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Interactive comment on "Size and time-resolved roadside enrichment of atmospheric particulate pollutants" *by* F. Amato et al.

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Replies to the comments by R.M. Harrison (Referee)

We would like to thank Prof. Harrison's for his suggestions as to how the data analysis could be extended, which we followed and which have resulted in the addition of a new and very interesting section to the text.

Comment 1: Regarding his comment on "road traffic signatures" for trace elements and OC/EC, we calculated the increment ratios for EC and OC, as well as for the tracer elements of road traffic (those with roadside enrichments REs>35% at all sites). The results were described in a new section entitled "Road traffic signatures" and a new Table (see below). In short, we obtained OC/EC ratios for the roadside and urban

increments which were comparable to those obtained by Harrison & Yin (2008). As for trace elements, we obtained very similar ratios for the roadside and urban increments for Cu, Sb, Sn and Fe, which could be used as marker ratios in source apportionment analyses. The results are also highlighted in the abstract and conclusions.

The new section reads as follows: "3.3. Road traffic signatures The analysis of the concentration increments of specific elements and components at the HT site with respect to the T site, and at T with respect to UB, allows for the determination of ratios which may be characteristic of road traffic emissions. These ratios may be considered signatures of road traffic emissions, and be used in, i.e., source apportionment studies. Based on the EC and OC increments at HT with respect to T, and T with respect to UB, OC/EC ratios were calculated (Table 3). These ratios were determined as follows: the difference between HTOC and TOC was calculated, and the same was done for HTEC and TEC, and then the ratio between the two values (OC/EC ratio of the roadside increment) was obtained. The same was done for T and UB to obtain the urban increment. In this way, the OC/EC ratio of the roadside increment (HT vs. T) was 0.28, whereas the ratio of the urban increment (T vs. UB) was 0.52, mainly resulting from the larger EC than OC increment registered at HT. These ratios are of the same order of magnitude as the roadside and urban increments for OC/EC registered in Birmingham (0.38 and 0.29, respectively, Harrison & Yin, 2008), even if the urban increment was relatively higher in our study. In addition, EC/TC ratios were also analysed and compared with that characteristic of emissions from heavy duty diesel vehicles (EC/TC=0.78; USEPA, 2002). EC/TC ratios in our study were 0.78 and 0.66 for the roadside and urban increments, respectively, and are thus consistent with those characteristic of diesel road traffic emissions. According to national statistics, 70% of all new vehicles in 2010 and 40% of the total vehicle fleet is comprised of diesel vehicles in Barcelona (DGT, 2011). A similar analysis was carried out for trace element concentrations. Roadside and urban increments were determined for Group I elements with REs >35% for all types of sites, as well as for Group II and II elements (variables not enriched at the site with higher traffic volume, only certain ratios calculated for comparison). As shown in Table 3, similar ratios were obtained for roadside and urban increments between Group III elements (Cu, Sb, Sn, Fe), thus confirming the ability of these ratios to represent road traffic emissions. The lowest variability and thus higher stability of the ratios (see standard deviations in Table 3) was obtained for Cu, Sb and Sb (Cu/Sb=6.8-8.0; Cu/Sn=4.7-5.4; Sn/Sb=1.49-1.50), in comparison with Fe (Fe/Sn=93-109; Fe/Sb=137-158; Fe/Cu=17-29). Despite this relative variability, enrichment ratios for these elements may be considered comparable in the roadside and urban environments, and thus characteristic of road traffic emissions. Conversely, the ratios for Group II and II variables were markedly different in the roadside and urban environments (ratios calculated for a few number of variables, as an example for comparison)."

Please see attached pdf of Table 3

Table 3. Road traffic trace element signatures based on the ratios between the roadside and urban increments calculated for each element as the difference between the concentrations (in ng/m3) at the HT and T sites, and at the T and UB sites. Ratios calculated on a sample-by-sample basis.

Comment 2:

Prof. Harrison mentions a number of issues here:

- Wind directional effects: We agree with Prof. Harrison in considering that street canyon recirculation may have provoked an overestimation of pollutant increment at the kerbside sites (VAL and COR). For an exhaustive evaluation of this issue we followed the same approach of Harrison et al., 2004, investigating the relationship between pollutant increments and wind speed from distinct sectors. For hourly increments we observed a decreasing trend with an increase of hourly averaged wind speed from the sector 45-225°. This sector corresponds to the sea-breeze activation (10am-10 pm) and as expected by literature studies (Berkowicz, 2000; Harrison et al., 2004) it provoked a recirculation plume inside the street with pollutant accumulation at the

leeward side of the street. Therefore, being the mobile laboratory station located at the windward side, lower concentrations of traffic markers such as Cu and Fe were registered as wind speed from the 45-225° was increasing (Fig. D1). This yields to a slight overestimation of kerbside increments of pollutants presented in Tables 2 and 3 of the original manuscript. However when plotting the increments against wind speed from the opposite sector, no increasing trend was observed (Fig. D2) and range of delta concentrations was the same of the wind sector 45-225°, revealing that probably street canyon effects in the study area exist but are not so strong like in previous studies in London for example (Harrison et al., 2004).

Figure D1. Increment of coarse Cu during hours with wind direction 45-225° (sea-breeze scenario).

Figure D2. Increment of coarse Cu during hours with wind direction 225-45° (land-breeze scenario).

However, it must be noticed that wind data from the 225-45 sector, correspond with nightly hours, with very few traffic emissions, except for the first morning hours (6 to 8 am). For this reason we are going to re-plot our graphs (Figure D2) only for this time-window, to see if an increasing trend can be observed.

For daily measurements we believe that the particular atmospheric scenario of Barcelona, with alternate intra-daily winds (sea-breeze during the day, land-breeze during the night) make this analysis not suitable for our purpose.

- Method used to derive the regression equation: we first performed a L1 norm approximation (Barrodale and Roberts, 1977), minimizing the absolute value of (Y-y) instead of (Y-y)2 in order to reduce the influence of outliers. However we agree that the variable on the x axis has the same sources and type of uncertainty of variable in y axis: therefore we will apply the RMA regression (Ayers, 2001) and plot the new regression lines.

âĂć Regression line forced through the origin: When we will calculate the new regression lines we will not force them to pass from the origin in order to compare our results with those from Harrison et al., 2004. We expect to find regression lines with an intercept for all traffic–related pollutants given that both our traffic sites are street canyons. A discussion will be done, whether our results agree with the interpretation form Harrison et al., 2004 or not.

We hope our replies have helped clarify the manuscript so far. We believe the changes have certainly improved it.

References:

Ayers, G.P., 2001. Comment on regression analysis of air quality data. Atmospheric Environment 35, 2423–2425.

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USEPA, 2002. Health Assessment Document for Diesel Engine Exhaust. EPA/600/8-90/057F. National Center for Environmental Assessment, Washington, DC.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 453, 2011.

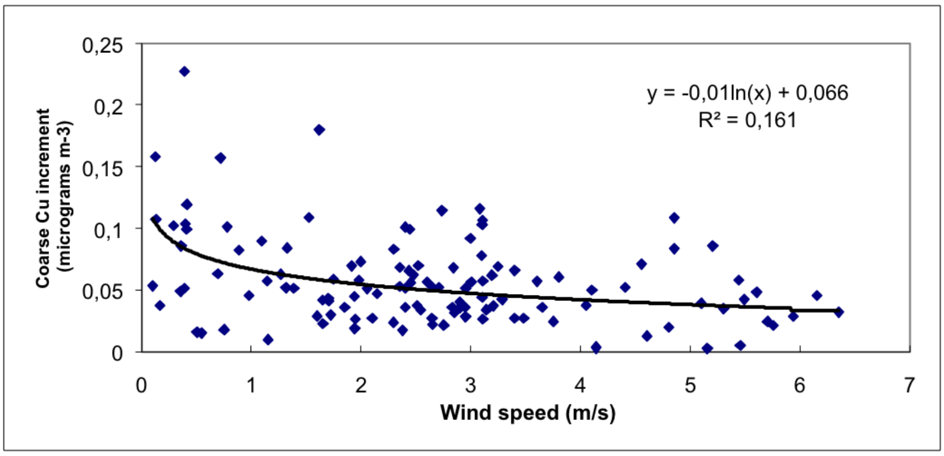


Fig. 1. Figure D1. Increment of coarse Cu during hours with wind direction 45-225° (sea-breeze scenario).

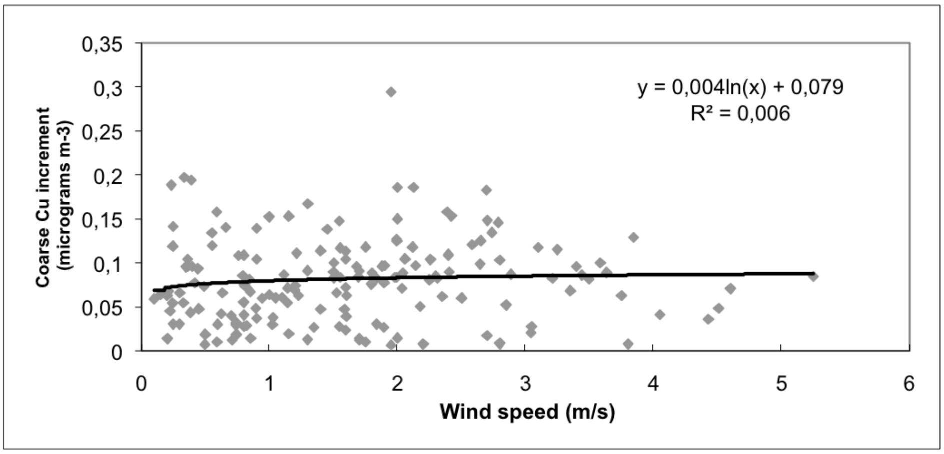
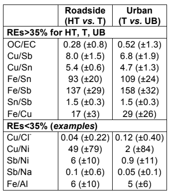


Fig. 2. Figure D2. Increment of coarse Cu during hours with wind direction 225-45° (land-breeze scenario).



	Roadside (HT *vs.* T)	**Urban (T *vs.* UB)**
REs>35% for HT, T, UB		
OC/EC	0.28 (±0.8)	0.52 (±1.3)
Cu/Sb	8.0 (±1.5)	6.8 (±1.9)
Cu/Sn	5.4 (±0.6)	4.7 (±1.3)
Fe/Sn	93 (±20)	109 (±24)
Fe/Sb	137 (±29)	158 (±32)
Sn/Sb	1.5 (±0.3)	1.5 (±0.3)
Fe/Cu	17 (±3)	29 (±26)
REs<35% (*examples*)		
Cu/Cl^-	0.04 (±0.22)	0.12 (±0.40)
Cu/Ni	49 (±79)	2 (±84)
Sb/Ni	6 (±10)	0.9 (±11)
Sb/Na	0.1 (±0.6)	0.05 (±0.1)
Fe/Al	6 (±10)	5 (±6)

Fig. 3. Table 3. Road traffic trace element signatures based on the ratios between the roadside and urban increments calculated for each element as the difference between the concentrations (in ng/m3) at the