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Relationships between size-fractionated indoor and outdoor trace elements at four retirement communities in Southern California

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Dear Reviewers,

Thank you for sharing with us your valuable suggestions and for reviewing this manuscript. We have made substantial efforts to address all of your comments and, as a result, we are confident that the attached version of our paper has been improved. Below is a document in which we detail our responses to all of your remarks.

Sincerely,

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Reviewer #1

General comments

This discussion paper presents an extensive dataset of outdoor and indoor measurements of trace elements in quasi-ultrafine, accumulation mode and coarse particles. As the authors rightfully state, several studies have provided information on the elemental composition of outdoor PM10 and PM2.5, but substantially fewer studies have considered also indoor PM. Indoor measurements were conducted in the main buildings of 4 retirement communities located at varying distances from Los Angeles, California. Elderly people have previously been shown to be susceptible to the adverse health effects of particulate air pollution, which adds to the relevance of this paper. In general, people spend 80-90% of their day indoors and people with sedentary life style, including many elderly people with chronic diseases, even more. Thus, indoor concentrations of trace elements measured in this study are not that far from actual exposures.

The paper would benefit from some shortening and focusing – now all the results seem to be presented with similar levels of details, even those not contributing to the main messages of the paper.

We feel that the two main sections of this manuscript complement each other well and we would prefer to leave the structure of this paper as is. To the best of our knowledge, the infiltration of trace elements associated with quasi-ultrafine particles has been reported here for the first time. The second part of this work is also quite relevant, because it suggests that using the I/O_S ratio as a surrogate of the infiltration factor for $PM_{2.5}$ might lead to an overestimation of the fraction of indoor $PM_{2.5}$ of outdoor origin (at least in the communities considered in our study).

I'm also a bit worried about the large number of rather speculative explanations for the outdoor and indoor levels of various elements in the study. The speculations should be linked more tightly to the actual sources of outdoor PM at the study area (based on e.g. emission inventories and source-apportionment studies), as well as to PM generating indoor activities during the study period.

Although we understand the reviewer's concerns, we would like to point out that information about sources of quasi-ultrafine-related outdoor and (especially) indoor metals that could be used to expand our discussion are very limited.

To use potassium as an example, I would assume that wood combustion is relatively common in California, and so are wildfires, which should lead to e.g. high concentrations; indoors cooking and smoking are known sources of potassium.

The reviewer is correct but, in our view, those are also speculative comments.

Specific comments

-Page 4935, line 10: cut-off sizes are given in a misleading way, it should be explained that there is also the lower limit (e.g. for accumulation mode 0.25 um).

We agree with the reviewer and we modified the definitions of quasi-ultrafine, accumulation and coarse mode PM as follows (see the beginning of the method section):

- Quasi-ultrafine PM: particles with an aerodynamic diameter less than 0.25 µm
- Accumulation PM: particles with an aerodynamic diameter between 0.25 and 2.5 µm
- Coarse PM: particles with an aerodynamic diameter between 2.5 and 10 µm

-page 4937, determination of air exchange rate: authors should explain how they took into account changes in outdoor CO (Abt et al. used sulfur hexafluoride), and which were the dominant indoor sources of CO

Unless we are mistaken, the reviewer is confusing the way that AER was estimated (using CO data) with the way Finf for $PM_{2.5}$ was calculated (using IN/OUT ratios of BAM data). As explained in the main text and in Polidori et al (2007; also referenced in the present paper), only time-periods when the CO concentration peaked at values significantly higher than the background CO level and was followed by a non-source period (mostly observed in the morning and probably associated with cooking activities) were considered in our calculations.

-page 4938, determination of infiltration factor: I/O ratios <1 do not guarantee that indoor sources are not active – was there no information on indoor activities during the measurements available?

Measurement taken at one of the San Gabriel sites during the first phase of CHAPS (from 08/23/2005 to 10/15/2005) showed substantial morning peaks in indoor organic carbon (OC), particle number concentration (PN) and $PM_{2.5}$ between 06:00 and 09:00 am, probably from cooking activities in the kitchen adjacent the indoor sampling site where breakfast, lunch and dinner were all cooked at this time using gas stoves/ovens. Interestingly, cooking did not affect elemental carbon (EC), CO, and NO_X, whose indoor and outdoor levels were mostly influenced by morning rush hour traffic. With the exception of these morning peaks, indoor and outdoor particle and gas concentrations tracked each other well, although indoor levels were generally lower than outdoor levels. As discussed in one of our previous publications (Polidori et al. 2007) this suggests that indoor sources of OC, PN and $PM_{2.5}$ were not significant other than during the morning cooking events, and that indoor EC mainly originated from outdoor sources. Indoor cooking affected the concentrations of the least and the most volatile OC fractions (OC_1 and OC_{2-4}, respectively) equally.

-table 1: information on mass and total trace element concentrations in different size fractions during the two seasons should be given, and used in the interpretation of the results

To comply with the reviewer's request, Table S2 was added to the Supplemental Information document, and the initial part of the Result section was modified as follows.

"Indoor and Outdoor Elemental Composition

Table 1 provides geometric means (± standard deviation) of weekly averaged indoor and outdoor concentrations of selected TEs…….. Most of these TEs were consistently present in both indoor and outdoor samples and, generally, the sum of their concentrations tracked the corresponding PM level well within each size-fraction (Table S2)."

Table S2 Geometric means (µg/m^3 ± standard deviation) of indoor (IN) and outdoor (OUT) weekly concentrations for PM mass (Mass) and the sum of all measured trace elements (TTE) detected at the 4 retirement communities during CHAPS. Data were segregated by site (SG1, SG2, SG3, and RIV), season (warmer, W, and the colder, C), and size fraction (quasi-ultrafine, accumulation, and coarse mode PM). The 3 San Gabriel Valley sites and the site in Riverside have been denoted as SG 1, SG 2, SG 3, and RIV, respectively.

-page 4940, lines 15-16: should read "outdoor-indoor" instead of "indoor-indoor"?

The reviewer is correct. The correction was made.

How were the deductions concerning outdoor origin made in practice?

For the purpose of this study the indoor/outdoor ratios (I/O) of these trace element and the corresponding Spearman correlation coefficients (SCC) were used to determine how efficiently each of these species penetrated indoors (e.g. I/O and SCC close to 1 were indicative of outdoor origin). In a previous publication (Polidori et al. 2007) we used a more rigorous single compartment mass balance model to assess the mean contributions of indoor and outdoor sources to measured indoor OC, EC, PM$_{2.5}$ and PN concentrations. However, this type of analysis was behind the scope of this paper and has not been repeated for trace metals. Moreover, it is important to point out that the single mass balance approach is best suited for continuous measurements and not 24-hr data like those discussed in the present study.

-page 4941, variability in I/O ratios, S and R: information on the ventilation systems of the main buildings (including efficiency classes of the filters), would help interpreting the variability

The variability of the I/O, S and R-values for the trace elements present in each size fraction has been included in the text when appropriate. For example,

- on page 4939 (starting on line 23) we stated that "…at all retirement communities, outdoor quasi-UF S, Cr, Ba, Mo, Zn, Pb and Cu were well correlated with each other (Spearman correlation coefficient, or R, ranged from 0.60 to 0.95; $p<0.05$)…”.

- Also, on page 4940 (starting on line 14) we noticed that “Consistent with our expectations, outdoor species in coarse mode PM associated with re-suspended soil dust such as K, Mg, Al, Ca, Ti, Fe and Mn were highly correlated with each other both at the San Gabriel sites and in Riverside, with Spearman correlation coefficients ranging from ~0.7 to 0.99 ($p<<0.05$). Moreover, statistically significant correlations (from 0.40 to 0.85; $p< 0.05$) were observed at all locations among outdoor Ni, Zn and Fe (three elements with potential industrial sources), especially in the coarse mode.”

Although specific information on the ventilation systems is not available, we stated explicitly that “the AERs at the four retirement communities were relatively low (average AERs varied from 0.25 to 0.40 h^{-1} in the warmer seasons and from 0.26 to 0.33 h^{-1} in the colder seasons; Table 2). The low AERs estimated in this study are consistent with the structural characteristics of the sampling locations (two recreational areas, a dining room, and a hallway; all well insulated environments), the low number of open windows and doors, and the presence of central air conditioners.”

-page 4941, high I/O ratio of Zn: is smoking a plausible explanation in the current study? Was smoking allowed and if yes, how frequent were smoking events?

Smoking was not allowed in the studied retirement communities.

-page 4944, line 1: Zn and Fe are also closely associated with non-exhaust traffic emissions

At the end of page 4944 we stated that “….Zn is mostly a product of tire attrition (Singh et al., 2003),…”.

-page 4944, line 17: I’m not convinced that based on similar indoor and outdoor EF profiles one can judge that most of the trace elements were of outdoor origin

We agree that this could be lead to some confusion. Thus, the sentence starting on page 4944, line 14 was modified to “The indoor and outdoor EF profiles in each size fraction were very similar both at the San Gabriel valley sites and in Riverside, suggesting that at all retirement communities the PM composition was influenced by a similar natural / anthropogenic source mix.”

-page 4945, elements as tracers of outdoor PM: it should be stated more clearly that the use of tracers for PM of ambient origin is dependent on size distribution. Thus, maybe the apparent overestimation of infiltration factor using S in the present study was not just due to presence of semi-volatiles, but also due to differences in the size-distribution of PM2.5 between locations?

The reviewer observation is correct in principle. However, S, Ni, Zn, and Fe, have typical mass median diameters of about 0.5–1.0 µm (S, Ni, Zn) and 3–4 µm (Fe) (Milford and Davidson, 1985). Also, in one of our recent publications (Arhami et al. 2009) we have found, among other things, that the size distribution of S and $PM_{2.5}$ in the Los Angeles area is quite similar.

Arhami M., Sillanpää M., Hu S., Geller M.D., Schauer J.J. and Sioutas C.*. " Size-segregated Inorganic and Organic Components of PM In the Communities of the Long Angeles Harbor Across Southern Los Angeles Basin, California." *Aerosol Science and Technology*, 43(2), 145-160, 2009

-page 4946, lines 7-17: how do the rather similar I/O, R and intercept for S and Ni lead to conclude that using S (but not Ni, implicitly) as a surrogate for PM2.5 infiltration leads to overestimation?

For any given species:

IN concentration = (IN concentration of outdoor origin) + (IN concentration of indoor origin)

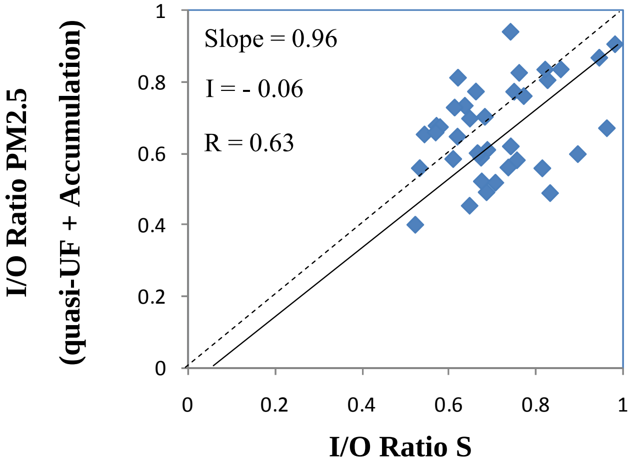
or

IN concentration = (IN/OUT ratio × OUT concentration) + (IN concentration of indoor origin)

Using the IN/OUT ratio for Sulfur (0.93; see Figure 4b) as the infiltration factor for PM2.5 would lead to an overestimation of indoor concentration of outdoor origin for PM2.5. This is assuming that the "actual" IN/OUT ratio for PM2.5 (as determined by continuous BAM measurements) is between 0.38 and 0.52 (page 4946; line 16). Using the IN/OUT ratio for Ni (0.97; Figure 4b) as the infiltration factor for PM2.5 would also result in an overestimation of indoor concentration of outdoor origin for PM2.5.

Further, shouldn't sulfur levels in quasi-ultrafine and accumulation mode PM be summed in order to estimate infiltration for PM2.5?

The reviewer's observation is correct. However, since accumulation mode particles represent the majority of the PM2.5 mass and the typical mass median diameters of S is between 0.5 and 1.0 µm, the plot of "I/O Ratio PM2.5" vs "I/O Ratio S" (below) is not very different from that shown in Figure 4b for accumulation particles.



–page 4948, outdoor PM concentrations as surrogates of indoor-infiltrated PM in time-series studies: when the analyses in the present paper have not covered any longitudinal aspects, in minimum presented longitudinal indoor-outdoor correlations for elements, conclusions cannot be drawn about the use of outdoor measurements in longitudinal epidemiological studies

We are not sure why the reviewer believes that we have not covered "any longitudinal aspect". We have collected a series of measurements at 4 different locations over a period of time of 2 years. The authors believe that out statement on page 4948 is well justified.

Reviewer #2

General Comments

The authors have done an exhaustive chemical characterization of ambient and indoor aerosol concentrations in 3 size ranges at four sites. This paper provides an extensive data set to examine the infiltration of coarse, fine and ultrafine particles into the indoor environments. Indoor concentrations of particulate matter are crucial because people spend more than 80% of their time indoors, and are especially important for susceptible subpopulations, in this case the elderly. It was found that Sulfur might not be an especially good tracer for west coast sites because its penetration efficiency is high with regards to the rest of the accumulation mode, and its deposition rates are slower than other particle types. In addition, many semi-volatile species, the prime example being ammonium nitrate, may evaporate indoors due to the low concentrations of the corresponding gas phase species. The results of descriptive paper like this are instructional. The authors need to decide if this is an overview paper or is it an attempt to build a case for using another tracer besides Sulfur for these studies. If the former is the case, more quantitative effort needs to be made between trace elemental concentrations and sources.

We believe that these points have been properly addressed in the manuscript. As explained in the result section, our results suggest that using the I/O_S ratio as a surrogate of the infiltration factor for $PM_{2.5}$ might lead to an overestimation of the fraction of indoor $PM_{2.5}$ of outdoor origin, at least in the communities considered in our study and, likely, at most other residences located in the Western US, where the contribution of ammonium nitrate and that of other semi-volatile species to the measured ambient PM2.5 concentration is substantial. In the conclusions, we also speculated that it is not prudent to use a conservative compound (S or Ni) to monitor the infiltration behavior a "non-conservative" species ($PM_{2.5}$). Thus, we recommended using continuous indoor and outdoor BAM measurements to calculate the infiltration factor of $PM_{2.5}$ instead.

Coupling these results with a receptor model would be beneficial.

We agree with the reviewer, but expanding the data analysis of this paper to include a receptor modeling section would be behind the scope of the current study.

If it is to build a case for another tracer, then the discussion needs to be tightened to focus only on sulfur and then propose from the quantitative analysis of the other TE data, which one would be better served for this purpose. If the authors want to make the case that vaporization of aerosol components are important, data showing lower I/O ratios and Ss for NH4NO3 might do it.

In the result section we pointed out that "The average F_{inf} for ammonium nitrate reported by Lunden et al. (2003) and Sarnat et al. (2006) during 2 previous studies conducted in Southern California homes was ~0.2."

Specific comments

The data in Figure 2 are quite difficult to read. Because there is so much data presented, deciding above which tack to take will perhaps clear this up.

The authors believe that presenting the median indoor / outdoor concentration ratios (I/O) of the most abundant trace elements along with the corresponding regression slopes ($\underline{S}$), and Spearman correlation coefficients (R) for all size fractions and at all sites represents the most efficient way to summarize and compare these results.

Page 4938 lines 1-4. What were the AERs calculated for each of the buildings? How were k's calculated?

As explained in the "Data Analysis" section the average AERs varied from 0.25 to 0.40 h^{-1} in the warmer seasons and from 0.26 to 0.33 h^{-1} in the colder seasons (see Table 2 for details). Also, k values were not calculated, as infiltration factors were estimated from indoor and outdoor mass measurements.

Page 4940 lines 24 through 26. Relatively short residence time of which size fraction? Coarse particles have a short residence time. So do ultrafines. Which size range is being discussed here?

As stated on page 4940 (starting on line 23) "In the quasi-UF mode (Fig. 2a), the magnitude of I/O, S and R values for TEs of both crustal and anthropogenic origin was highly variable. This likely reflects the spatial heterogeneity of combustion sources, such as motor vehicle emissions, the relatively short atmospheric residence time of this size fraction, and the fact that…"

Page 4943 lines 13 and 14. This sentence should be near the calculation of EF, perhaps line 9.

We agree with the reviewer's comment, and the sentence "For each individual element, values close….." was moved at the end of line 9.