonyl byproducts and strong oxidants that may deteriorate indoor air quality (Sarwar et al., 2002; Weschler et al., 1992).

4.2. Sorption and desorption

The importance of sorption/desorption processes is demonstrated by the range of values calculated for *k/a*, the lower bound of the removal vs. air exchange rates. For the less-reactive compounds, these numbers, in fact, are incompatible with the reaction rates given in Table 1.1, by orders of magnitude. The case of benzene in Helsinki is exemplary, for even at an unlikely air exchange rate of only 0.1 h^{-1}, removal rates exceed atmospheric reaction rates by three orders of magnitude. The large role of sorption in determining indoor concentrations dynamically has been specifically demonstrated (Schlitt and Knöppel, 1997), with longer lag times for the less polar compounds. House dust seems to have an important effect as a sorption/desorption surface.

It is relevant to examine whether the ability of the objects and surfaces in the indoor environment to act as temporary reservoirs for VOCs may have important consequences in terms of individual exposure. The diurnal variations in concentration typically peak in the morning and evening for traffic VOCs, and around midday for solvents (Mollmann-Coers et al., 2002). Under normal circumstances then, the home would capture part of the daytime peak and return it during the night. Indoor workplaces, on the other hand, would lower the daytime personal exposure. A further level of complexity is introduced when temperature variations are considered, since sorption is enhanced by

lower temperatures. The strength of the temperature dependence is governed by the van't Hoff law and is highly variable for different compounds (Elkilani et al., 2003; Won et al., 2001).

To reduce overall exposure, it is desirable to promote sorption when people are present and desorption when rooms are vacant. Two possible strategies may achieve this goal. Increasing the amount sorbing materials (e.g. carpets, soft furniture) in the workplace and decreasing it in homes would take advantage of the diurnal concentration cycle, by limiting both direct and delayed peak exposure. In practice, the situation is quite the opposite, with typical homes having more sorbents than typical offices or commercial establishments. Another strategy, based on temperature, would be viable in warm climates or seasons, through the shrewd use of air conditioning, letting the temperature rise when rooms are unoccupied. Conversely, a heating strategy that let temperature drop when people are not present would lead to higher exposures.

The actual significance of these sorption/desorption strategies for personal exposure depends on the magnitude of daily temperature excursion and on the day/night variability of outdoor concentrations, as well as the thermodynamic characteristics of individual compounds. Clearly, at present, these should be regarded as hypotheses for investigation in controlled conditions, trying to simulate real inhabited environments as closely as possible.

4.3. Limitations and biases

Since there are a number of approximations and possible sources of bias in this model, it is important to summarize them and discuss their impact on the results and their interpretation.

a) The outdoor concentration at the workplace was not measured, and it is replaced in this model by the home outdoor concentration. This necessary approximation introduces two biases: 1) a nighttime concentration is used for daytime conditions 2) outdoor concentrations in residential settings are used for a workplace location. The direction of both biases is likely to increase the contribution of workplace indoor-generated contributions for many compounds, as workplaces in the sample were more often located in central locations than homes, and as daytime levels of the VOCs associated with traffic are expected to be higher than at night. In spite of these positive biases, workplace-generated contributions were generally small for most compounds. Actual contributions are then likely even smaller at the population level.

b) Another source of bias is the exclusion from the analysis of all cases with a personal exposure below the limits of detection, as the results would be essentially random. This sub-population, however, does not represent the higher range of exposures in the actual non-smoking population of each city, and often consists of very few samples. Personal exposure values for the analyzed non-smoking populations, with or without the inclusion of samples below LOD, usually differed less than 10%.

c) Sample sizes were very small (less than 10) in some cases and their ability to represent the actual population of that city is correspondingly marginal. Their separation here is solely dictated by different baseline levels of outdoor air pollution. Generalizations for cross-city comparisons, in these particular cases, should not be made.

d) The approximation of no primary emissions in case of net sorption (Approximation II) introduces a bias that overestimates the outdoor contributions to the expense of the indoor ones. The small number of cases where net sorption was observed, however, generally dilutes the effects of this bias. Its effects are important however, for benzene in all cities and in general for the city of Oxford.

5.   Conclusions

Some approximations can be made to separate the contributions of different microenvironments to personal exposure. In the cities in the EXPOLIS study, sources in the home, outdoors and in other microenvironments all appeared to be important in determining VOC exposure, while workplace microenvironments consistently played a less important role. From a public health standpoint, then, more attention should be given to investigate indoor air quality in residential, rather than commercial buildings. The indoor microenvironments appeared to play a sometimes very significant role as reservoirs for outdoor-generated VOCs through sorption/desorption processes. Depending on the diurnal concentration and temperature variability, these processes could be exploited to reduce personal exposure, although the extent of this effect must be ascertained through specific research.

Part II

Intake Fractions

6.   Introduction

6.1. Rationale for Intake Fractions

Emissions from sources of air pollution set in motion a complex chain of events that may ultimately lead to observable health effects in a population. This series of events, usually considered under the collective label of "Fate & Transport", has historically been the object of traditional environmental science. The critical stages of contact between a pollutant and (human) targets, in particular, have been addressed by exposure assessment. This traditional, highly analytic approach, however, has inevitably blurred the essential, causal link between source and health effects. The need to express clearly this relationship has produced, over time, a variety of modeling approaches and a sometimes confusing terminology. Recently, the concept of Intake Fraction has been introduced and has gained acceptance as a synthetic tool to express the immediate link between source and exposure. The original definition (Bennett et al., 2002) of intake fraction (iF) is

$$iF = \frac{\text{mass intake of pollutant by an individual}}{\text{mass released into the environment}} \qquad (2.1)$$

The concept express a source to target relationship stopping at the intake level, that is, short of any toxicological consideration about absorption and distribution to specific organs and tissues. In principle, however, the concept can be readily extended to include those processes, by use of appropriate coefficients, where such information is known.

One of the advantages of this concept is, in fact, its flexibility. Intake fractions are not only adaptable in terms of cause-effect, as noted, but also in the ability to describe single or multiple sources and targets, and different time horizons. While equation (2.1) expresses the intake fraction for one individual and one source, the calculation is readily extended to a population.

Another major advantage of the use of intake fractions is the possibility of easy comparisons. Different policy scenarios and even estimates from different studies can be compared at a glance. In particular, the incremental risks can be judged directly by comparing intake fraction estimates, whenever there is a linear relationship between intake and risk. Indeed, this advantage is the main reason given for its development (Bennett et al., 2002).

6.2. Simplified formula for indoor sources

To apply this concept to indoor sources of VOCs, a further specification of the original definition is expedient. For air pollutants the definition can be put in the form (Marshall et al., 2003)

$$iF = \frac{\int_{t_0}^{\infty} C(t)Q(t)\,dt}{\int_{t_0}^{t_e} E_i(t)\,dt} \tag{2.2}$$

where t_s and t_e are the starting and ending times of the emission, $C(t)$ is the concentration, $Q(t)$ is the inhalation rate, and $E(t)$ is the emission rate. For continuous or periodic emissions, t_e is infinite and the two integrals are evaluated over the same interval t.

From mass balance equations, the emissions can be written as a function of the indoor concentration, at steady state

$$C_i(t) = \frac{E_i(t)}{V\,a(t)} \tag{2.3}$$

where C_i is the concentration of pollutant attributable to the i-th source and $a(t)$ is the air exchange rate. Moving from the continuous to the discrete domain, and substituting for the emission rate, eq. 2.2 becomes

$$iF = \frac{\sum Q_i C_i\,\Delta t}{V \sum C_i a_i\,\Delta t} \tag{2.4}$$

Using the definition of average, one can write

$$iF = \frac{\overline{QC}}{V\,\overline{aC}} \tag{2.5}$$

Recalling the definition of covariance as the average of a product minus the product of the averages, 2.5 can be written as

$$iF = \frac{\overline{Q}\cdot\overline{C} + \mathrm{cov}(Q,C)}{V\left(\overline{a}\cdot\overline{C} + \mathrm{cov}(a,C)\right)} \tag{2.6}$$

if both covariances are small compared to the respective products of the means, the expression can be approximated by

$$iF \approx \frac{\overline{Q}}{V\,\overline{a}} \tag{2.7}$$

which is independent of the concentration of the compounds. This simplified formula to calculate intake fractions of indoor air pollutants is also hinted to in the original intake fractions definition (Bennett et al., 2002), in calculating intake fractions of Environmental Tobacco Smoke.

In practice, the covariance terms will be small when one variable changes little with respect to the other. Note that two variables may be highly correlated and still have a very low covariance compared to the product of their means (Fig. 17). A detailed discussion of the approximation errors introduced by neglecting the covariance terms is given in Appendix A.
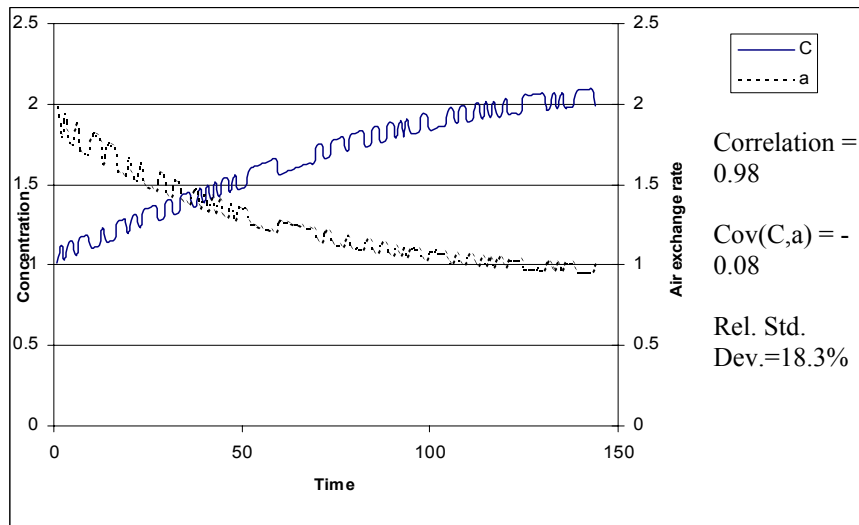
Figure 17. Hypothetical evolution of concentration (C) and air exchange rate (a), over time, in arbitrary units. Concentration is inversely proportional to air exchange rate, with random perturbations. Note that, in spite of the high correlation, the approximation error produced by using the averages and neglecting the covariance remains quite small.

Because people spend only part of their time in a particular indoor environment, a further correction must be applied to equation 2.7, for continuous sources

$$iF \approx f \frac{\overline{Q}}{\overline{V}\overline{a}} \tag{2.8}$$

where f is the fraction of the time spent in that particular indoor environment. This correction applies only for continuous sources and only under the condition that concentration are not substantially different when a person is present or not in a particular microenvironment. Other sources, such as cooking, depend on the individual's presence. For these sources, the correction by the fraction spent at home may be less accurate. However, compounds emitted during cooking may linger indoors longer than the individual might stay there, perhaps participating in sorption/desorption interactions with the indoor environment.

7.   Methodology

7.1. Modeling approach

The four factors that determine intake fractions in equation 2.8 have complex, sometimes highly skewed, frequency distributions. The resulting intake fractions are therefore likely to have as wide a range of values in a population. An estimate focusing only on the central value (mean, median,…) would provide only a very limited picture of intake fractions from indoor emissions in the cities of interest. A complete distribution of intake fraction values in the selected populations would provide a more complete understanding of the internal heterogeneity of the populations in this respect. This information could be used, in particular, to identify "problem" situations.

Although desirable, this task presents some challenges. Even discounting the complexity of combining several statistical distributions, in some cases the actual distributions are not clearly characterized. These facts make it impossible to derive analytically a frequency distribution of the intake fractions. A numerical simulation approach is therefore necessary.

Monte Carlo models are routinely used in exposure and risk analysis in analogous situations, to model the distribution of dependent variables based on distributions of the associated independent variables. A Monte Carlo model simulates a real population by sampling values of the independent variables and calculating the correspondent values of the dependent variables, for a fixed but large number of times. Values of the independent variables are sampled according their specified probability distributions, which constitute the input of the model. In the end, a population of values of the dependent variable is created, that has a frequency distribution similar to that in the actual population.

7.2. Description of input variables

The distributions of factors used to model intake fractions based on equation 2.8 had different origins. Some distributions were taken from the literature, while some others were obtained by fitting the data available in the EXPOLIS database. The latter were chosen based on the Kolmogorov-Smirnov (K-S) statistic. This statistic is free from the arbitrariness of the chi-squared statistic, but is not very discriminating in detecting differences at the tails of the distributions (Palisade Corp., 2000). Furthermore, a p-value cannot always be computed exactly for this statistic. To take into consideration differences far from the center, chi-squared statistics were also computed. Any discrepancy between the two statistics in ranking the fit of distributions is noted in the description of the individual distributions. The p-value associated with the statistics (if computable) is the probability associated with the null-hypothesis that the observed distribution was generated by the continuous distribution being tested. Low p-values indicate that the hypothesis must be rejected, as there is little agreement between the two distributions.

Fraction of time at home

Distributions for the fraction of time spent at home was obtained directly from the EXPOLIS time-activity data. The total time spent indoors at home at home (field *hi* in table *TMAD total minutes*) was divided by 48 hours. The entire data set available in EXPOLIS was used, including the individuals who were not part of the exposure sub-sample. The individual distributions for each city are shown in Figures 18 to 22.

Athens

Distribution:	Normal
Parameters:	Mean $\mu = 0.635$ Std. Dev. $\sigma = 0.183$
Fits Statistics:	K-S = 0.42 p >0.15 X^2=3.6 p = 0.963
Comment:	This continuous distribution fits the data adequately
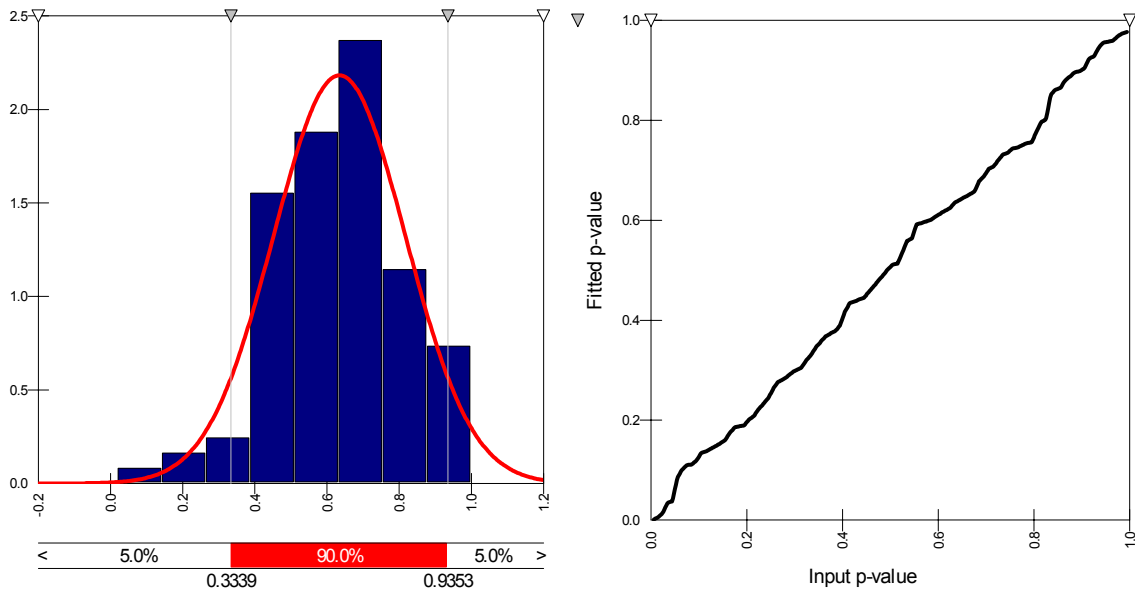
Figure 18. Distribution fit of EXPOLIS data for the fraction of time spent at home in Athens.

Basel

Distribution:	Loglogistic
Parameters:	location γ = -0.537 scale β = 1.0899 shape α = 13.813
Fits Statistics:	K-S = 0.056 X^2=29.9 p = 0.031
Comment:	The fit of a log-logistic distribution is marginal according to the chi-squared statistic; note the sharp change in the steepness of the curve at high p-values
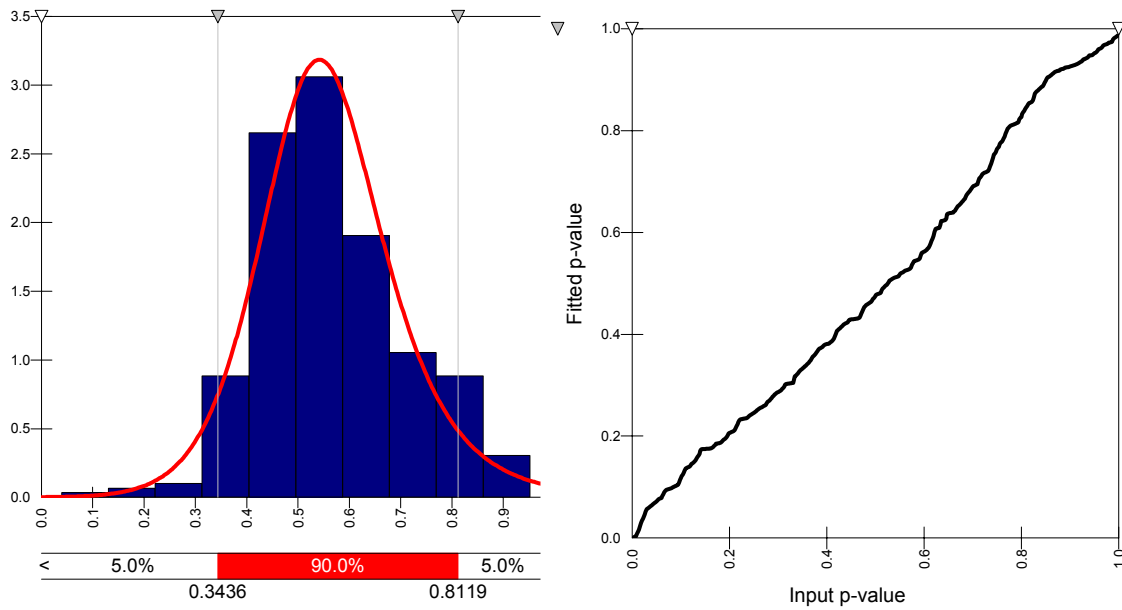
Figure 19. Distribution fit for the fraction of time spent at home in Basel.

Helsinki

Distribution:	Loglogistic
Parameters:	location γ = -0.0558 scale β = 0.6063 shape α = 9.5322
Fits Statistics:	K-S = 0.0724 p>0.15 X^2=61.1 p = 0.000
Comment:	The fit of a log-logistic distribution is poor according to the chi-squared statistic; but acceptable for the K-S statistic, more important as discrepancies are near the center of the distribution
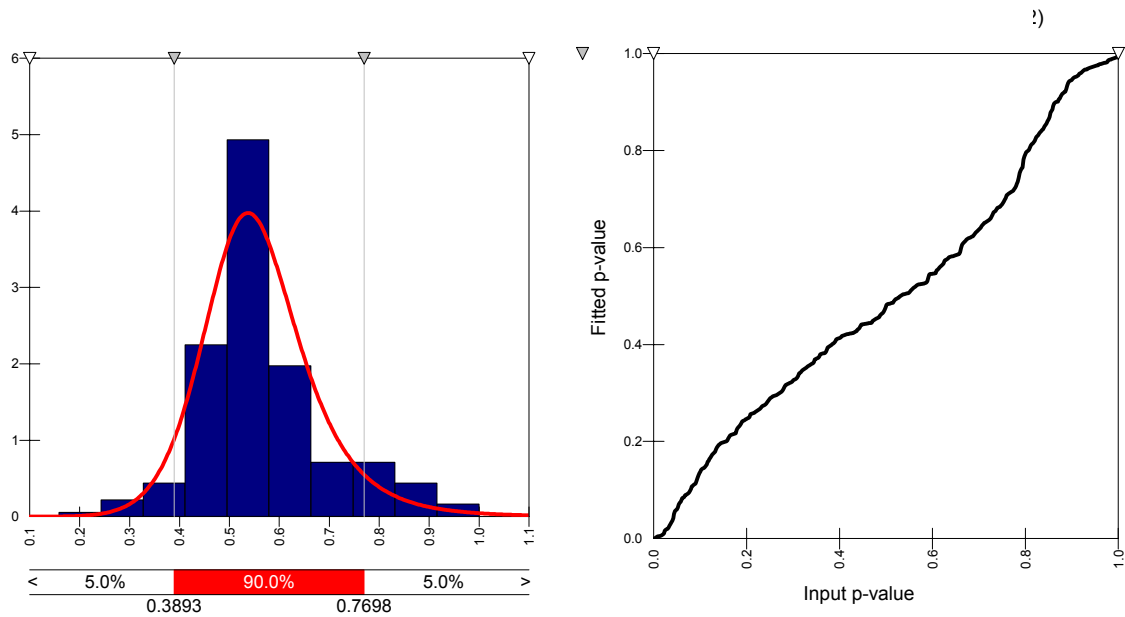
Figure 20. Distribution fit for the fraction of time spent at home in Helsinki.

Oxford

Distribution:	Normal
Parameters:	Mean $\mu = 0.625$ Std. Dev. $\sigma = 0.157$
Fits Statistics:	K-S = 0.0687 p >0.15 X^2=8.4 p = 0.679
Comment:	This distribution fits the data accurately
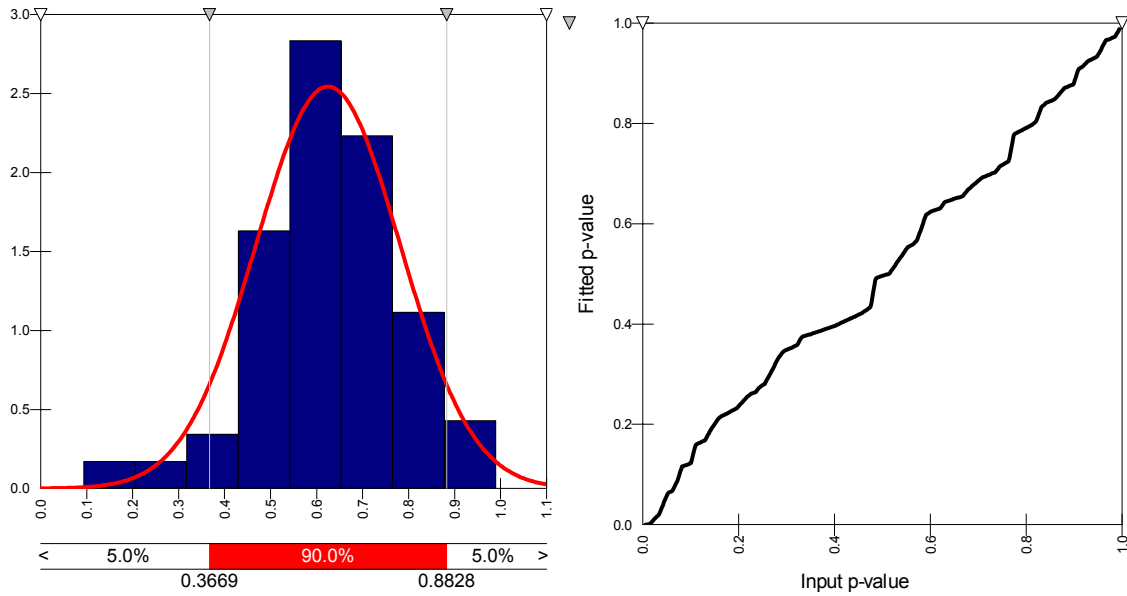
Figure 21. Distribution fit for the fraction of time spent at home in Oxford.

Prague

Distribution:	Loglogistic
Parameters:	location γ = 0.0853 scale β = 0.4804 shape α = 6.0911
Fits Statistics:	K-S = 0.0758 X^2=11.4 p = 0.248
Comment:	This continuous distribution fits the data adequately
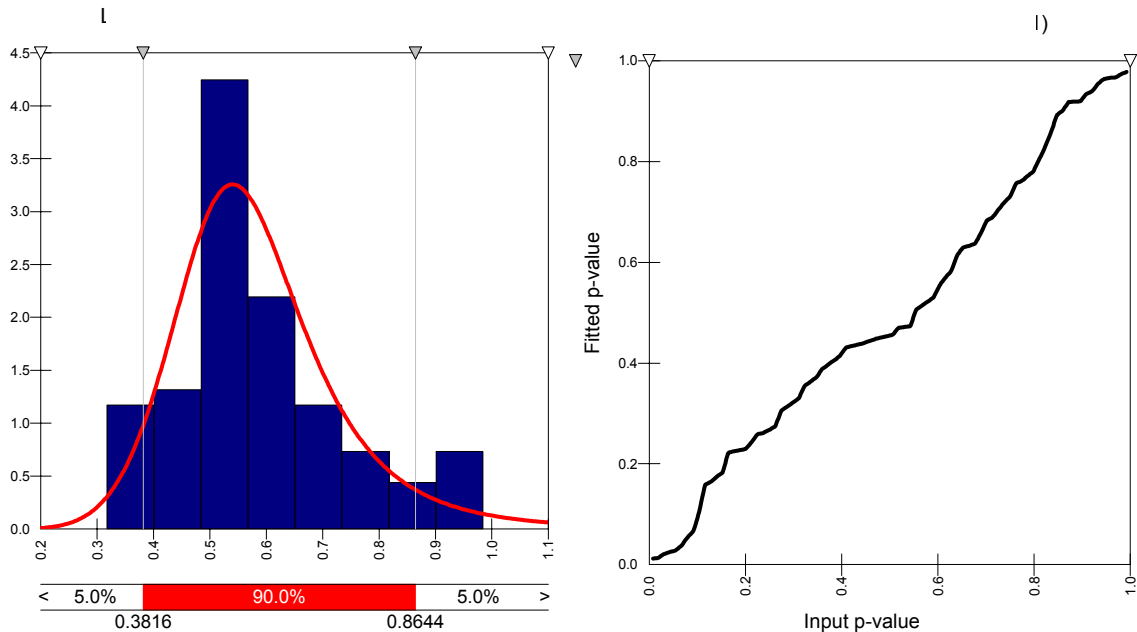
Figure 22. Distribution fit for the fraction of time spent at home in Prague.

Residential flow rate

The distributions of flow rates in the sampled residences was calculated as the product of the residence volume in the data base and the air exchange rates calculated by Hänninen *et al.* (2004), for each individual residence available. These air exchange rates were calculated by regression of indoor vs. outdoor sulfur concentrations in PM$_{2.5,}$ measured during the EXPOLIS study. The air exchange rate estimates were available for all cities except Oxford, for which an alternate method was used.

The flow rate values used in the simulation were limited to a minimum of 2 m^3/hr (corresponding typically to an AER of about 0.01 hr^{-1}) to prevent unrealistic situations leading to meaningless intake fractions above 1. As a consequence, the upper extremes of the intake fraction distributions may be very dependent on this arbitrary choice and should not be taken at face value. This possibility is discussed for the distributions modeled for each city in section 8.4.

Athens

Distribution:	Loglogistic
Parameters:	location γ = 86.781 scale β = 170.14 shape α = 1.9326
Fits Statistics:	K-S = 0.0632 X^2=3.29 p = 0.656
Comment:	This continuous distribution fits the data adequately
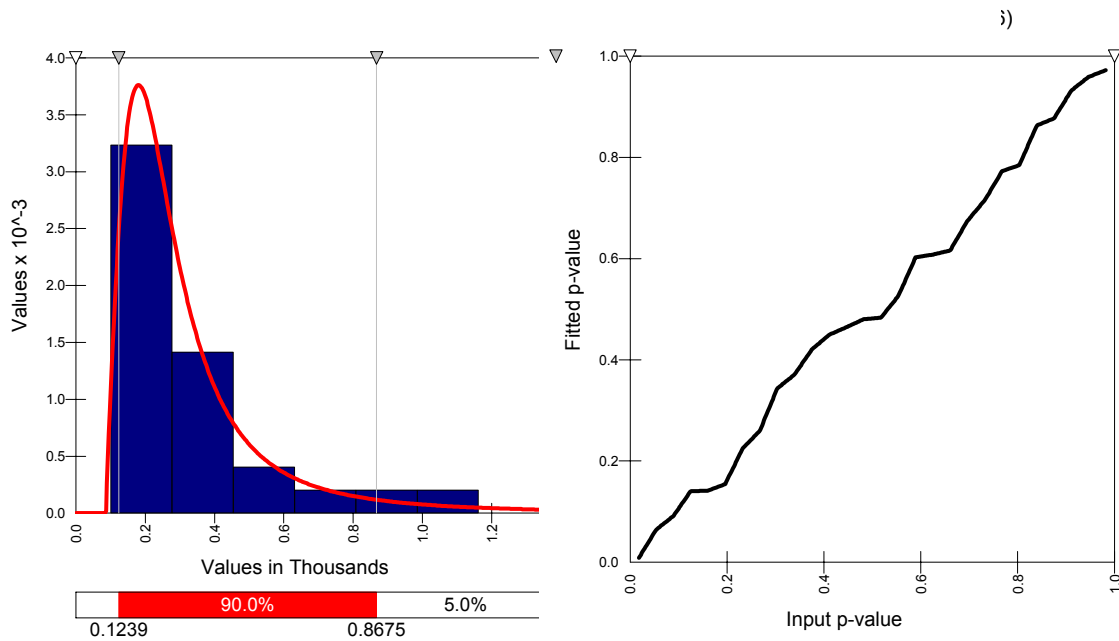
Figure 23. Distribution fit for the residential flow rate in Athens, from EXPOLIS data, as calculated from (Hänninen et al., 2004). Units in m^3 hr^{-1}.

Basel

Distribution:	Loglogistic
Parameters:	location $\gamma = 17.771$ scale $\beta = 150.90$ shape $\alpha = 2.1667$
Fits Statistics:	K-S = 0.0758 X^2=0.8 p = 0.977
Comment:	This continuous distribution fits the data adequately
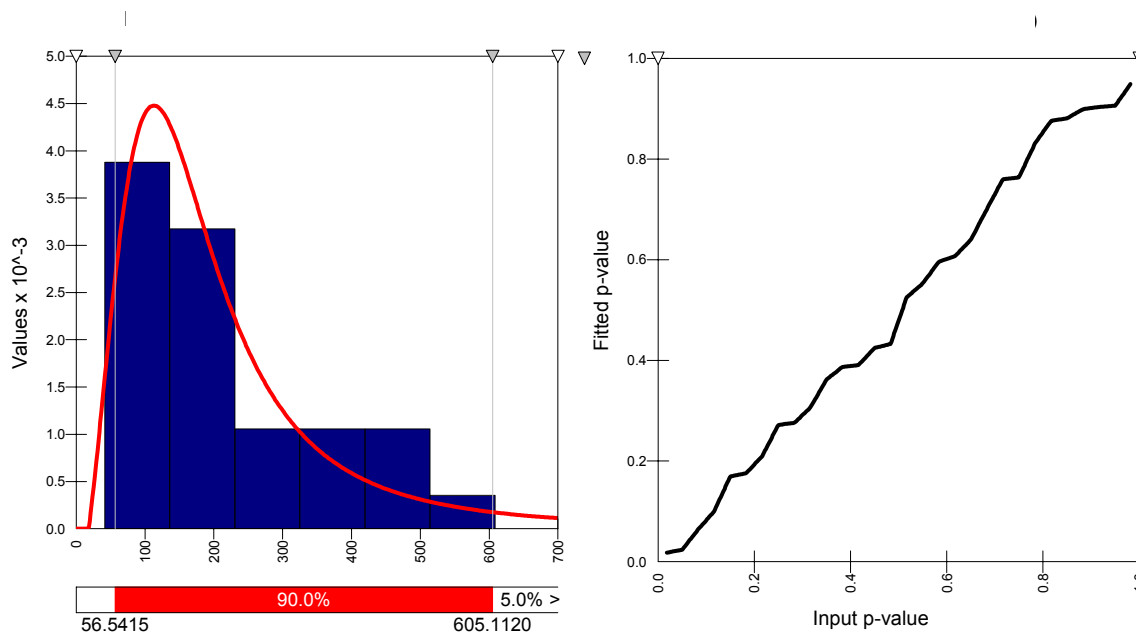
Figure 24. Distribution fit for the residential flow rate in Basel, from EXPOLIS data, as calculated from (Hänninen et al., 2004). Units in $m^3 hr^{-1}$.

Helsinki.

Distribution:	Lognormal
Parameters:	Mean of normal μ = 4.874 std. dev. of normal σ = 0.8234
Fits Statistics:	K-S = 0.0527 X^2=3.39 p = 0.947
Comment:	This continuous distribution fits the data adequately

Figure 25. Distribution fit for the residential flow rate in Helsinki, from EXPOLIS data, as calculated from (Hänninen et al., 2004). Units in m³ hr⁻¹.

Prague

|	
Distribution:	Extreme value
Parameters:	Location a = 144.327 Shape = 92.019
Fits Statistics:	K-S = 0.121 X^2=0.125 p = 0.939
Comment:	This continuous distribution fits the data adequately

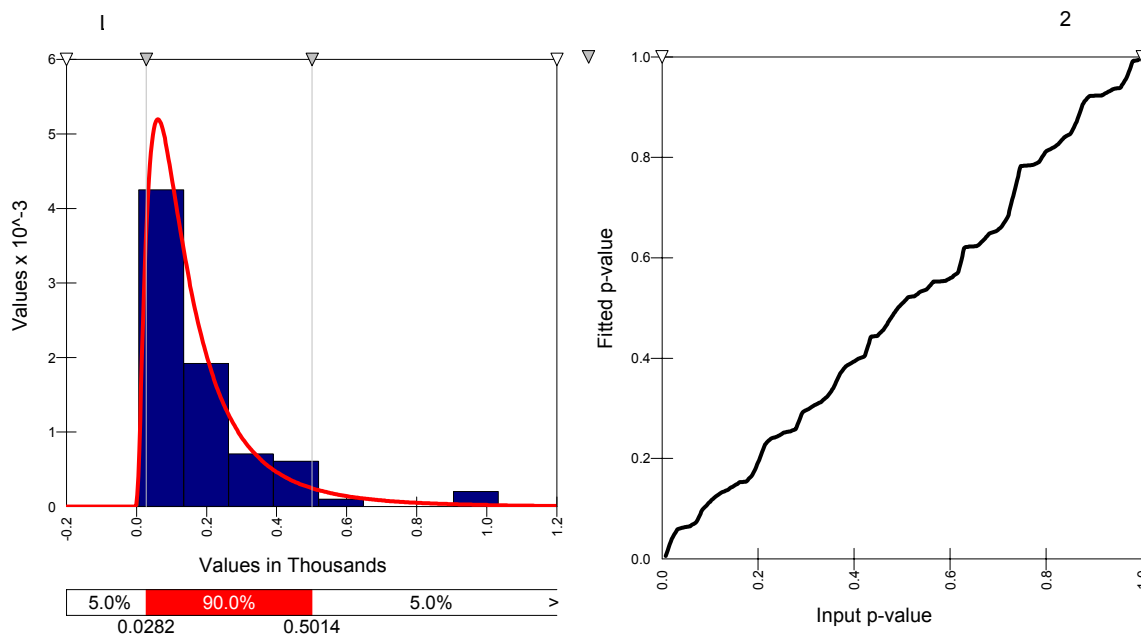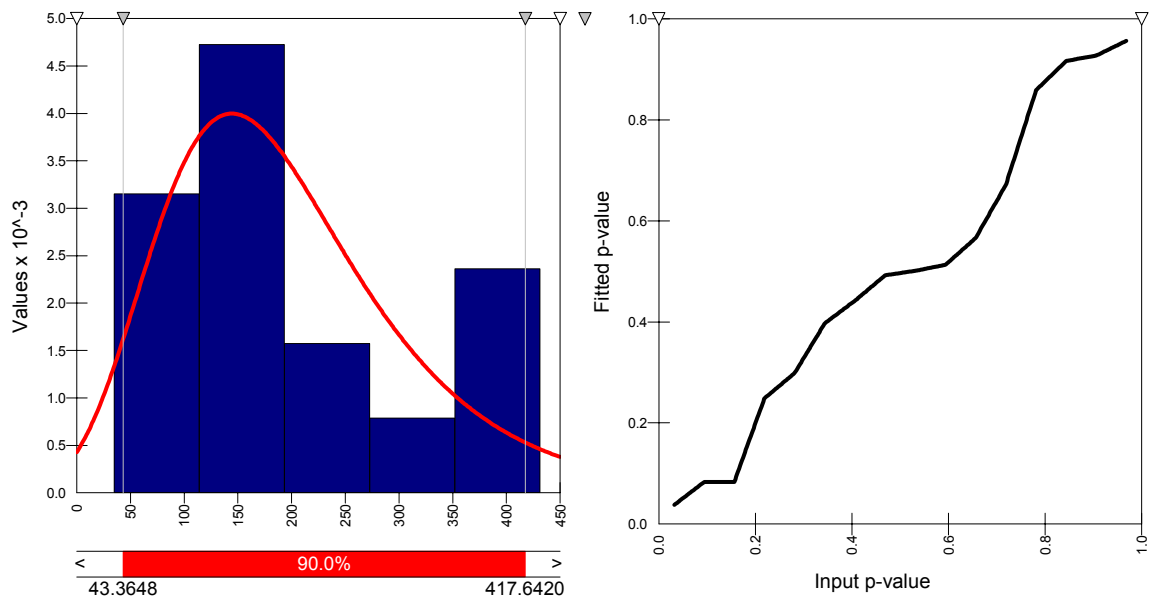**Figure 26. Distribution fit for the residential flow rate in Prague, from EXPOLIS data, as calculated from (Hänninen et al., 2004). Units in $m^3 \ hr^{-1}$.**

Residential volume and air exchange rate distributions for Oxford

As noted in the previous section, no estimate of air exchange rate was available for the city of Oxford from Hänninen *et al.* (2004), so that the flow rate could not be calculated for each individual residence. For this city, the residential volume distributions from EXPOLIS were used in the Monte Carlo simulation along with the distribution of air exchange rates in British residences calculated by the UK Department of Environment, Food and Rural Affairs (Ashmore et al., 2000). Lognormal distributions with means of 0.7 and 1.0 hr^{-1} are reported for winter and summer respectively, with a standard deviation of 0.27 hr^{-1}. Slightly higher values were reported for kitchens, but the figures quoted refer to the bedroom and lounge. The Monte Carlo model drew samples in equal proportions from the two seasonal distributions.

Residential volume distribution

Distribution:	Lognormal
Parameters:	Mean of normal μ = 5.2733 std. dev. of normal σ = 0.3134
Fits Statistics:	K-S = 0.765 X^2=4.07 p = 0.907
Comment:	This continuous distribution fits the data adequately
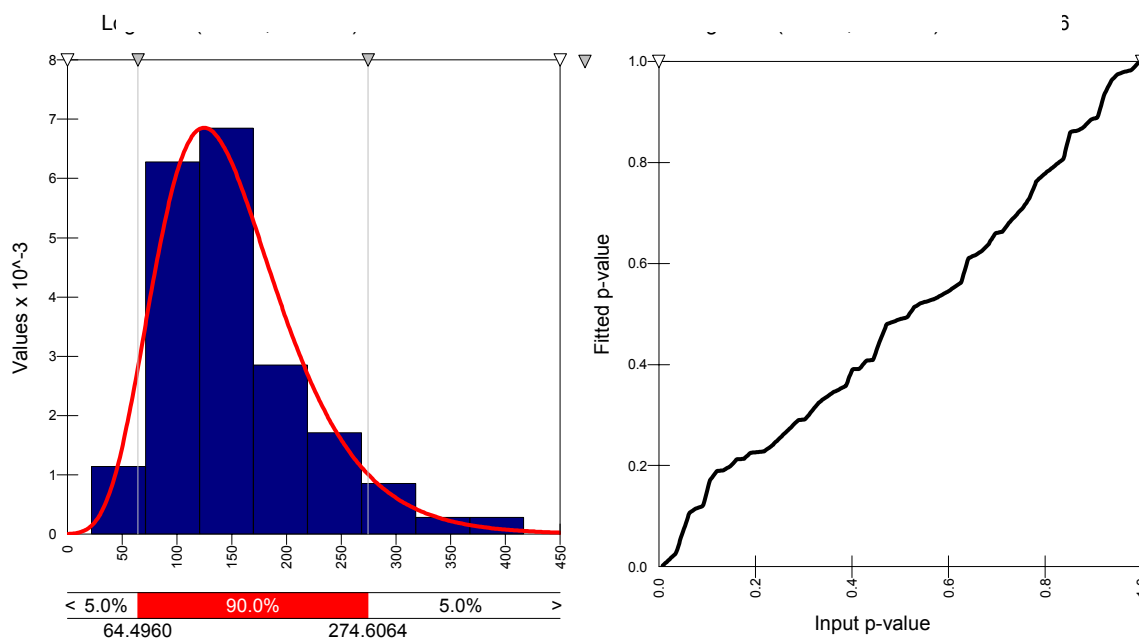
Figure 27. Distribution fit for residential volume in Oxford, from EXPOLIS data. Unit in m^3.

Flow rate was calculated as the product of volume and air exchange rates sampled. Theoretically, air exchange rate and volume are related by an inverse proportionality relationship. Empirical observation of their actual relationship in the other cities (for which coupled values were available) indicated, however, that individual variability in air exchange rates overshadows any theoretical relationship. No correlation between these two variables was therefore implemented in the Monte Carlo model, and the two variables were treated as independent.

Alternative Flow Rate distribution for Helsinki

To evaluate the possible impact of calculating flow rate distributions for Oxford in a different way from the other cities, an alternative flow rate distribution was calculated for Helsinki, using the same approach. The residential volume distributions from EXPOLIS were used as input to the Monte Carlo model along with the distribution of air exchange rates in Finnish residences (Ruotsalainen et al., 1992). Furthermore, this alternative distributions was used to validate the estimates of air exchange rates made by Hänninen et al. (2004) using EXPOLIS data against independent literature.

Volume

Distribution:	Lognormal
Parameters:	Mean of normal $\mu = 5.4665$ std. dev. of normal $\sigma = 0.32388$
Fits Statistics:	K-S = 0.268 $X^2 = 8.94$ p = 0.974
Comment:	This continuous distribution fits the data adequately
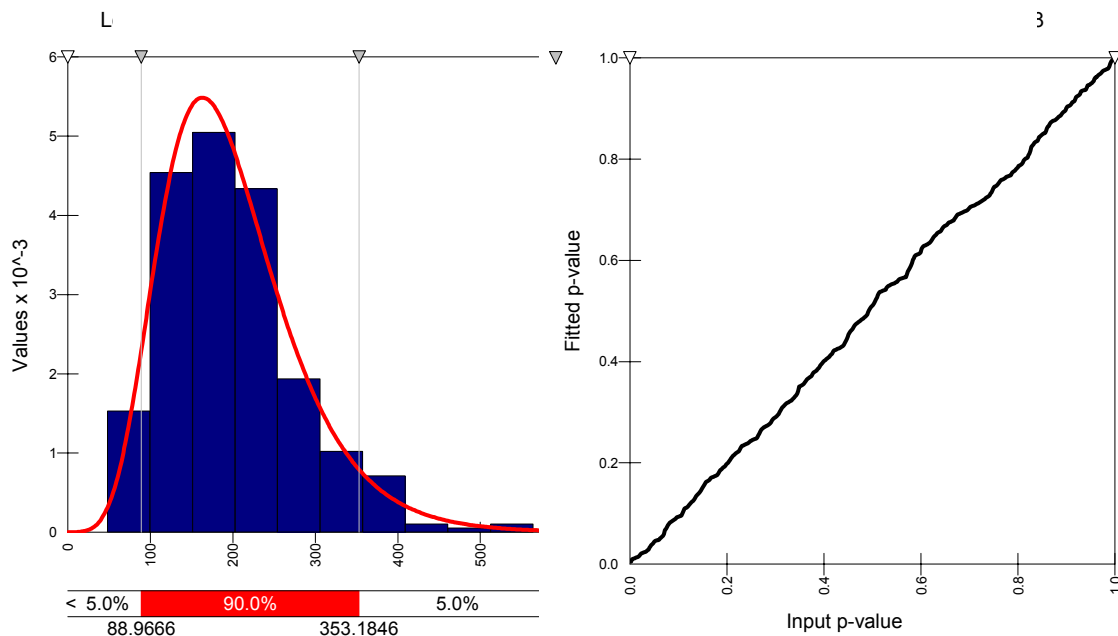
Figure 28. Distribution fit for residential volume in Helsinki, from EXPOLIS data. Unit in m³.

Air Exchange

Distribution:	Lognormal
Parameters:	Mean of normal μ = -0.45723 std. dev. of normal σ = 0.39449
Fits Statistics:	Root Mean Square Error = 0.0134 (only used for ranking, not for statistical testing)
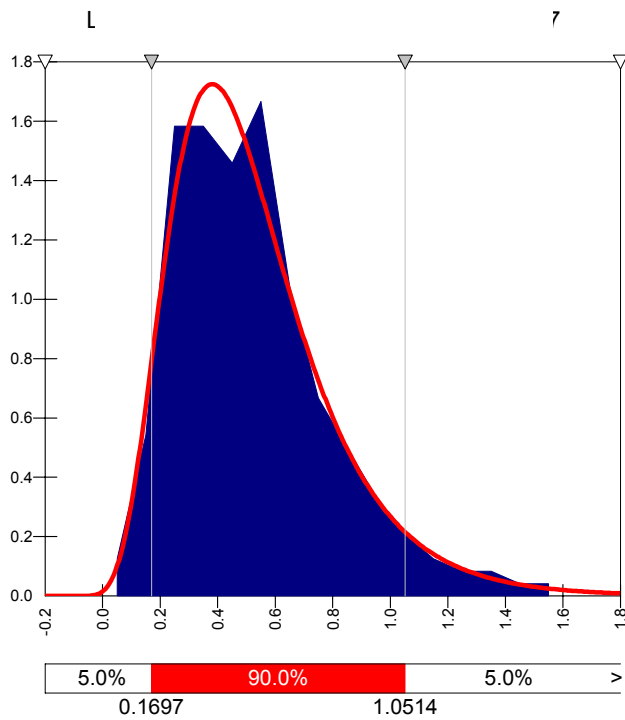
Figure 29. Distribution fit for air exchange in Helsinki. Data from (Ruotsalainen et al., 1992), units in hr^{-1}.

The resulting flow rate distribution is in remarkably good agreement with the one calculated exclusively from EXPOLIS data (Figure 25). While this method provides a validation of the air exchange estimates from Hänninen et al. (2004) only for the case of Helsinki, some degree of confidence in the reliability of the estimation procedure can be obtained for the other cities as well. In addition, it demonstrates the appropriateness of treating volume and air exchange rate as independent variables when calculating flow rate distributions for Oxford.
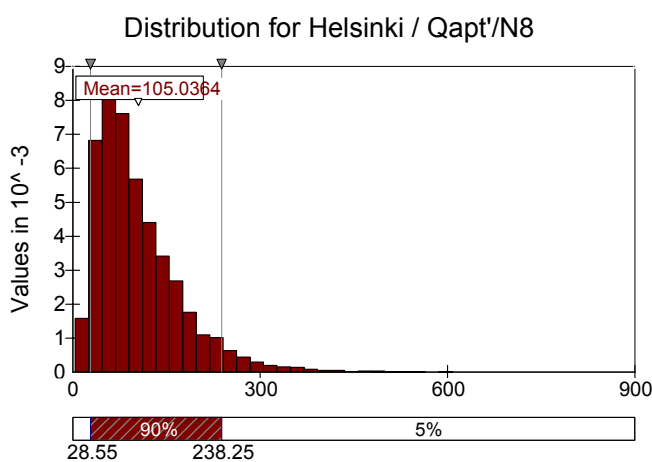
Figure 30. Resulting flow rate distribution for Helsinki, using the alternative data set.

Inhalation rates

Inhalation rates depend considerably on individual characteristics, as well as the activity performed by an individual. Numerous studies have tried to determine the empirical relationship between specific activities and individual metabolic factors on one hand, and inhalation rates on the other for specific individuals (see (USEPA, 1997) for a comprehensive review). The distribution of the inhalation rates in the population has been much less researched, although special groups (asthmatics, children, etc.) have received a certain level of attention. The distributions used for this model are from a study conducted by the US Environmental Protection Agency (1985), as reported in table 5A-7 of the Exposure Factors Handbook (USEPA, 1997). Since only a range and a mean were calculated, without information on the shape of the distributions, triangular distributions were used for the Monte Carlo model. Separate distributions were used for males and females (sampled with identical frequency) and for different levels of activity (*rest* vs. *light*). These levels of activity were based on a range of four possible levels (from *rest* to *high*) defined in the study. Although these studies were conducted on a sample of the US population, there are no reasons to suspect that metabolic and inhalation rates would be much different in the European population.
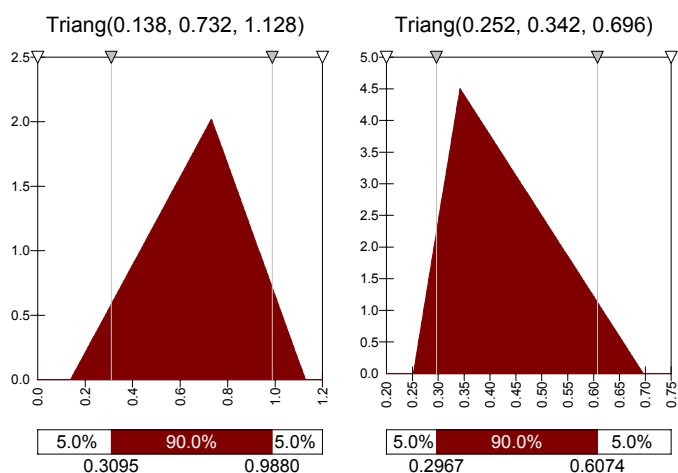
Figure 31. Distributions of inhalation rates for adult males and females, at rest. Values expressed in m³ hr⁻¹

Figure 32. Distributions of inhalation rates for adult males and females, at light activity level. Values expressed in m³ hr⁻¹

Activity level

Given the effect of the level of exertion on the individual inhalation rate, and the variety possible lifestyles, it is necessary to include a distribution of activity rates in the Monte Carlo model. To properly weigh the rest/light-activity inhalation rates, the proportion of time at home was modeled based on the activity patterns reported in Table 15A-6 of the Exposure Factors Handbook (USEPA, 1997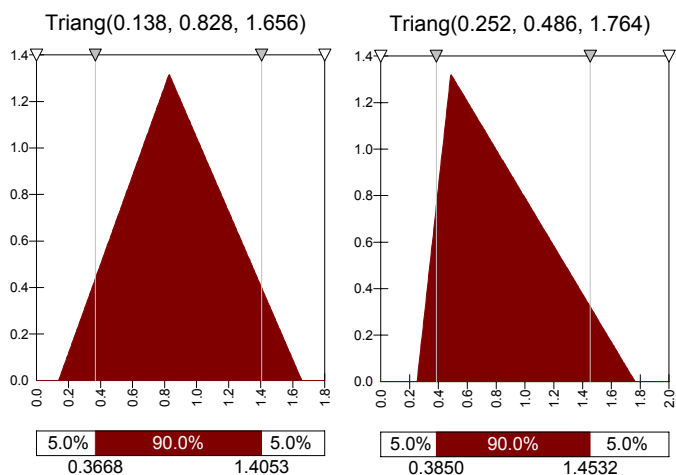), based on research by Hill (1985).. The 15 most common activities reported were assigned to either *rest* or *light-level* according to the definitions for the inhalation rates used (Table 2.3). Assuming a normal distributions for the time spent in all these activities, each group was converted in a proportion of time at *rest* or *light activity* by simple summation. The standard deviation of this proportion was derived through error propagation formulas.

Although this data is very comprehensive and particularly suited to this modeling study, it is important to recognize that time-activity patterns for the European population could differ somewhat from those used in this model, which were collected for the US population. The possible significance of this difference will be discussed in section 8.4 (Sensitivity Analysis).

Table 2.3. The 15 most common daily activities, used to compute the distribution of time at rest vs. light activity. Selected data from (USEPA, 1997), Table 15A-6.

Activity Factors	Mean	Std dev.		
	hours/day	hours/day		
Light Activity				
Meal preparation	0.66	0.71		
Meal cleanup	0.20	0.28		
Indoor cleaning	0.44	0.64		
Laundry	0.20	0.39		
Baby care	0.09	0.34		
Child care	0.09	0.24		
Washing/dressing	0.70	0.42		
Domestic crafts	0.17	0.56		
Rest				
Meals at home	0.92	0.53		
Sleeping	8.04	1.21		
Naps/rest	0.70	0.00		
Watching TV	2.05	1.63		
Reading	0.54	0.64		
Other entert.	0.22	0.49		
Conversation	0.27	0.36		
Total	15.3			
Rest	12.7	± 2.3	83.4%	± 14.9%
Light activity	2.5	± 1.3	16.6%	± 8.8%

Normal(0.895, 0.149) Trunc(0,1)

< 5.0%	90.0%	5.0%
0.6306		0.9825
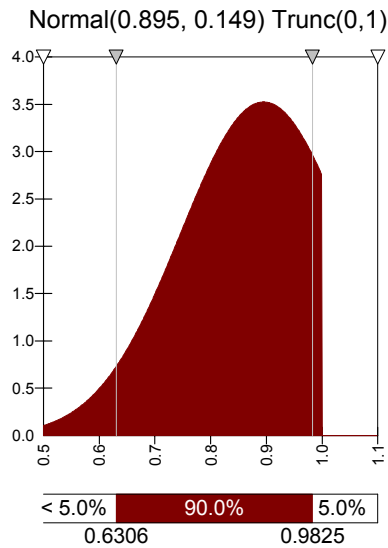
Figure 33. Distribution of the fraction of time spent at rest, while at home, as defined in Table 2.3.

7.3. *Monte Carlo Model Definition*

Formulation

The Monte Carlo simulation of intake fraction distributions was based on equation 2.8. To account for the variability in inhalation rates, which is in turn influenced by gender, and activity level, a more explicit formulation was actually used. For all cities except Oxford, the model output was defined as

$$iF = f \frac{\left[T_{rest}Q_{rest,male} + (1 - T_{rest})Q_{light,male}\right]R + \left[T_{rest}Q_{rest,female} + (1 - T_{rest})Q_{light,female}\right](1 - R)}{F} \quad (2.9)$$

where
f is the fraction of time at home, sampled from the distribution defined for each city
T_{rest} is the proportion of time at rest while at home, sampled from the distribution of time at rest
Q is the inhalation rate for each gender and activity level, sampled from the corresponding distributions
R is a random variable, taking a value of either 1 or 0, with equal probability.
F is the residential flow rate, sampled from the distributions defined for each city

The use of the dichotomous random variable R ensures that for each sample drawn, only the inhalation rate for a male or for a female is evaluated, but not both simultaneously.
For the city of Oxford, which did not have a distribution of flow rates available directly from the EXPOLIS data, the residential flow rate F was not sampled from a distribution but calculated as follow

$$F = V\left[a_{summer}R + a_{winter}(1 - R)\right] \quad (2.10)$$

where
F is the residential flow rate, sampled from the distributions defined for each city

V is the residential volume, sampled from the distribution defined for Oxford
a is the air exchange rate sampled from the winter and summer distributions for residences in the UK
R is, again, a random variable, taking a value of either 1 or 0, with equal probability

Once again, the use of the dichotomous random variable *R* ensures that for each sample drawn, only a winter or summer air exchange rates are evaluated, but not both. For the alternative distribution calculated for Helsinki, for which only one distribution of air exchange rates was available, the flow rate was more simply calculated as the product of volume and air exchange sampled from the corresponding distributions.

7.4. Simulation settings

The Monte Carlo simulations were carried out using *@Risk* add on for Excel, version 4.0.1 (Palisade Corp., Newfield, NY, USA). The simulations were set at 10,000 sampling iterations. Latin Hypercube was used as sampling method. This method differs from standard Monte Carlo sampling in that it uses stratification of the input probability distribution to reproduce more accurately the low-probability regions of that distribution. The downside is that this method is more sensitive to the requirement of variable independence. Test runs using traditional Monte Carlo vs. Latin Hypercube sampling did not produce meaningful differences. In addition, several runs of the simulation used different seeds for the random number generator did not lead to meaningful differences in the output distributions either. The performance of these tests indicates that the simulation is robust with respect to the specific computational settings.

8.   Results

8.1. Simulation convergence

The criterion for convergence of the simulation was that changes in the percentiles, the mean and the standard deviation of the distribution should be below 2%. These changes are documented in Table 2-4 for the simulation results presented.

Table 2-4. Convergence details in the Monte Carlo simulation. All changes are below the 2% level set in advance.

	% Change in Percentile	% Change in Mean	% Change in Std Dev
Athens	0.07%	0.01%	-0.17%
Basel	-0.04%	0.07%	0.10%
Helsinki (1)	0.02%	0.34%	-0.61%
Helsinki (2)	0.01%	-0.07%	-0.55%
Oxford	0.05%	0.07%	0.33%
Prague	-0.32%	-0.48%	-1.46%

8.2. Calculated Intake Fractions Distributions

The individual distributions resulting from the Monte Carlo simulation were fitted to the closest continuous distribution using the Kolmogorov-Smirnov statistic (K-S). For interpretation and use of the parameters of the continuous distribution, see definitions in Appendix B.

Athens

Observed Statistics	
Mean	$1.55 \ 10^{-3}$
Mode	$0.65 \ 10^{-3}$
Std.Dev.	$1.01 \ 10^{-3}$
Range	$0.02 - 8.6 \ 10^{-3}$
Fitted distribution	
Type	Lognormal
K-S statistic	0.174
Parameters	$\mu = -6.370$
	$\sigma = 0.507$
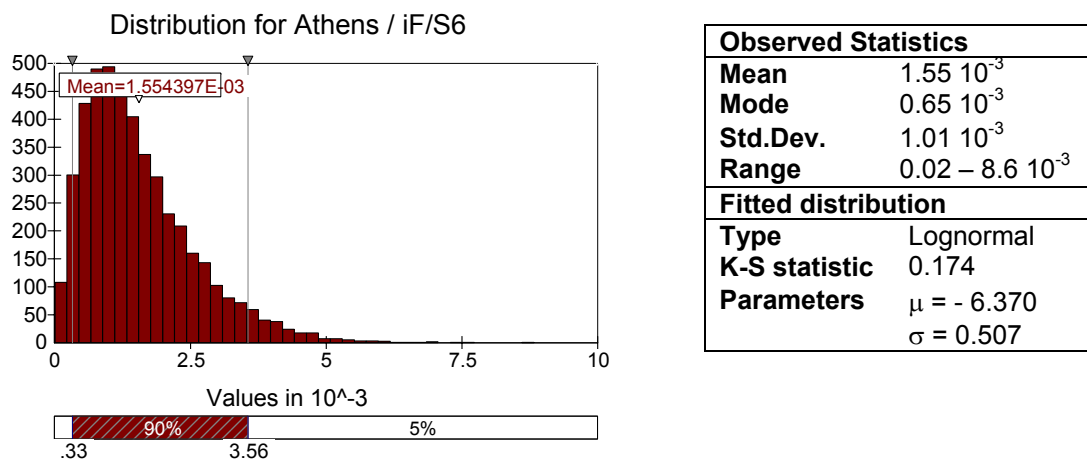
Figure 34. Intake fraction distributions for indoor sources in Athens

Basel
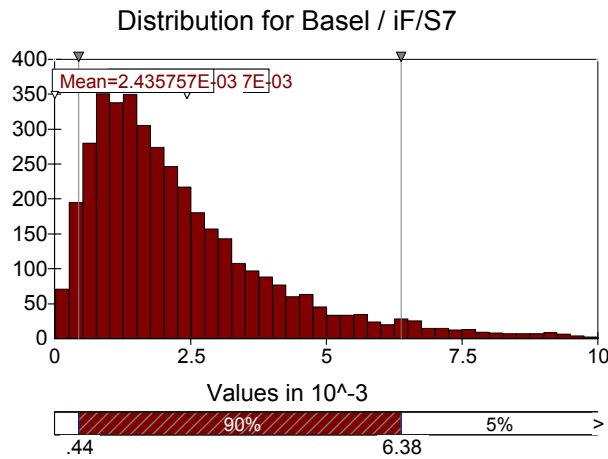
Observed Statistics	
Mean	2.44 10^{-3}
Mode	0.87 10^{-3}
Std.Dev.	2.14 10^{-3}
Range	0.00 – 27.9 10^{-3}
Fitted distribution	
Type	Lognormal
K-S statistic	0.008
Parameters	$\mu = -6.199$
	$\sigma = 0.714$

Figure 35. Intake fraction distributions for indoor sources in Basel

Helsinki

As noted, two separate distributions have been calculated for Helsinki. The first one, in which air flow rates were calculated based on EXPOLIS data only
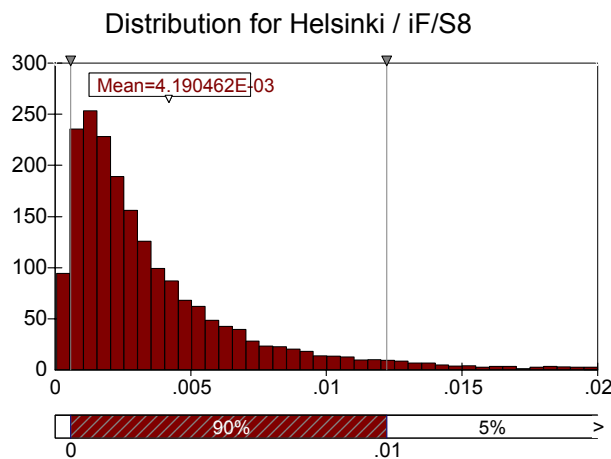
Observed Statistics	
Mean	4.19 10^{-3}
Mode	1.25 10^{-3}
Std.Dev.	6.44 10^{-3}
Range	0.06 – 272 10^{-3}
Fitted distribution	
Type	Lognormal
K-S statistic	0.013
Parameters	$\mu = -5.974$
	$\sigma = 0.951$

Figure 36. Intake fraction distributions for indoor sources in Helsinki. EXPOLIS data

The alternative distribution was made with independent estimates of air exchange rates (Ruotsalainen et al., 1992)

Distribution for Helsinki / iF'/T8
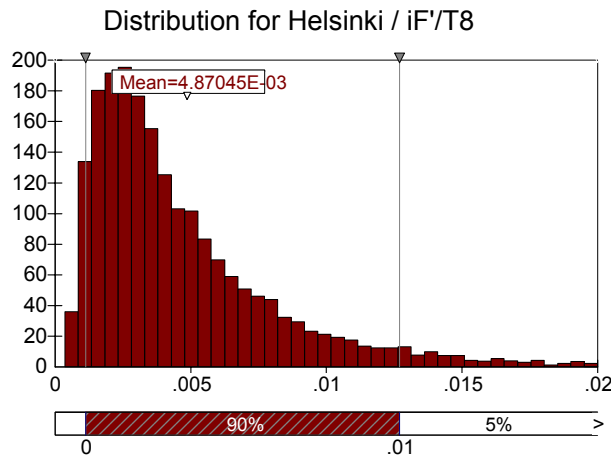
Observed Statistics	
Mean	4.87 10^{-3}
Mode	2.60 10^{-3}
Std.Dev.	4.33 10^{-3}
Range	0.36 – 99 10^{-3}
Fitted distribution	
Type	Lognormal
K-S statistic	0.006
Parameters	$\mu = -5.651$
	$\sigma = 0.770$

Figure 37. Intake fraction distributions for indoor sources in Helsinki. Alternative estimate

Oxford

Distribution for Oxford / iF'/T11

Observed Statistics	
Mean	3.85 10^{-3}
Mode	2.20 10^{-3}
Std.Dev.	3.04 10^{-3}
Range	0.08 – 58 10^{-3}
Fitted distribution	
Type	Lognormal
K-S statistic	0.009
Parameters	$\mu = -5.745$
	$\sigma = 0.634$

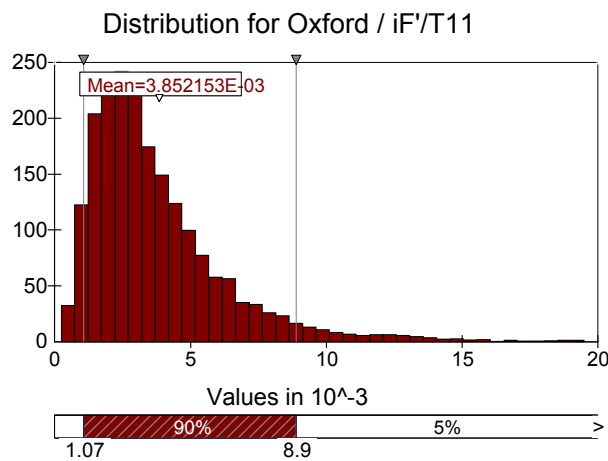**Figure 38. Intake fraction distributions for indoor sources in Oxford**

Prague

Distribution for Prague / iF/S12
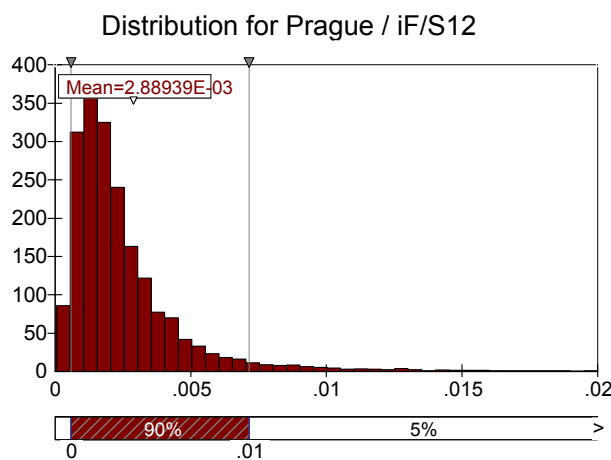
Observed Statistics	
Mean	2.89 10^{-3}
Mode	1.04 10^{-3}
Std.Dev.	5.53 10^{-3}
Range	0.09 – 215 10^{-3}
Fitted distribution	
Type	Lognormal
K-S statistic	0.037
Parameters	$\mu = -6.280$
	$\sigma = 0.813$

Figure 39. Intake fraction distributions for indoor sources in Prague

8.3. Uncertainties

Uncertainties in individual factors

An uncertainty is produced during any data collection due to necessarily limited precision and accuracy of the measurements. Furthermore, the data manipulation during the analysis normally introduces further approximations. Both these errors propagate through the data analysis process and ultimately affect the precision of the final estimates. We shall evaluate the different approximations and the precision of the variables involved.

Concentration and air exchange rates are two variables clearly strongly dependent on each other, according to equation 2.3. In the case of constant emission rates, in particular, they are inversely proportional. The approximation error produced in these conditions can be shown (see Appendix A) to be proportional to the square of the relative standard deviation (RSD) of the concentration

$$Err(iF) \approx -\left(\frac{\sigma_C}{\overline{C}}\right)^2 \qquad \text{for } \frac{\sigma_C}{\overline{C}} < 0.5 \qquad\qquad (2.11)$$

In other words, the error of the approximation will be 9% for a concentration RSD of 30%. The analysis of real-time and seasonal indoor VOC concentration profiles reported in the literature (Persily et al., 2003; Schlink et al., 2004) indicates that typical values of RSD are up to 30-40%. Since these values of RSD correspond to concentration profiles displaying a large variability, it is safe to assume that most situations are well approximated by the simplified intake fractions formula (eqn. 2.8), in the case of constant source strength. The expected error is then within -20%. It can be noted that the error of the estimate is always negative, meaning that the simplified formula always underestimates the intake fractions in these cases.

In the case of variable source strengths, the relationship between air exchange rate and indoor concentration will be weaker than in the case of constant source strength. The covariance term is then correspondingly smaller and the approximation even more accurate.

An error of underestimation is made in calculating the volume of a residence by neglecting the volume of furniture and other objects present. The value of this ratio is likely to change in different cities based on different furnishing traditions. No estimates of furniture/room volume ratios could be located in the literature. A few experiments with interior design software *(Home Design Architectural Series 18*, v. 6.0, Punch Software, Kansas City, MO, USA) indicate that the solid volume (i.e. not inclusive of contained spaces, such as drawer or cabinet interior) occupied by furnishings ranges in the 1-5% of the room volume. We shall adopt - 5% as a conservative estimate of this error.

The basic uncertainty in the estimate of time spent at home is given by the resolution of the diary recording (15 min) divided by the time spent at home (mean 26-30 hours). In the case of the sampled populations, since at least two measurements are made in the two days of sampling, this uncertainty must be multiplied by √2 to account for the two measurement errors. Thus, the final estimate of the uncertainty in the fraction of time at home is about ± 21 min, which translates in approximately ± 1.5%.

It is difficult to characterize the uncertainty for the other variables (inhalation and air exchange rates) as their inherent variability is confounded with true uncertainty in the estimate. Both quantities have been derived from a manipulation of heterogeneous values reported in the literature, that are not amenable to a complete error propagation analysis. Technically, the standard error of the mean is the estimate of true uncertainty for the mean of a distribution. In practice, however, that is a rather different concept from the uncertainty estimated for the previous quantities. In addition, that value cannot be extended to individual data points. In the absence of better information we will limit the error in the AER to the error in measuring $PM_{2.5}$ concentrations. Based on the analysis of duplicate

filters in EXPOLIS, the uncertainty in the measurement is 4-10% (EXPOLIS Study Group, 1999). We shall use ± 10% as an estimate of error for the AER.

Similarly, the error in inhalation rate will be limited to the typical measurement error in inhalation studies. Since estimates of inhalation rates were taken from several different sources compiled by USEPA, and since the accuracy was not estimated, no values are available from the original literature (USEPA, 1985). We shall assume a ± 10% uncertainty on this estimate, as well, for lack of better information.

Overall estimates of uncertainty

Because uncertainty estimates are not symmetrical, separate upper and lower bound uncertainty estimates must be made. Some uncertainties cannot be explicitly quantified, such as ignoring the inhalation rate-concentration covariance.

Upper bound

The uncertainty resulting from neglecting the concentration-AER covariance, being negative, only contributes to the upper bound. Similarly the uncertainty in estimating the volume of air in the residence due to furniture only contributes to uncertainty in the same direction. Therefore, we can write the uncertainty (relative) of the intake fraction from the relative uncertainties of its factors

$$\varepsilon_{\sup}\left(iF\right) = \sqrt{\varepsilon_{\text{cov}}^{2} + \varepsilon_{V}^{2} + \varepsilon_{f}^{2} + \varepsilon_{a}^{2} + \varepsilon_{Q}^{2}} \qquad (2.12)$$

where ε indicates the uncertainty and the subscripts refer to uncertainty in covariance (*cov*), volume (*V*), fraction of time at home (*f*), AER (*a*), and inhalation rate (*Q*).

Using the estimates of relative uncertainties described above (respectively $\varepsilon_{cov} = 0.2$ $\varepsilon_{V} = 0.05$ $\varepsilon_{f} = 0.015$ $\varepsilon_{a} = 0.1$ and $\varepsilon_{Q} = 0.1$), the overall upper uncertainty is 25%.

Lower bound

The lower bound of uncertainty is not affected by the covariance or volume errors. So we can simply write

$$\varepsilon_{\inf}\left(iF\right) = \sqrt{\varepsilon_{f}^{2} + \varepsilon_{a}^{2} + \varepsilon_{Q}^{2}} \qquad (2.13)$$

where, again, ε indicates the uncertainty and the subscripts refer to uncertainty in fraction of time at home (*f*), AER (*a*), and inhalation rate (*Q*).

Applying the same values above for the uncertainty of the individual factors, we obtain the overall lower bound uncertainty as 14%

It is therefore possible to express all intake fraction estimates within a +25 -15 % uncertainty interval. It should be remembered, however, that not all the possible contributing factors could be considered in these calculations and the actual uncertainty is likely to be somewhat higher. Furthermore, this uncertainty estimate does not include the uncertainty resulting from approximating the true distributions of factors with a continuous function, or from incomplete knowledge of the actual distributions (e.g. in the case of triangular distributions).

8.4. Sensitivity analysis

Sensitivity analysis explores the relative influence that the different input variables (right hand side of equation 2.8) have on the distribution of the output values (intake fractions). The results give information on how sensitive the results are to choice in input values. The purpose of the analysis is to

determine to what extent incomplete information (such as unknown distributions) or arbitrary choices determine the answers. If the less detailed information plays a minor role, then the model is robust with respect to that information and is more generally applicable. If, on the other hand, the critical parameters are those poorly characterized, the results are not very reliable.

One way to analyze the input-output relationship is to perform a regression, with the output values as dependent variable and the input values as independent variables. Those variables that have the highest, significant correlation coefficients are those to which the output distributions are more sensitive.

Another way to consider the problem is to examine the highest and lowest ends of the output distributions (intake fractions) and check the corresponding distributions of the input variables. This is referred to as scenario analysis. In other words, one can see if, for example, the highest values of the output distributions are attributable in particular to high or low values of one or more specific input variables, rather than simple statistical fluctuations (e.g. all input variables are high). In the following analysis we will focus on the upper 10th percentile and the lowest quartile in the intake fraction distributions as representative of high and low values.
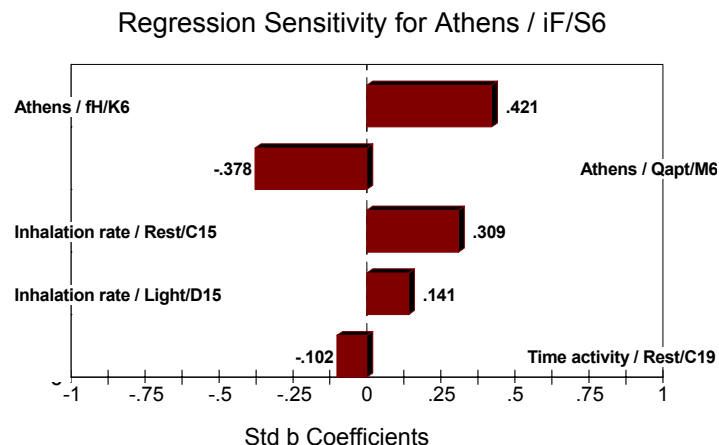
Athens

Figure 40. Regression sensitivity for Athens

The fraction of time spent at home is the most important factor in determining intake fractions in Athens. Ventilation rate and rest inhalation rate are also important, as would be expected. The choices in assigning inhalation rate at light activity level and the time fraction spent in rest are not crucial in determining the final distributions of intake fractions.

A scenario analysis indicates that the highest 10th percentile of the intake fraction distribution is the result of a high fraction of time spent at home ($>77^{th}$ percentile) and a high inhalation rate at rest ($>73^{rd}$ percentile), rather than of modest ventilation rates. Hence, the high-end estimates are not sensitive to the arbitrary choice of a lower limit for ventilation rates and are to be considered reliable. The lowest quartile intake fraction distribution, conversely, results from situations where little time is spent at home ($<28^{th}$ percentile) and ventilation rates are high ($>86^{th}$ percentile).

Basel

The ventilation rate is the most important factor in determining intake fraction distributions in Basel. A less important role is played by the fraction of time at home, and the inhalation rate at rest. Scenario

analysis indicates that the highest intake fractions are those relative to people that spend a rather high fraction of time at home (>71st percentile). Conversely, the lowest intake fractions are for those participants whose home have very high ventilation rates (>86th percentile).

Regression Sensitivity for Basel / iF/S7

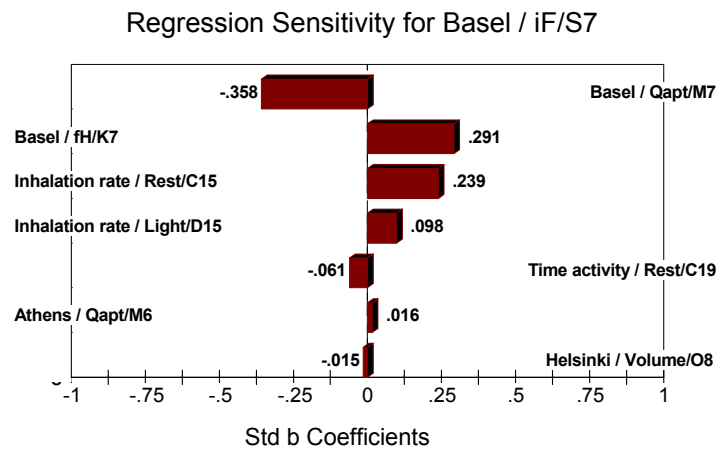|		
-.358		Basel / Qapt/M7
Basel / fH/K7	.291	
Inhalation rate / Rest/C15	.239	
Inhalation rate / Light/D15	.098	
-.061		Time activity / Rest/C19
Athens / Qapt/M6	.016	
-.015		Helsinki / Volume/O8

Std b Coefficients

Figure 41. Regression sensitivity for Basel. Note that the correlation is also computed with input values referred to other cities, which as expected, have no meaningful influence.

Helsinki

In the case of Helsinki, using ventilation rates estimated from the EXPOLIS database, no one input variable seems crucial in driving the intake fraction distribution estimates. The ventilation rate in the residence is the most important factor (beta = 0.2). This is rather in contrast with the second estimate (using independent air exchange rates from the literature), that is much more sensitive to AER and volume (Figure 44). Inhalation rate at rest and fraction of time spent at home also seem more important in determining this second estimate. It would then appear that the estimate made using the EXPOLIS data only is generally more robust, since the volume vs. AER rate relationship used in the model is left undefined, which is likely not the case in reality.

High (>87th percentile) and very low (<5th percentile) ventilation rates are responsible for the lowest and highest intake fractions respectively, in a scenario analysis for the EXPOLIS-only estimate. The highest (up to 0.27) intake fractions are therefore to be taken with caution, as they are affected by the arbitrary, conservative choice of minimum ventilation rate. In all likelihood, such low values of ventilation (and hence such high intake fractions) are not observed in reality.

These results are also confirmed by the scenario analysis of the second estimate, where the lowest intake fractions are produced by high (>76th percentile) residence volumes and AER (>80th percentile). The highest intake fraction values are produced at low residential volume (<14th percentile) and low AER (<11th percentile), but also somewhat higher rest inhalation rates (>69th percentile).
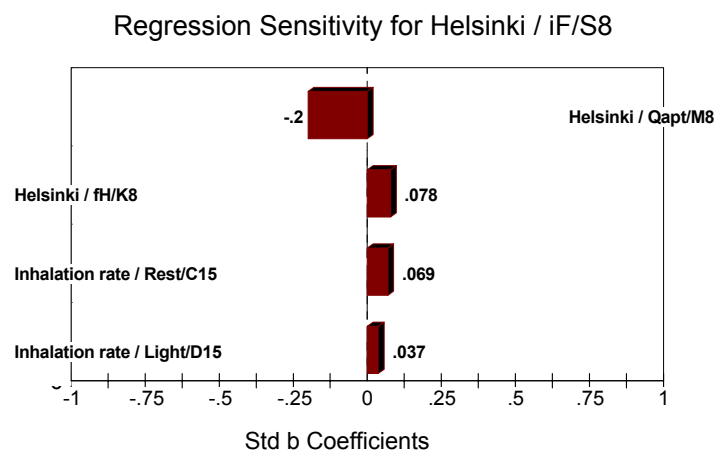
Regression Sensitivity for Helsinki / iF/S8

Figure 42. Regression sensitivity for Helsinki, EXPOLIS data.
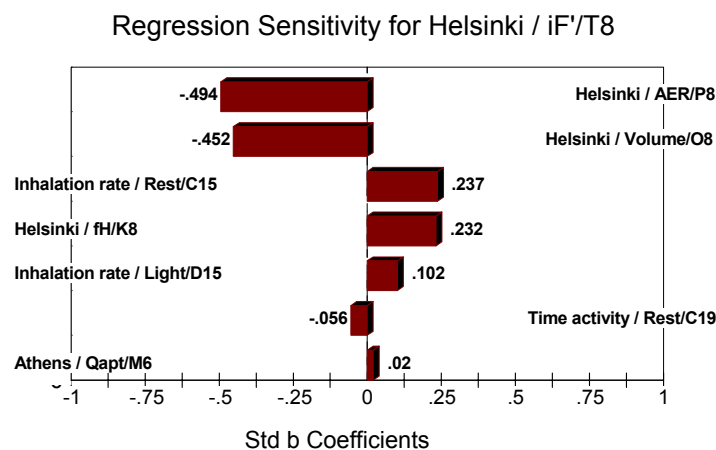
Regression Sensitivity for Helsinki / iF'/T8

Figure 43. Regression sensitivity for Helsinki, alternative estimate. Note that the correlation is also computed with input values referred to other cities, which as expected, have no meaningful influence.

Oxford

In Oxford, volume and AER are the most critical factors in determining intake fractions. The fraction of time at home and the inhalation rate at rest are also important. The highest intake fractions in Oxford do not appear to be due to a particular factor, but are rather resulting from the combination of much time spent at home (>73rd percentile), small residential volume and low AER (<9th and <19th percentile respectively) and somewhat high inhalation rates (>69th percentile). Low intake fraction values are produced in situations where volume and AER are even moderately elevated (>78th and 72nd percentile respectively) and the fraction of time at home is low (<25th percentile).

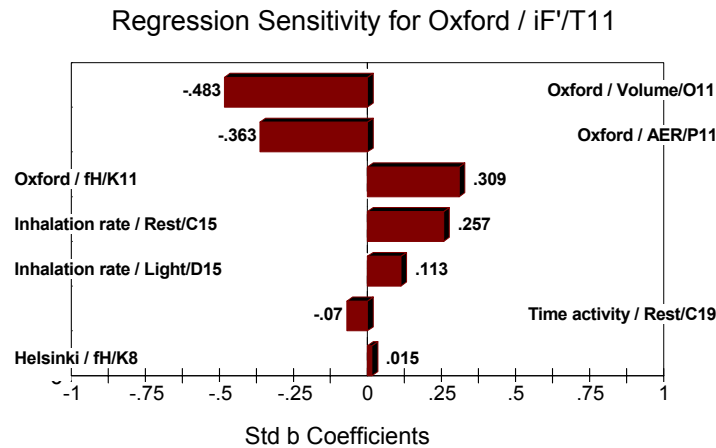## Regression Sensitivity for Oxford / iF'/T11

Figure 44. Regression sensitivity for Oxford. Note that the correlation is also computed with input values referred to other cities, which as expected, have no meaningful influence.

Prague

For Prague, the ventilation rate of the residence dominates the outcome of the simulation, although its absolute level of correlation is moderate (std b = -0.30). Other factors do not seem to be important. Indeed, the scenario analysis confirms this observation, revealing that the lowest intake fractions are those obtained at high ventilation rates (>86th percentile) and the highest ones are the result of very low (5th percentile) ventilation rates. These high values (up to 0.2) of intake fractions are therefore to be considered with caution, because they are sensitive to the arbitrary, conservative limit set to the minimum ventilation rate. In all likelihood, such low values of ventilation (and hence such high intake fractions) are not observed in reality.

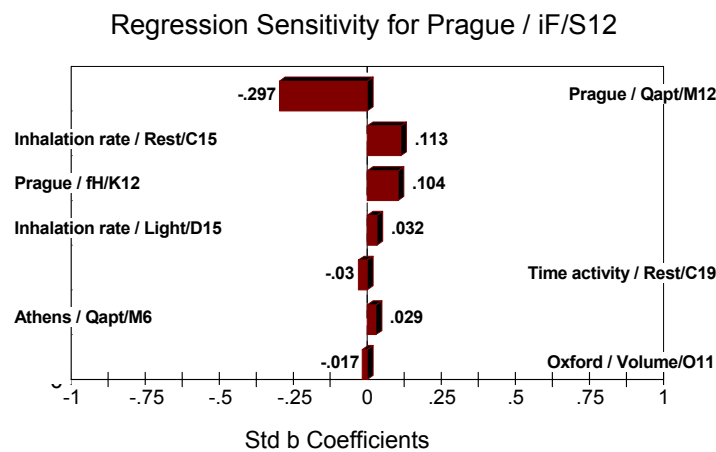## Regression Sensitivity for Prague / iF/S12

Figure 45. Regression sensitivity for Prague. Note that the correlation is also computed with input values referred to other cities, which as expected, have no meaningful influence.

9.   Interpretation

The values of intake fractions from indoor sources calculated in the model are distributed lognormally in all cities. All distributions indicate that for 90% of the population values typically range between 10^{-3} and 10^{-2}. The distributions are only moderately skewed, so that the mean and the 95th percentile differ by only a factor of 2 to 3.This indicates that the variability within each population is not large, so that the majority of people within each city have very similar intake fractions.

Considering the upper tail of the distributions, values as high as $270 \ 10^{-3}$ and $210 \ 10^{-3}$ were produced during the simulation for Helsinki and Prague respectively, but sensitivity analysis showed that these values are likely to be artifacts. More reliable estimates of the top 5th percentile range from $10 \ 10^{-3}$ to $60 \ 10^{-3}$.

The distributions of intake fractions appear to span similar ranges in the different cities. When the uncertainty of the estimates is taken into account, the range overlap would be further reinforced. The estimated uncertainty can be applied to point estimates as well (Figure 47 considers the means). The lowest estimates are for the city of Athens, followed by Basel and Prague, at very similar levels. Oxford and Helsinki have higher, similar values, although the alternative estimate for Helsinki (more directly comparable to that for Oxford) covers a slightly higher range, with less overlapping. This order appears to reflect very closely the climate differences in the various cities, from the Mediterranean climate of Athens, to the continental of Basel and Prague, to the oceanic and sub-arctic of Oxford and Helsinki. These would, in turn, be reflected in the different degrees of insulation of the residences, and in the opportunity to open windows.
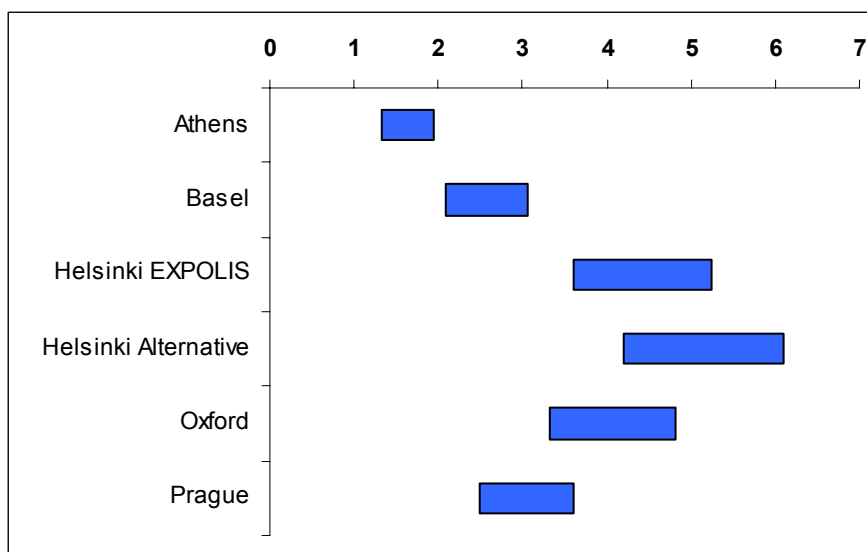

Figure 46. Means of the iF distributions in the different cities, adjusted for the estimated uncertainty. Values in 10^{-3} units.

When evaluating the robustness of the model with respect to the assumptions, we note that, as a rule, the results are more sensitive to the data obtained from the EXPOLIS study (flow rate, time at home, residence volume) than to data from other sources. This finding indicates that the results are more sensitive to the best-characterized, city-specific data than to the supplemental information used, since inhalation rate distributions were poorly approximated (triangular distributions) and the fraction of time at rest was not based on the activity patterns of the European population..

9.1. Comparisons with other estimates

As intake fractions are a relatively recent development in exposure assessment, and as most of the research has focused on outdoor sources, there are not many examples in the literature to compare with the estimates from the present study. As an example supporting the original intake fraction definition (Bennett et al., 2002), it was calculated that the intake fraction of benzene from environmental tobacco smoke would be approximately $7 \cdot 10^{-3}$. From another study, examining the situation in developing countries (Smith, 1993a), the intake fraction for emission from unvented stoves can be estimated at $3 \cdot 10^{-3}$. In both cases, these mean estimates for indoor sources are in the same exact range observed for the distributions calculated in the present study. Intake fractions for outdoor sources, on the other hand, vary over several orders of magnitude, ranging from $6 \cdot 10^{-5}$ for traffic emissions of benzene in Los Angeles (Marshall et al., 2003), to 10^{-6} for power plants (Smith, 1993b), to 10^{-8} for 1,3-butadiene in the US (Bennett et al., 2002). In general, intake fractions for outdoor sources are much lower than for indoor sources, being 2 or more orders of magnitude those calculated for indoor sources. Although higher values for indoor sources are not surprising, the magnitude of this differences is remarkable and provides a measure of the effects of indoor environments in limiting the dilution of compounds emitted by indoor sources.

9.2. Limitations and applicability

For a proper interpretation of the results of this study, it is important to point out some limitations.

1) The estimated distributions do not take into account the proximity to a source that may take place during use of consumer products. This is likely to result in the underestimation of the intake fractions for a variety of sources, ranging from cooking emissions to cleaning products.
2) Similarly, the residential indoor environment was assumed as a single space, and possible differences in the use of different rooms are not accounted for. This may again be important for sources that are room specific.
3) For reactive pollutants, the distributions overestimate the intake fractions, the more so the greater the compound reactivity. In this context, reactive pollutants are to be considered those whose atmospheric lifetime is smaller than one residence time for the air (reciprocal of air exchange rate).

In general, however, these limitations and a degree of uncertainty do not affect the practical value of the intake fraction estimates, which lies in the immediacy of comparisons with other estimates. Since the intake fractions from different sources vary over several orders of magnitude, approximate values are often sufficient for the use.

Finally, it is worth pointing out, that because of the independence of the calculation from the residential indoor concentration the scope of these results is in principle broader than simply indoor VOC sources. These results apply to all indoor air pollution sources, within the limits of the study and as long as the same assumptions are met. The associated estimates of uncertainty are less portable, however, and should be calculated on an individual basis.

9.3. Example application

Intake fractions for indoor sources can be used to calculate the approximate dose reaching the occupants of a residence from the mass content in building materials and consumer products, without need to determine emission rates, which are highly variable in time. As a quick example, the average concentration of m-xylene in household cleaners/polishes is 1.4% (Sack et al., 1992). The dose to

which 90% of European residents would be exposed through inhalation from the use of an entire 1 kg bottle will then be approximately

1.4% x 1000 g x (10^{-3} to 10^{-2}) = 14 to 140 mg of m-xylene.

Clearly, this is only a gross estimate, and the actual users of the product will receive higher doses due to their proximity during application, but the figure is a good approximation for the other residents, who are exposed through product evaporation from surfaces and cleaning tools

10.   Conclusions

The intake fractions for indoor sources are distributed lognormally in all the cities, with mean values in the 10^{-3} to 10^{-2} range. The lowest values were observed in Athens and the highest in Helsinki, reflecting the different ventilation patterns due to climate differences.

In general, the intake fractions within a population display a limited variability. Since means and 95th percentiles differ by a factor of 2-3 (rather than by orders of magnitude), the capacity to reduce exposure based on realistic ventilation and activity rates is limited. Although the information collected during the EXPOLIS study does not have the power to capture the most extreme conditions, it still represents the population of the cities sampled. it appears that the range of exposures to VOCs from residential indoor sources is rather limited, insomuch as it depends on individual activities and indoor ventilation. What is most likely to determine a wider range of actual exposures is the strength of the different sources.

The fact that intake fractions for indoor sources are orders of magnitude greater than those for outdoor sources should not be interpreted that the body burden from the indoor sources is correspondingly larger. These depend on the total amount released in the environment. However they do indicate the effect of close proximity between sources and target populations is very significant

11.   Implications and Recommendations

It has been shown that sources located both indoors and outdoors produce major contributions to personal exposure to VOCs in European cities. The relative proportion of these contributions varies for different compounds, but those associated with traffic emissions show higher outdoor contributions as it is to be expected. Indeed, exposure to those compounds owes a large contribution to other locations/activities, such as time spent in traffic. It is apparent, then, that strategies of air pollution management that address only outdoor sources would ignore much of the potential population exposure. While this conclusion is not new, the difficulties of intervention in indoor air quality and traffic management must be acknowledged. In addition, there is a strong indication that some of the indoor sources of VOCs are actually secondary, i.e. they release over time adsorbed compounds whose origin lies outdoors.

Although both workplace and residential indoor environments contribute to personal exposure, the role of the latter was overwhelming, in the sampled population. The need to investigate occupational exposure is certainly essential for specific sub-populations and even more so for individuals. And the importance of air quality in the workplace, with its consequences on productivity, is undeniable. It would seem, however, that from a public health standpoint, the possible impact of residential air quality is very significant, though it appears to have received much less attention in scientific investigations. An increased focus on residential along with commercial buildings is certainly encouraged.

The sorption phenomenon appears to play a large role in determining human exposure, but it requires more detailed studies in terms of its implications. While some compounds may be permanently adsorbed, little is known of the saturation capacity of materials in the household. Sorbing materials effectively trap volatile compounds inside the home for a while, and upon desorption, they behave essentially as indoor sources. As emissions from indoor sources are 2-3 orders of magnitude more likely to reach a human target, it would appear that, in general, sorption leads to an increase in exposure. The actual effect in terms of risk, however, needs to be evaluated in the specific context of each compound, with regards to the type of hazard (acute or chronic toxicity).

Exposure reduction strategies aimed at indoor sources should focus more on reducing the content of hazardous compounds in household and building products rather than on ventilation or building strategies. This recommendation derives from two considerations. In the first place, while differences exist between different locations (e.g. intake fractions from Athens and Helsinki), practical constraints of climate and energy costs limit intervention on ventilation. Similarly, a recommendation of larger residences (which indeed would reduce exposure) would face similar obvious limitations. Secondly, the majority of the population in each location have very similar intake fractions, indicating that intervention on the extreme exposures would not affect the total population exposure appreciably. It is apparent, then, that given the limited ability to reduce intake fractions, the only viable alternative to reduce exposures lies in reducing the source strength of consumer products or building materials, depending on the compounds of interest.

Acknowledgments

12. Appendix A

Error approximations for sources of constant strength

A simplified formula to estimate intake fractions for indoor sources was derived in equations 2.3 to 2.8. While the covariance of the breathing and concentration rates is not expected to be high, the covariance of air exchange rate and concentration needs to be explored, as the two variables are related by physical processes. The error involved in using the simplified formula in place of the complete one is

$$\text{Rel. Err (iF)} = \sqrt{\left(\frac{\text{cov}(Q,C)}{\overline{Q}\cdot\overline{C}}\right)^2 + \left(\frac{\text{cov}(a,C)}{\overline{a}\cdot\overline{C}}\right)^2} \qquad (A1)$$

Ignoring the error due to covariance of breathing rate and concentration and focusing on the second term, yields

$$\text{Rel. Err (iF)} = \frac{\text{cov}(a,C)}{\overline{a}\cdot\overline{C}} \qquad (A2)$$

If the source strength (E) is constant, we can write from equation 2.3

$$C = \frac{E}{V\,a} = \frac{k}{a} \qquad (A3)$$

The covariance of C with k/C is then

$$\text{cov}(C,k/C) = \frac{\sum\limits_i \left(C_i - \overline{C}\right)\left(\dfrac{k}{C_i} - \dfrac{k}{\overline{C}}\right)}{N} \qquad (A4)$$

Hence the relative error due to ignoring the covariance is

$$\text{Rel. Err (iF)} = \sum \frac{-\left(C_i - \overline{C}\right)^2}{N\,C_i\cdot\overline{C}} \qquad (A5)$$

When the dispersion around the average concentration is small, then the concentration in each instant is not too far from the mean

$$C_i \approx \overline{C} \qquad (A6)$$

and the relative error approaches the quantity

$$\text{Rel. Err (iF)} \approx -\sum \frac{\left(C_i - \overline{C}\right)^2}{N\overline{C}\cdot\overline{C}} = -\left(\frac{\sigma_C}{\overline{C}}\right)^2 \qquad (A7)$$

that is, the square of the relative standard deviation (RSD). To test the goodness of this error approximation, we experimented with several functions simulating the concentration evolution over time (an example is shown in Figure 48). These included both monotonous and periodic functions, together with a random component. Air exchange and concentration were always set to be inversely proportional. The resulting RSD of the concentration was plotted against the approximation error, calculated as the covariance divided by the product of the means.

As can be observed in Figure 48, the data points are interpolated by a power-law function, which approaches the quadratic relationship indicated by equation A7. The scattering around the interpolating function increases with the RSD, as indicated in deriving the expression of the relative error (equation A5). Thus, the relationship given by equation A7 to estimate the error becomes less useful, as the RSD grows. Its use is not recommended with RSD above 50%.

The error introduced in calculating intake fractions with the simplified formula remains modest even when indoor concentrations display a relatively high variability (high RSD) over the period of interest.

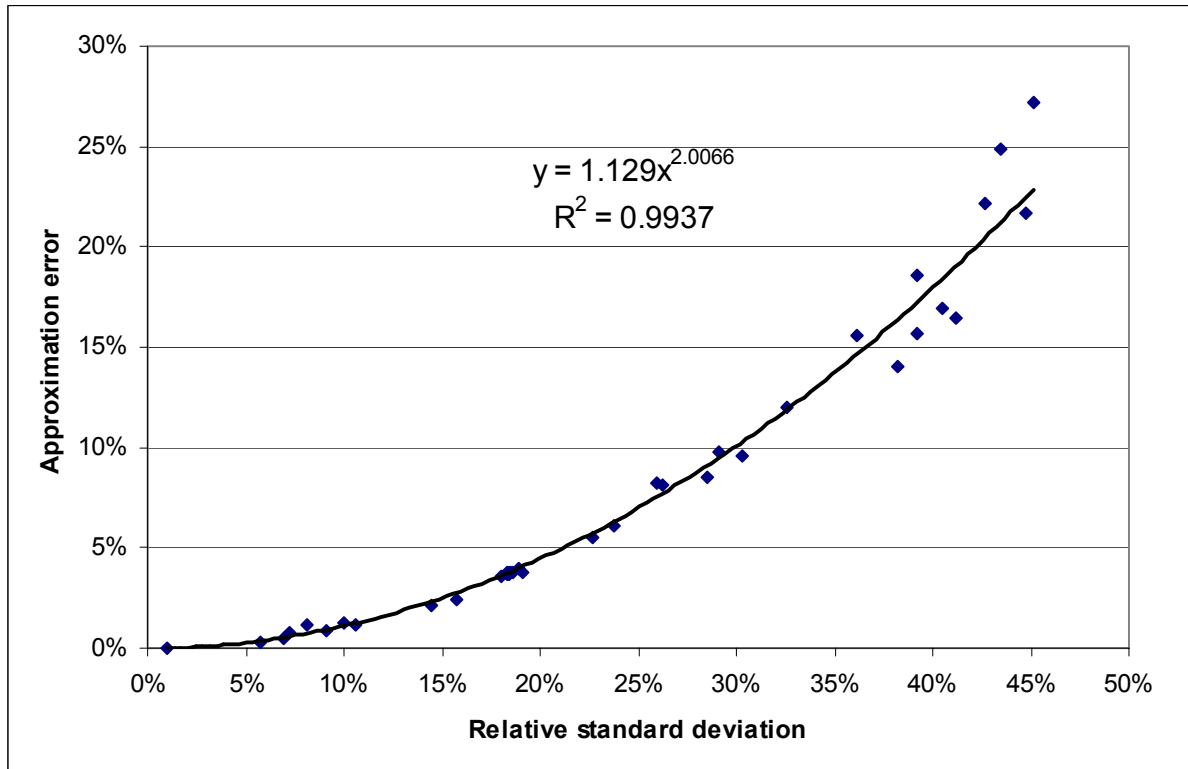$$y = 1.129x^{2.0066}$$
$$R^2 = 0.9937$$

Figure 47. Empirical relationship between the relative standard deviation (RSD) of the concentration and the approximation error produced by ignoring the concentration-air exchange rate covariance term in the simplified formula for intake fractions. The interpolation approaches equation A7. As the RSD increases, so does the dispersion around the interpolation line, and the relationship to estimate the error becomes less accurate.

13.   Appendix B

Definitions of statistical distributions

Due to the multiplicity of ways in which some distributions, in particular lognormal distributions, can be expressed, the parameters used in fitting the various statistical distributions are defined below (as reported by Palisade Corp. (2000)).

Lognormal
Throughout the present document, a lognormal distribution is defined by the expression (density function)

$$f(x) = \frac{1}{x\sqrt{2\pi\sigma^2}} \exp\left(- \frac{(\ln x - \mu)^2}{2\sigma^2}\right)$$

The values of μ and σ in the text are as expressed in the equation above. Therefore, the mean and variance of a lognormal distribution with parameters μ and σ will be

Mean: $\exp\left(\mu + \frac{\sigma^2}{2}\right)$

Variance: $\exp(2\mu + \sigma^2)\left[\exp(\sigma^2) - 1\right]$

Extreme Value

Throughout the present document, an extreme value distribution is defined by the expression (density function)

$$f(x) = \left(\frac{1}{b}\right) \exp\left(-\frac{x-a}{b}\right) \exp\left[-\exp\left(-\frac{x-a}{b}\right)\right]$$

Loglogistic

Throughout the present document, a Loglogistic distribution is defined by the expression (density function)

$$f(x) = \frac{\alpha\left(\frac{x-\gamma}{\beta}\right)^{\alpha-1}}{\beta\left[1 + \left(\frac{x-\gamma}{\beta}\right)^{+\alpha}\right]^2}$$

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