Chemistry and sources of PM_{2.5} and volatile organic compounds breathed inside urban commuting and tourist buses

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Abstract

Inhalable particulate matter (size <2.5µm: PM_{2.5}) inside commuting and tourist buses moving through the city of Barcelona, Spain, was chemically analysed. The analyses show PM dominated by organic carbon (mostly 10-20 µg/m³) and elemental carbon (mostly 3-6 µg/m³; OC/EC=3.4), followed by SO₄²⁻, Fe, Ca, K, Al₂O₃, Mg, and Na, with calculated mineral content being around one third that of total carbon. Elemental carbon levels are higher inside diesel buses than those powered by natural gas or electricity, and higher in the upper floor of open-top double decker tourist buses than in the lower floor. Overall, major element concentrations inside the buses are typically 2-8 times higher than 24h-averaged urban background levels, although some metallic trace elements, notably Cu and Sb, are exceptionally enriched due to the presence of brake particles, especially on routes involving higher gradients and therefore more brake use. In contrast, Cu and Sb concentrations in electric buses are unexceptional, presumably because these buses rely more on regenerative braking and are hermetically sealed when moving. Seasonal differences reveal PM to be more mineral in winter (Al₂O₃ 1.3 µg/m³ vs. summer average of 0.3 µg/m³), with summer enrichment in Na, Mg, P, V, Ni and SO₄²⁻ being attributed to marine aerosols contaminated by port emissions. Source apportionment calculations identify 6 main factors: road dust resuspension, metalliferous (brake wear and metallurgy), local urban dust, secondary sulphate and shipping (6%), vehicle exhaust (19%), and an indoor source (46%) interpreted as likely related to the textile fibres and skin flakes of bus occupants. Volatile Organic Compounds measured inside all buses except one were dominated by 2-Methylpentane (14-36 µg/m³), Toluene (10-30 µg/m³), Xylene isomers (10-28 µg/m³, with m- >> o- > p-Xylene) and n-Pentane (5-15 µg/m³). ΣBTEX concentrations were <70 µg/m³, with Toluene being commonest, followed by m-Xylene, with p-Xylene, o-Xylene and Ethylbenzene each below 7 µg/m³ and Benzene concentrations always less than the EU limit value of 5 µg/m³. The VOCs mixture is similar to that recently reported from inside Barcelona taxis (although inside the larger volume bus VOC concentrations are lower than in the taxis) and is interpreted as providing a chemical fingerprint characterising traffic-contaminated ambient air in the city road environment. The notable exception to the VOC content was a brand new hybrid diesel bus still offgassing volatiles to such an extent that Σ(alkane+alkene+aromatic) indoor concentrations exceeded 800 µg/m³, with ΣBTEX ten times higher than normal.

Keywords: Indoor air quality, commuting, public buses, electric bus, diesel bus, tourist bus

1. Introduction

Hundreds of millions of people in the world spend part of their workday commuting through a city ($\approx$ 8% of the daily time) and inhaling atmospheric pollutants, including organic and inorganic compounds in the form of gases or particles. In many cases these urban journeys provide a disproportionate percentage of the individual's average daily exposure to inhalable toxins, and recognition of this fact is reflected in a large body of scientific literature on commuting and air pollution that goes back over 50 years (e.g. Haagen-Smit 1966; Cepeda et al., 2017). The number of such publications has accelerated in recent years, accompanied by an increasingly wide recognition of the serious insult to human health inflicted worldwide by inhaling contaminated urban air. Given the sometimes radical differences in atmospheric microenvironments experienced by city travellers using different transport modes, many of these publications have turned their attention specifically to air quality found inside moving vehicles (e.g. Alameddine et al., 2016; Fruin et al., 2011; Hudda et al., 2011, 2012; Hudda and Fruin 2018; Jo and Yu, 2001; Leavey et al., 2017; Lee et al., 2015; Madl et al., 2015; Moreno et al., 2015; Tartakovsky et al., 2013; Xing et al., 2018; Yang et al., 2015; Zhu et al., 2007). In the context of legislative demands imposed by environmental authorities, the main focus of these studies has been on PM_{10} and $\text{PM}_{2.5}$ mass, numbers of ultrafine particles (UFP), concentrations of gaseous pollutants such as NO_x , CO and CO_2 and, more recently, volatile organic compounds (VOCs).

In this paper we turn our attention to a much less-studied aspect of in-vehicle air quality, namely that of the major and trace element chemistry of inhalable particles breathed by passengers using public transport. Such studies are few primarily because of the practical difficulties of obtaining enough PM sample to allow a comprehensive chemical analysis, a challenge we have overcome by using state-of-the-art portable equipment, having access to our own ICP-AES/MS geochemical laboratory, and a sampling team prepared to spend many hours inside the vehicles. Specifically, we have collected $\text{PM}_{2.5}$ samples from filters placed inside public transport buses moving through the city of Barcelona, as well as VOCs with in situ pumping and adsorption into cartridges packed with graphitized BC adsorbents, choosing different fuel-type buses, routes, and seasons of the year to investigate the main factors influencing commuting exposure to $\text{PM}_{2.5}$ pollutants. This study has been complimented by the addition of comparative chemical data from 24h averaged $\text{PM}_{2.5}$ obtained at an urban background site in the city (Palau Reial), and by source apportionment calculations using Positive Matrix Factorization.

2. Methodology

The air quality sampling was carried out within the BUSAIR project between May 2017 and March 2018 inside public buses operated by the Metropolitan Transports of Barcelona (TMB), Spain, which carries around 203 million of passengers a year and comprises 101 lines running along a network of 830 km built progressively since 1906 (2018 TMB data). All buses are equipped with an air-conditioning system (AC) which starts functioning in spring until the end of the summer. With this in mind the sampling was divided in two different campaigns, "summer", from May 2017 to September 2017, and "winter", from November 2017 to March 2018, to observe any differences in air quality between buses with and without AC. Buses were also selected to include a range of different engine-types operating in the fleet (diesel, natural gas, electric, hybrid). In addition, buses were chosen to include lines representative of the newly-introduced route system that emphasises "vertical" (i.e. running to and from the coastline, across the sloping piedmont that defines the city surface) and "horizontal" (parallel to the coastline) trajectories.

A total of 24 bus pairs were sampled, as listed on Table 1, including two tourist bus lines (open top double-decker buses) running along the “red” and “blue” routes through the city. The bus pair would run on their normal scheduled service, one usually 10 minutes or so behind the other. Thus, on each sampling day, two members of the research team travelled for around 2 hours along the same route but in buses of different fuel type (with the exception of the tourist buses). To take an explanatory example from Table 1, on 16 May the first bus of the chosen pair operating on “vertical” route V13 was a diesel Euro V, with a hybrid diesel being the next bus to arrive, and sampling equipment was placed inside each of these two buses for a 2-hour return journey. This procedure was repeated three times on dry weekdays to ensure enough PM sample was collected for chemical analysis (i.e. 6-hour samples collected over 3 days: in the example above, on 16, 17 and 18 May). In several cases schedule changes meant that sampling could not be done on strictly consecutive days, but it was always completed (without changing the filter) during the next available weekday and at the same time in the morning. Similar logistical problems with schedule changes meant that there are two bus pairs that were not repeated in summer and winter (left blank in Table 1).

Sampling equipment inside the buses was located in the middle of the bus in the space reserved for wheelchairs and strollers, facing the central double doors. Notes were written during the sampling, recording variables such as if the AC was on or if the windows/doors were open. Ambient environmental conditions such as temperature (T) and relative humidity (RH) were also measured. Summer average T and RH inside the buses ranged between 19-27°C and 38-64 % in summer, and 14-25°C and 28-45 % in winter.

For PM_{2.5} chemical composition determination, 37 mm quartz fibre filters (Pallflex® Air Monitoring Filters, Pall, LifeScience) were used loaded in a personal environmental monitor (761-203B PEM, SKC, usually known as portable emission monitoring system) connected to a personal air sampling pump (Leland Legacy, SKC) operating at 10 L/min. The filters were gravimetrically weighed prior to their use, having been first placed for 6 hours in an oven at 200°C (Mettler) to eliminate volatiles, and then kept at room temperature for 24 h before weighing them (XP105DR, Mettler Toledo) in an acclimatised room where T and RH are controlled to 20°C and 50 %, respectively. The same filter was used during 3 weekdays of sampling in order to achieve enough sample to be analysed. Once the sampling had been done, the filters were kept inside a box to maintain them in darkness before being subjected to the same procedure as for blank filters before weighing.

Given the fact that the sampling campaign took place over several months, all data in the study have been deseasonalised with reference to the Barcelona Urban Background station at Palau Reial (UB-PR), thus smoothing (not removing) the effect of meteorological parameters as a whole (Rivas et al., 2014). This calculation involved determination of an adjusted concentration $(C_i^j)_k^*$ of the i_{th} pollutant for the k_{th} day at the bus j_{th} as shown in Eq. (1):

$$(C_i^j)_k^* = (C_i^j)_k / [(C_i^{PR})_k / (\overline{C_i^{PR}})] \quad (1)$$

where $(C_i^j)_k$ is the concentration measured at the bus $(C_i^{PR})_k$ and $\overline{C_i^{PR}}$ are the 6h average corresponding to the 3 days k^{th} and campaign averages at UB-PR, respectively.

A total of 48 PM_{2.5} gravimetric samples collected on quartz fibre filters using the PEM samplers were chemically analysed. First of all, a 1.5 cm² section from the middle of the filter was cut in order to analyse organic and elemental carbon (OC, EC) by a thermal-optical technique using a Lab OC/EC Aerosol Analyser (Sunset Laboratory Inc.). The rest of the filter was acid digested with 2.5 mL of HF, 1.25 mL of HNO₃, 1.25 mL of HClO₄ for major and trace elements analysed using ICP-AES and ICP-MS respectively. For quality control, 0.1 g of 1633b Standard Reference Material (Trace Elements in Coal Fly Ash, NIST) was used to identify any possible analytical or calibration.

Volatile Organic Compounds were measured in 16 of the buses using stainless steel cartridges custom packed with activated graphitized BC adsorbents, using the same methodology as detailed in Moreno et al. (2019). With regard to the PM_{2.5} source apportionment calculations, these used Positive Matrix Factorization software (PMF v5, Paatero and Tapper, 1994; Amato et al., 2009), using relevant criteria (see Paatero and Hopke, 2003) that allowed selection of 11 strong species (OC, EC, Ca, Fe, Mg, SO₄, Mn, Cu, Sr, Sn, Sb) and 10 weaker species (Al₂O₃, K, Na, Ti, V, Ni, Zn, Ba, La and Pb). The data matrix was uncensored (i.e. negative) so that below detection and zero limit values were included in the analyses to avoid a bias in the results (Paatero, 2007).

3. Results

The chemical analyses of the 48 PM_{2.5} samples collected during the BUSAIR campaigns are presented in chronological order in Table S1 (supplementary information) which also records the bus fuel-type (diesel (EIV, EV), hybrid diesel (HD), compressed natural gas (CNG), hybrid compressed natural gas (HCNG) and electric), and the bus number/route (V = “vertical”; H = “horizontal”; TB tourist bus red and blue trajectories). The analyses are further grouped into 20 “summer” (AC on with closed windows; May to September) and 20 “winter” samples (November to February), the other 8 samples were considered mixed. The data from these various sub-groups based on bus engine type, season, and route are averaged in Table 2 which for comparison adds the values for the average for all buses (AB) and the urban background (UB) in Barcelona during the sampling period.

The highest concentrations, as recorded in Tables S1 and Table 2, and graphically presented in Figure 1a, are those of OC (most values 10-20 µg/m³) and EC (most values 3-6 µg/m³), followed by SO₄²⁻, Fe, Ca, K, Al₂O₃, Mg and Na. Average OC concentrations are in general around x3 those of EC average (OC/EC=3.4), and calculated mineral content is approximately one third that of total carbon content (EC+OC). With regard to the trace elements the highest concentrations are recorded for Zn and Cu, followed by Zr, Ti, Mn, Cr, Ni, Sb, Sn, V, Sr, Pb, Hf, Ce, and La. This distinctive inorganic trace element signature of interior bus air is further emphasised by comparing the BUSAIR chemical database with levels recorded within the Barcelona UB-PLR (Table 2; Figure 1a and b). Whereas concentrations of most elements and compounds recorded in the contaminated city road are raised typically 2-8 times higher than UB-PLR levels (AB/UB on Table 2), some elements stand out as unusually enriched (both Cu and Sb >10 times: Figure 1b).

We now consider the PM chemistry characterising exposure in each of the bus sub-groups shown in Table 2, then present the results of source apportionment calculations. Finally, we examine the pattern of VOCs present inside sixteen of the buses used during the winter campaign (Table S2, supplementary information).

3.1. Bus type

Although the results reveal considerable PM_{2.5} chemical variation, the majority of data fall within a relatively restricted range. In the case of EC, for example, most (73%) buses recorded levels of 3-7 µg/m³ although exceptionally, concentrations as high as 19 µg/m³ and as low as 1 µg/m³ were reached (Table S1). Most bus pairs show similar EC concentrations, with nearly half differing by <1 µg/m³ and only 3 pairs differing by more than 2.5 µg/m³ (Table 3). A notable exception to this general rule is a diesel EV/EIV pair (16 January) that records a difference in EC content 17 µg/m³ (Table 3).

A similar pattern is revealed by OC concentrations, which cluster around 10-15 µg/m³ and rarely (25%) exceed differences >5 µg/m³ between bus pairs. In the case of “mineral” concentrations (essentially mainly a mix of silicates and carbonates: Table S1) these again show very few

exceedances above $10 \mu\text{g}/\text{m}^3$, with 92% of bus pairs showing differences below $2 \mu\text{g}/\text{m}^3$, irrespective of whichever engine type was powering the bus.

Taken overall, the diesel buses record slightly higher average EC concentrations inside the bus when compared to CNG or electric models, this being interpreted as likely evidence for some degree of self-pollution (Table 2). In contrast, when compared to diesel buses the six electric buses show relatively lower average concentrations of many $\text{PM}_{2.5}$ components, but especially the metals Cu and Sb (Figure 2a). These electric buses have a window system which is hermetically sealed, climate control is regulated by the driver, and they are equipped with regenerative braking which reduces the use of friction brakes, all of which favour reduction of outside PM infiltration, including that sourced from their own brakes.

The data from the tourist buses offer insight into the differences between the upper floor, which is wide open to outdoor air, and the lower floor which, although ventilated via stairs leading to the open top floor, is more confined. The data demonstrate consistently higher EC levels in the upper floor (“out” in Table S1) than in the downstairs interior (“in”). If the concentration of EC inside buses can be viewed as a proxy for traffic emissions, this would indicate that passengers travelling on the open upper deck of the bus are more exposed to traffic exhaust emissions than those below. However, it should be noted that this difference between EC concentrations upstairs and downstairs in these buses is always $<2.5 \mu\text{g}/\text{m}^3$.

3.2. Season

The two subgroups selected on the basis of warmer (“summer”) and cooler (“winter”) seasons are listed in Table S1 and compared with UB-PLR concentrations in Figure 2b. The $\text{PM}_{2.5}$ chemistry for each of these two subgroups is quite different, with the winter samples being noticeably richer in mineral dust (summer average Al_2O_3 $0.3 \mu\text{g}/\text{m}^3$; winter average $1.3 \mu\text{g}/\text{m}^3$) and slightly more carbonaceous (summer OC+EC $19 \mu\text{g}/\text{m}^3$; winter OC+EC $24 \mu\text{g}/\text{m}^3$). Several trace elements occur in higher concentrations in winter, most notably Sb, Cu, Zn and Mn. The highest increase was recorded for Sb x6.5 above UB-PLR in summer and x21 in winter. In contrast concentrations of Na, P, V, Ni, Cr, SO_4^{2-} and especially Mg were considerably lower in summer. The likely controls on these seasonal chemical differences are discussed below.

3.3. Route

The “route” sub-groups listed on Tables S1 and Table 2 have been chosen on the basis of whether they run essentially horizontal and coast-parallel through the city (these routes being designated with the prefix H for “horizontal”), whether they operate across a considerable change of gradient between the coast and the northeast-southwest oriented hills that form the hinterland of Barcelona (prefix V: “vertical”), or whether the bus is neither H nor V but follows some more variable route through the city (buses 34, 39, 47, 19, and 60: “others” on Table 2). Vertical routes showed on average higher concentrations of carbon content (OC+EC = 25 for V vs. $18 \mu\text{g}/\text{m}^3$ for H), and mineral dust (6.2 V vs $3.6 \mu\text{g}/\text{m}^3 \text{ H}$). Other elements also occur in higher concentrations in V routes, especially Cu, Sb, Mg and K which are >50% higher in buses running along V routes (Figure 2c, Table 2) and presumably this is likely to reflect greater use of brakes on the routes with higher gradient.

3.4. Source apportionment calculations

Several PMF solutions were evaluated in terms of scaled residuals, G-space plots, profiles and contributions. The most-reliable solution provided 6 main factors responsible for the variability of $\text{PM}_{2.5}$ and its components (Figure 3):

- The first factor comprises mainly OC although it also explains a significant share of some metals such as Ti, Pb, Na, Sr and Ca. Previous studies in Barcelona have related indoor sources of high OC concentrations (without EC) to the textile fibres and skin flakes of occupants (Amato et al., 2014; Rivas et al., 2014). This is the dominant source of PM_{2.5} inside the bus (46%) increasing PM_{2.5} levels by 39.6 µg/m³ on average. In addition, this first factor is taken to include a Ca, Ti, Sr and Na grouping similar to that identified as linked to a cosmetic product source in a previous study in Barcelona (Minguillón et al. 2012). The largest contributions of this first factor were found in tourist buses, probably due to the higher occupancy.
- The second factor was traced by Cu, and mainly comprises OC and EC (OC/EC=1.8). This factor was labelled as vehicle exhaust, although it likely involves a partial contribution from brake wear as well. It is the second most important source of PM_{2.5}, contributing 16.3 µg/m³ (19%) on average. Interestingly the lowest contributions were obtained for electric buses, as already described for EC, Cu and Sb. The rest of fuel-types do not register significant differences.
- The third factor was traced by SO₄²⁻ and V (highest % of species) and was interpreted as secondary SO₄²⁻ and shipping. The mean contribution to exposure in buses was 4.8 µg/m³ (6%). Significant differences were observed between the winter (3 µg/m³) and summer (7 µg/m³) campaigns, as both oxidation processes and shipping emissions reach their maximum in summer months (Querol et al., 2001; Amato et al., 2009). The association of secondary sulphate and primary vanadium in the same factor has been reported in Barcelona before, as the ammonium sulphate particles are formed from SO_x emissions which are often emitted by heavy oil combustion processes (notably by shipping) containing high amount of Vanadium.
- The fourth factor was traced by Mg, Fe, K and Ca, with OC as main component. This factor had a contribution in only 2 bus pairs and was practically null for the rest of the campaigns. Since the 2 bus pairs included routes and vehicles used also in other days, we interpret this source as local urban dust, probably some minor building activities, which affected only 2 samples.
- The fifth factor was traced by Sb, Cu, Zn, Al₂O₃ and La and was interpreted as road dust resuspension. The main components are OC, EC and Fe, with an OC/EC ratio of 6.0. The lowest contributions of this factor were observed for electric and touristic buses, the reason for the latter remains unclear.
- The sixth factor was identified as metalliferous and accounts for most of the variance of metals originated from brake wear (Sn, Ba, Fe) and metallurgy (Mn, Pb and Zn) (Amato et al., 2009). The largest components are EC and Fe. The largest contributions were found in tourist buses, possibly due to their higher weight (higher braking emissions) and because they move mostly in the southern part of the city which is nearer to the metallurgical cluster of Baix Llobregat county.

3.5. Volatile Organic Compounds

A total of 44 VOCs were quantified inside 16 buses sampled during the winter campaign (Table S2, supplementary information). The overall VOC concentrations ranged from 69.9 to 173 µg/m³. However, bus 34 hybrid diesel was a notable exception because of the much higher concentrations (851 µg/m³). This bus is a special case in the context of the study because it was a brand new vehicle which was still degassing VOCs from the furnishing and coatings, including glues and other products. Excluding the above mentioned bus, the VOC distributions in the studied buses are rather similar. The aromatic compounds are dominant (27.5-50.2%), being mainly constituted of benzene, toluene, ethylbenzene, xylenes and trimethylbenzenes, which involve 87% of the total aromatic compounds. Toluene (10-29 µg/m³) and m-xylene (5-17 µg/m³) are common in all samples (Table S2). The overall

BTEX (Benzene, Toluene, Ethylbenzene and Xylene) signature of indoor air in the buses is remarkably similar. The typical distribution is predominated by toluene (10-30 $\mu\text{g}/\text{m}^3$) and followed by m-xylene (5-17 $\mu\text{g}/\text{m}^3$) > p-xylene (2-5 $\mu\text{g}/\text{m}^3$) > o-xylene (3-6 $\mu\text{g}/\text{m}^3$) > ethylbenzene (2-7 $\mu\text{g}/\text{m}^3$) and benzene (2-4 $\mu\text{g}/\text{m}^3$).

The alkanes (26.7-48.1%) constitute the second most abundant VOC group (Figure 4). They are dominated by 2-methylbutane (14-36 $\mu\text{g}/\text{m}^3$) followed by n-pentane (5-15 $\mu\text{g}/\text{m}^3$) which are found in all samples (Table S2). With regard to the remaining VOCs detected, only the monoterpene compound d-Limonene was present in concentrations >10 $\mu\text{g}/\text{m}^3$ and this in only four buses, one of which registered 65 $\mu\text{g}/\text{m}^3$ (Table S2).

As mentioned above, bus 34 (a hybrid diesel) registered exceptionally high VOC concentrations that together totalled over 850 $\mu\text{g}/\text{m}^3$. In this case aromatic compounds were present in higher overall concentrations (497 $\mu\text{g}/\text{m}^3$: 58% of total VOCs) than the alkane/alkene subgroup (332 $\mu\text{g}/\text{m}^3$; 39%). Most outstanding in the aromatic subgroup are anomalously high concentrations of the three xylene (= dimethylbenzene) isomers (especially o-xylene: these compounds were found in concentrations of 160 $\mu\text{g}/\text{m}^3$). Ethylbenzene was also present in exceptional concentrations (95 $\mu\text{g}/\text{m}^3$) which, like Isopropylbenzene and sec-butylbenzene, registered levels well over tenfold those in any other bus sampled (Figure 4). This bus shows a completely different BTEX hierarchy from normal, with o-xylene (160 $\mu\text{g}/\text{m}^3$) > ethylbenzene (95 $\mu\text{g}/\text{m}^3$) > p-xylene (91 $\mu\text{g}/\text{m}^3$) > toluene (44 $\mu\text{g}/\text{m}^3$) > m-xylene (43 $\mu\text{g}/\text{m}^3$) > benzene (5 $\mu\text{g}/\text{m}^3$). In the alkane/alkene sub-group the most abundant VOC was again 2-methylbutane (92 $\mu\text{g}/\text{m}^3$), as with the other buses. However, relative to levels in the other buses, the most striking alkane/alkene VOC increases were shown by cyclohexane (86 $\mu\text{g}/\text{m}^3$), n-decane (63 $\mu\text{g}/\text{m}^3$), n-octane (12 $\mu\text{g}/\text{m}^3$), and 2,3-dimethylpentane (10 $\mu\text{g}/\text{m}^3$). Other VOCs subgroups showed much lower concentrations, although relative to the other buses, there were unusually raised levels of the monoterpene p-cymene, the organochlorine 1,1,2-trichloroethane, as well as methyl methacrylate, tetrahydrofuran, and ethyl methacrylate (Table S2). As mentioned above, this bus was brand new and the high VOC concentrations presumably reflect significant off-gassing from the interior components.

4. Discussion

The data presented in this paper can be viewed as “state-of-the-art” in the sense that it is currently technically difficult to obtain gravimetric samples of inhalable particles breathed by commuters in public transport in enough quantity to allow comprehensive chemical analysis. The limitations of the personal environmental monitor used in the study meant that the same filter had to be used for three journeys (on the same route and at approximately the same time) in order to obtain just one chemical analysis, so that each of the results listed on Table 1 are an average of 6 hours, collected over three days. Such logistic limitations, added to the difficulties of negotiating permission with transport companies, have perhaps inevitably resulted in very few publications on the chemistry of indoor bus air. In this context, and despite these limitations, the information presented here represents by far the largest bus air chemical database publicly available to date, involving 132 days of direct sampling inside urban commuter buses under normal working conditions.

The design of the PM BUSAIR sampling programme was based on the expectation that several factors influence air quality inside buses, but that some of these factors are likely to be more influential than others. Thus, we sampled bus pairs powered by different engines in different seasons and following different routes through the city, adding the open-topped tourist buses as an interesting “extra” to compare with normal commuting routes. Given such variety, the number of buses sampled (48) is rather small, but it is enough to make several observations. The first of these is the distinct difference between interior bus air chemistry of PM_{2.5} in summer and winter (Figure 2b).

The air chemistry inside the buses sampled in summer is noticeably richer in Na, Mg, V, Ni, Cr and SO₄. Given the coastal position of Barcelona, a city with a large and active port catering especially for cruise ships, combined with more active landward-driven sea breezes in early summer, it seems likely that this seasonal difference in chemical signature is due to a greater influence of marine aerosols contaminated by shipping emissions and to the higher summer SO₂ oxidation (Querol et al., 2001; Amato et al., 2009). Another seasonal difference is registered in winter, when most PM_{2.5} elemental concentrations are not only higher inside the buses, but the chemical mix is noticeably richer in several trace metals, including a quite spectacular enrichment in Cu and Sb.

The data presented here fail to reveal any great difference in major element chemistry between the chosen bus pairs following the same route one after another, even though the buses were driven always by different engine types. Thus, the differences between bus pairs of measured OC, EC and “mineral” concentrations were most commonly <5 µg/m³, <2.5 µg/m³, and <2 µg/m³ respectively (Table S1). Taken overall, however, our data do suggest poorer interior bus air quality, measured as increased carbon and mineral content, is more likely to be associated with diesel buses when compared to, for example, electric buses (Figure 2a). This implicates part of the PM contamination present inside the moving vehicle as being a result of emissions from the bus itself (“self-pollution”), a phenomenon well documented in previous publications (e.g. Fondelli et al., 2008; Zhang et al., 2013; Chernyshev et al., 2019).

Another, and stronger, indication of self-pollution affecting interior bus chemistry, however, emerges from a consideration of the trace element signature of the PM_{2.5}. One of the more striking observations repeatedly noted in this study is the ubiquity and abundance of Cu- and Sb-bearing fine particulates in bus air. Previous publications have demonstrated how these elements are good tracers for brake particles (Adamice et al., 2016; Amato et al., 2011; Grigoratus and Martini, 2015). In a previous publication on public transport air quality in Barcelona we published the results of a pilot study on just three buses, demonstrating the same enrichment in Sb and introducing a Mn, Ti, Sb_x10 ternary diagram to show how bus air can be contrasted with PM_{2.5} samples collected from subway and outdoor city air (Moreno et al., 2015). On Figure 5 we plot our new BUSAIR database onto the same ternary diagram, adding the urban background data from the Palau Reial monitoring site during the sampling campaigns. The same relative enrichment in Sb and Cu inside the vehicle also strongly suggests that brake particles are more common in the buses operating along a significant slope, with the “vertical” buses (from coast line to the hills) recording concentrations >50% higher than the coast-parallel “horizontal” buses (Figure 2c, Table 2). Even more interesting is the fact that electric buses do not show such enrichment (Figure 2a), an observation that may reflect the fact that these buses have more hermetic closure and/or that they use regenerative braking and so emit fewer brake particles. Another conclusion arising from this difference in braking patterns is that it is the brake-contaminated PM plume generated by the bus itself (“self-pollution”) that is infiltrating into the bus, presumably through open windows and when doors are opened after braking upon arrival at bus stops.

The open-topped tourist buses provide a special case in that upstairs they are open to the city highway air which also enters the lower floor of the bus. This higher degree of ventilation is reflected in the fact that the PM_{2.5} mass represented by OC content is relatively low in the tourist buses (11 µg/m³) when compared to all other bus types (17-23 µg/m³) except electric (13 µg/m³) (Table 2). We also observe that those passengers travelling in the open top upper floor of the tourist bus breathe higher levels of EC, Cu and Zr, presumably sourced from fresh traffic exhaust and brake emissions (Table 2).

Our source apportionment data indicates that although almost half of the particles inhaled when travelling in the bus are most probably related to vehicle passenger emissions such as textile fibres

and skin flakes (Amato et al., 2014; Minguillón et al. 2012; Rivas et al., 2014), independently of the bus type. The infiltration from outdoor sources such as vehicle exhaust and brake wear particles both from the same bus (self-pollution) and from other vehicles, also represents an important source of pollution (19%).

Concerning VOCs, comparison of the concentrations in the inner bus atmospheres with those in open air collected in the Route Blue and Red Tourist buses, shows similar concentrations for gasoline vehicle pollutants such as benzene, toluene, ethylbenzene, xylenes, and trimethylbenzenes. Thus, the concentrations of toluene are 11-26 $\mu\text{g}/\text{m}^3$ in the external atmosphere and 10-29 $\mu\text{g}/\text{m}^3$ in the inner bus air, and total xylenes are 19-23 $\mu\text{g}/\text{m}^3$ and 11-28 $\mu\text{g}/\text{m}^3$, respectively. Traffic emissions infiltrating from outside will be also rich in alkanes, but also contain BTEX and other aromatic compounds as well as several alkanes (Yang et al., 2017). Evaporative emissions will normally favour aromatics over alkanes (Yue et al., 2017), whereas exhaust emissions of alkane and aromatic VOC are likely to be mostly toluene, 2-methylbutane and p- & m-xylenes derived from gasoline (petrol) combustion (Chin and Batterman 2012; Montells et al., 2000).

The present Barcelona bus data confirm that the most common and typical VOCs measured in the vehicle interior are 2-methylpentane (14-36 $\mu\text{g}/\text{m}^3$), toluene (10-30 $\mu\text{g}/\text{m}^3$), xylenes (10-28 $\mu\text{g}/\text{m}^3$, with m- >> o- > p-Xylene) and n-pentane (5-15 $\mu\text{g}/\text{m}^3$). Total BTEX concentrations measured in our study were generally rather low (<70 $\mu\text{g}/\text{m}^3$), with toluene being commonest, followed in turn by m-xylene, p-xylene, and o-xylene. Benzene (2-4 $\mu\text{g}/\text{m}^3$) and ethylbenzene (2-7 $\mu\text{g}/\text{m}^3$) were both consistently present in low concentrations. Such aromatic VOCs levels can be favourably compared to other studies, for example that by Chen et al. (2011) in Changsha city, China, where mean ΣBTEX values inside buses were 464 $\mu\text{g}/\text{m}^3$ and included highly undesirable levels of benzene (69 $\mu\text{g}/\text{m}^3$). A comparable study inside buses in Bangkok found ΣBTEX concentrations of 169 $\mu\text{g}/\text{m}^3$, with 12 $\mu\text{g}/\text{m}^3$ benzene (Ongwandee et al., 2010). A study in Taegu, Korea, reported mean ΣBTEX levels of 131 $\mu\text{g}/\text{m}^3$ inside buses and 195 $\mu\text{g}/\text{m}^3$ inside taxis, including 22 $\mu\text{g}/\text{m}^3$ and 33 $\mu\text{g}/\text{m}^3$ benzene respectively (Jo and Yu 2001). However, not all studies of VOC levels in public transport have been conducted in busy, polluted cities, as demonstrated by measurements made inside public buses operating in the relatively small and uncongested Spanish city of Pamplona where ΣBTEX concentrations of 10-22 $\mu\text{g}/\text{m}^3$ were recorded (Parra et al., 2008).

Pairwise comparison of the concentrations of the individual VOCs found in the buses compared in each route shows statistically significant correlations for the concentrations of aromatic compounds in all routes and alkanes in all routes except 34 (Hybrid Diesel and Electric) (Table 4). Despite these correlations significant statistical differences in the composition of aromatic compounds were observed in routes H4 (Hybrid and Euro V Diesel), V3 (Euro IV and V Diesel), H12 (compressed natural gas hybrid Diesel) and 34 (Hybrid Diesel, Electric). They also show significant differences when comparing between inner and external atmospheres (routes BT and RT) (Table 4).

The composition of alkanes shows significant differences in route V3 (Euro IV and V Diesel), H16 (Electric and CNG), H12 (CNG and Hybrid Diesel) and 34 (Hybrid Diesel and Electric), and significant differences between the inner and external atmospheres of route BT but not in route RT (Table 4).

With regard to the compounds related to personal care, such as the monoterpenes, these are present in higher concentrations in the inner bus atmospheres than in the external air. This is the case of p-cymene, 0.15-0.17 $\mu\text{g}/\text{m}^3$ in the outer atmosphere and 0.11-0.54 $\mu\text{g}/\text{m}^3$ in the inner atmosphere (Table S2), δ -limonene, 0.94-1.6 $\mu\text{g}/\text{m}^3$ and 0.49-65 $\mu\text{g}/\text{m}^3$, respectively, and β -ocimene, ND-0.03 $\mu\text{g}/\text{m}^3$ and ND-0.64 $\mu\text{g}/\text{m}^3$, respectively. The same is the case of VOCs exhaled from human breath such as isoprene (Marco and Grimalt, 2015), e.g. 0.78-1.3 $\mu\text{g}/\text{m}^3$ in the external atmosphere and 0.80-10 $\mu\text{g}/\text{m}^3$ in the inner bus air. Compounds that are commonly found in furniture tissues such as methyl methacrylate are also found in higher concentrations in the inner bus atmospheres,

0.12-0.19 $\mu\text{g}/\text{m}^3$ and <LOD-0.89 $\mu\text{g}/\text{m}^3$, respectively. The organochlorinated VOCs do not show a defined trend when comparing both atmospheres (Table S2).

The obvious exception to the general rule of relatively low VOCs concentrations inside buses in Barcelona is that of the brand new hybrid diesel bus sampled on 27 March and seriously contaminated by interior VOC off-gassing (Table S2). In this new bus many VOCs concentrations were much higher, and with a different distribution: o-xylene (160 $\mu\text{g}/\text{m}^3$), ethylbenzene (95 $\mu\text{g}/\text{m}^3$), 2-methylbutane (92 $\mu\text{g}/\text{m}^3$), p-xylene (91 $\mu\text{g}/\text{m}^3$), and cyclohexane (86 $\mu\text{g}/\text{m}^3$). However, despite the fact that levels of BTEX approached 500 $\mu\text{g}/\text{m}^3$ in this bus (over x10 higher than normal), the benzene concentrations still remained relatively subdued at 4.5 $\mu\text{g}/\text{m}^3$, below the European Union limit value of 5 $\mu\text{g}/\text{m}^3$ (EU air quality directive 2008/EC/50; Kerchich and Kerbach, 2012) because the occurrence of this compound is related to the inputs from external air and the general pollution by traffic. Although our VOCs data from this bus are much higher than what is normal for a commuter bus in Barcelona, others studies have demonstrated that levels of interior BTEX in brand new passenger vehicles can be even higher. A study of newly built coaches less than a month from the production line in China reported BTEX levels that in some cases exceeded 8,000 $\mu\text{g}/\text{m}^3$, with the highest concentrations peaking at around 15 days after delivery (Lu et al., 2016).

It is also interesting to compare our BUSAIR chemical data with a recent study of air quality inside Barcelona taxis (Moreno et al., 2019). The taxi interiors recorded exactly the same “top-five” distribution of VOCs as observed inside the buses, although at significantly higher concentrations: 2-methylpentane (43-60 $\mu\text{g}/\text{m}^3$), toluene (37-56 $\mu\text{g}/\text{m}^3$), xylenes (32-50 $\mu\text{g}/\text{m}^3$, with m- >> o- > p-xylene) and n-pentane (17-28 $\mu\text{g}/\text{m}^3$). This VOC signature is typical of Barcelona city roadside air and, although varying in concentration, is quite homogeneous in terms of composition. The observation that taxi interior air is higher in VOCs than bus air is consistent with the results of the Taegu study mentioned above (Jo and Yu 2001), and likely reflects poorer air quality in the more confined breathing space inside smaller vehicles.

5. Conclusions

1. The chemistry of $\text{PM}_{2.5}$ measured inside Barcelona public buses is dominated by the presence of OC (typically 10-15 $\mu\text{g}/\text{m}^3$) and EC (usually 3-6 $\mu\text{g}/\text{m}^3$), followed by SO_4 , Fe, Ca, K, Al_2O_3 , Mg and Na. Average OC values are around x3 those of EC average (OC/EC=3.4), and calculated mineral content is approximately one third that of total carbon content. Most bus pairs used in the study, following the same route but using differing bus models, show little difference in major element $\text{PM}_{2.5}$ chemistry, typically varying in EC, OC and mineral content by <2.5 $\mu\text{g}/\text{m}^3$, <3 $\mu\text{g}/\text{m}^3$, and <2 $\mu\text{g}/\text{m}^3$ respectively. However, major element concentrations of $\text{PM}_{2.5}$ in bus interiors are typically 2-8 times higher than urban background levels, reflecting the compromised air quality of the traffic-contaminated city streets.
2. Enhanced concentrations of certain trace metals and metalloids, notably Cu and Sb, inside the buses are attributed to the presence of brake particles entering the bus through doors and windows. In extreme cases, Sb concentrations can exceed x20 that of urban background.
3. Interior bus PM chemistry is not especially affected by the type of fuel used by the bus (with the exception of the electric and diesel bus), and can be affected by seasonal changes in ambient outdoor air. In the case of Barcelona in summer bus $\text{PM}_{2.5}$ can contain relatively higher levels of Na, Mg, V, Ni, Cr and SO_4^{2-} , attributed to the ingress of outdoor marine aerosols contaminated by port emissions and the higher SO_2 summer oxidation ratio. In winter, when air conditioning is off and city air is commonly more contaminated, the air inside the bus can be richer in mineral particles, with enhanced levels of trace metals/metalloid such as Mn, Sr, Zn, Zr, Sb and Cu.

4. Interior bus air chemistry can be influenced by both route taken and bus model. Higher gradients favour the ingress of more brake particles and thus affect the chemistry of the PM being inhaled by passengers. In contrast, buses designed to use more engine-braking (such as the Barcelona electric buses) are less contaminated by their own brake PM, especially if the windows are kept closed. Open-topped double decker tourist buses are more directly exposed to fresh traffic emissions (especially on the upper floor) but enhanced air exchange rates maintain elemental PM concentrations slightly below that more typical of enclosed commuter buses.
5. Based on the chemical tracer, the two main sources of particles inside the bus are deduced to be from passenger emissions such as textile fibres and skin flakes () (46%) and infiltrated vehicle exhaust and brake wear particles (19%). Other sources include road and urban dust, regional sulphate and shipping and industrial metalliferous particles.
6. The chemical signature of VOCs present in most Barcelona buses is remarkably uniform, irrespective of bus engine type, being dominated by alkanes and aromatics in the following order: 2-methylpentane (14-36 $\mu\text{g}/\text{m}^3$), toluene (10-30 $\mu\text{g}/\text{m}^3$), xylenes (10-28 $\mu\text{g}/\text{m}^3$, with m- >> o- > p-xylene) and n-pentane (5-15 $\mu\text{g}/\text{m}^3$). This is the same mixture recorded inside Barcelona taxis (although inside buses VOC concentrations are usually lower than in taxis) and presumably records the ingress into the vehicle of mostly gasoline-sourced exhaust emissions from outside. Ambient benzene concentrations measured inside the buses were always <5 $\mu\text{g}/\text{m}^3$. A notable exception to this rule occurs in new buses which can exhibit a very different, and greatly enhanced, VOC signature due to offgassing of interior coatings and materials. In this study one such bus (HD34) recorded exceptionally high concentrations in particular of o-Xylene (160 $\mu\text{g}/\text{m}^3$), Ethylbenzene (95 $\mu\text{g}/\text{m}^3$), 2-Methylbutane (92 $\mu\text{g}/\text{m}^3$), p-Xylene (91 $\mu\text{g}/\text{m}^3$), and Cyclohexane (86 $\mu\text{g}/\text{m}^3$).
7. BTEX concentrations in Barcelona buses typically range from 25-68 $\mu\text{g}/\text{m}^3$ in a hierarchy of Toluene (10-30 $\mu\text{g}/\text{m}^3$) > m-Xylene (5-17 $\mu\text{g}/\text{m}^3$) > p-Xylene (2-5 $\mu\text{g}/\text{m}^3$) > o-Xylene (3-6 $\mu\text{g}/\text{m}^3$) > Benzene (2-4 $\mu\text{g}/\text{m}^3$) and Ethylbenzene (2-7 $\mu\text{g}/\text{m}^3$). The exceptional levels of VOC offgassing recorded in the new hybrid diesel bus produced interior BTEX concentrations closely approaching 0.5 mg/m^3 , although benzene levels still remained below the European Union limit value of 5 $\mu\text{g}/\text{m}^3$.

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Table 1: Bus pair comparisons made per seasonal campaign including information on each line and date. V = “Vertical” (coast to mountain) routes; H = “Horizontal” (coast-parallel) routes. Other bus routes (19, 34, 39, 47, 60) run along more mixed trajectories. Bus types are diesel Euro IV and V, hybrid diesel (HD), natural gas (CNG), hybrid natural gas (HCNG) and electric. The tourist buses run using diesel Euro IV engines along “red” (more southerly, including Montjuic Hill) and “blue” (mostly north of the Diagonal) routes.

Table 2: Summary of chemical analyses of PM_{2.5}: all bus average (AB), urban background (UB), and sub-groups based on bus engine types, season, and route (see Table TS1).

Table 3: Elemental Carbon concentrations (µg/m³) in PM_{2.5} sampled from bus pairs chosen for this study (see Table 1).

Table 4: Statistical analysis in the composition of aromatic alkanes in all routes studied.

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Figure 1: Elemental concentrations measured inside Barcelona buses and urban background. 1a. Boxplot showing concentration median, lower and upper quartiles, and ranges (vertical “whisker” bar) of major and trace elements measured from PM_{2.5} sampled in buses and compared to urban background (black dot); 1b. Histogram demonstrating the relative enrichments of elements measured from PM_{2.5} sampled in buses relative to Barcelona urban background.

Figure 2: Histograms comparing Barcelona BUSAIR data with urban background in: 1a. Diesel v electric buses; 2b. Winter v summer, 2c. “Vertical” (sea-to-mountain) v “Horizontal” (coast-parallel) routes. Note the consistent especial enhancement of Cu and Sb, interpreted as sourced from brake emissions.

Figure 3: Positive matrix factorisation results showing the factor profiles identified.

Figure 4: Percentages of abundances of VOCs measured in 17 Barcelona buses and a brand new hybrid diesel bus contaminated by severe interior offgassing. See Table S2 and text for details.

Figure 5: MnTiSbx10 ternary plot comparing PM_{2.5} measured inside Barcelona buses, showing enrichment in Sb typical of brake PM-contaminated air. Fields for Subway, walking/streetworks, and bus from Moreno et al. (2015).

Supplementary Tables

Table S1: Individual chemical analyses of PM_{2.5} obtained over 6-hour sampling period in TMB buses during the BUSAIR campaign. The sub-groups listed are selected from these individual analyses, namely warm season (“summer”), cooler season (“winter”), diesel (Euro IV, Euro V), hybrid diesel (HD), compressed natural gas (CNG), hybrid compressed natural gas (HCNG), fully electric, route (“Vertical” (V) coast to mountain; “Horizontal” (H) coast-parallel); tourist open-top double decker buses operating on either red (TR) or blue (TB) trajectories (“in” = inside, lower floor; “out” = outside, upper floor); other routes show bus number only, namely 34, 39, 47, 19 and 60.

Table S2: Concentrations of Volatile Organic Compounds (VOCs) measured inside Barcelona buses. HD = Hybrid Diesel; CNG = Compressed natural gas; HCNG = Hybrid Compressed Natural Gas; EIV & EV = Euro IV & Euro V diesel engines; H = “Horizontal” coast-parallel routes; V = “Vertical” coast-to-mountain higher gradient routes. Bus interiors are dominated by alkanes and aromatics, and especially by 2-Methylpentane (14-36 µg/m³), Toluene (10-30 µg/m³), Xylenes (10-28 µg/m³, with m- >> o- > p-Xylene) and n-Pentane (5-15 µg/m³). An exception is provided by the brand new hybrid diesel bus 34 which has

635 greatly enhanced VOCs concentrations due to interior offgassing (see text for details). LOD= limit of
636 detection.

Bus pair	SUMMER		WINTER	
	Line	Date	Line	Date
Euro V vs Euro IV	V13	10, 11, 12 May	V3	16, 17, 18 Jan.
Euro V vs HD	V13	16, 17, 18 May	H4	14, 15, 16 Nov.
Euro V vs CNG	V3	30, 31 May, 1 Jun.	V3	1, 12, 13 Dec.
Euro V vs Electric	34	14, 15, 18 Sep.	-	-
Euro IV vs HD	47	10, 12, 14 July	19	14, 15, 19 Dec.
Euro IV vs CNG	V17 vs V11	20, 21, 28 Sep.	V3	23, 24, 30 Nov.
Euro IV vs Electric	-	-	60	10, 12, 13 April
HD vs CNG	H12	18, 19, 20 Jul.	H12	26 Feb., 1, 2 Mar.
HD vs Electric	34	23, 24, 25 May	34	27, 28 Mar.
CNG vs HCNG	39	13, 14, 15 Jun.	39	10, 11, 12 Jan.
CNG vs Electric	H16	8, 9, 12 Jun.	H16	19, 20, 21 Feb.
Tourist inside vs outside	Blue	20, 21, 22 Jun.	Blue	23, 24, 25 Jan.
Tourist inside vs outside	Red	26, 27, 28 Jun.	Red	30, 31 Jan., 1 Feb.

Table 1

	URBAN BACKGROUND	ALL BUSES (AB)		BUS TYPE							SEASON		ROUTE		
	UB	AB	AB/UB	Diesel	HD	CNG	HNG	Electric	Tourist outside	Tourist inside	Summer	Winter	Vertical	Horizontal	Others
n		48		14	8	10	2	6	4	4	16	16	14	10	16
µg/m ³															
OC	2.39	16.3	6.8	19.2	17.0	16.6	23.0	12.9	10.7	11.2	14.7	19.1	17.9	14.2	18.9
EC	1.04	4.8	4.6	6.6	4.6	4.2	4.8	3.8	4.1	2.9	4.8	5.1	6.6	4.0	4.4
CO ₃ ²⁻	0.35	1.6	4.5	2.0	1.2	1.8	2.3	1.4	0.5	0.7	1.4	1.7	1.9	1.1	2.0
SiO ₂	0.54	2.1	3.8	2.6	1.8	2.6	4.0	1.8	0.6	0.6	0.7	4.0	2.3	1.9	2.8
Al ₂ O ₃	0.18	0.7	4.0	0.9	0.7	0.9	1.3	0.6	0.2	0.2	0.3	1.3	0.8	0.6	1.0
Ca	0.23	1.0	4.5	1.4	0.8	1.2	1.6	0.9	0.3	0.5	1.0	1.1	1.3	0.8	1.3
Fe	0.19	1.4	7.3	1.9	0.9	1.6	1.4	1.3	0.5	0.5	1.2	1.6	2.0	1.0	1.5
K	0.11	1.0	8.8	1.6	0.5	1.1	1.5	0.9	0.5	0.6	0.9	0.9	1.6	0.4	1.2
Na	0.15	0.3	2.0	0.2	0.5	0.3	<0.1	0.3	0.4	0.4	0.4	0.2	0.1	0.3	0.4
Mg	<0.1	0.4	9.3	0.8	0.1	0.4	0.2	0.6	0.1	0.2	0.6	0.1	0.7	0.1	0.7
P	<0.1	1.2	122	3.0	0.1	0.6	0.2	1.6	<0.1	0.1	1.9	0.1	0.8	0.1	3.1
SO ₄ ²⁻	1.72	1.8	1.0	1.8	1.8	1.6	2.1	1.6	1.9	2.0	2.5	0.9	1.6	1.8	1.8
OC+EC	3.43	21.1	6.2	25.9	21.5	20.8	27.7	16.8	14.8	14.1	19.5	24.2	24.6	18.1	23.3
Mineral	1.65	5.5	3.3	8.0	4.0	6.0	7.9	5.1	1.7	2.0	4.6	7.5	6.2	3.6	8.2
ng/m ³															
Ti	6.64	19.47	2.93	20.06	13.98	18.43	106.83	11.09	9.11	8.23	22.32	21.70	14.14	14.06	34.09
V	4.04	6.78	1.68	7.21	5.33	6.42	31.20	7.53	4.80	4.05	9.56	2.39	7.23	4.38	10.31
Cr	1.53	9.72	6.37	9.36	14.16	6.82	5.25	4.84	12.68	13.25	8.11	7.75	8.46	6.15	11.47
Mn	4.10	12.03	2.93	15.39	10.32	13.69	17.51	7.03	8.37	7.94	6.91	19.17	15.09	12.13	11.22
Ni	2.38	8.89	3.74	10.48	9.11	5.59	1.91	7.43	12.96	13.95	8.64	5.54	9.95	5.83	7.43
Cu	6.70	82.37	12.29	96.29	107.86	107.17	174.89	19.94	30.19	20.17	84.42	119.10	113.83	71.86	89.99
Zn	23.70	90.25	3.81	123.28	73.70	113.69	92.50	42.71	55.82	53.82	47.53	135.02	135.24	75.23	78.00
Sr	0.88	4.27	4.86	6.21	3.96	4.52	6.26	2.12	1.57	2.23	2.71	6.28	5.42	3.34	5.21
Zr	5.08	36.65	7.21	44.44	38.10	40.25	33.47	39.76	23.12	12.31	29.87	43.05	47.88	36.86	36.93
Sn	1.78	4.74	2.67	6.18	4.48	4.57	3.93	3.99	3.57	3.34	4.28	5.64	6.05	4.79	4.20
Sb	0.94	10.72	11.46	15.31	7.79	14.58	23.75	4.04	2.78	2.35	6.24	19.87	16.56	9.32	10.58
La	0.12	0.64	5.49	0.61	0.42	1.30	1.04	0.39	0.26	0.25	0.25	1.25	0.78	0.56	0.75
Ce	0.23	1.81	7.79	2.18	1.27	2.65	2.39	1.20	0.67	0.88	0.40	3.45	2.21	1.25	2.47
Hf	0.24	2.19	9.13	2.77	2.29	2.40	2.29	2.30	1.16	0.55	1.40	2.97	2.90	2.12	2.34
Pb	3.05	3.30	1.08	3.39	3.46	3.11	4.43	2.48	3.36	3.51	2.95	3.91	2.84	4.04	3.04
OC/EC	2.29	3.37	1.47	2.90	3.67	3.98	4.83	3.39	2.62	3.81	3.09	3.71	2.70	3.56	4.25

Table 2

Bus pair	SUMMER		WINTER	
	Line	Elemental Carbon	Line	Elemental Carbon
Euro V vs Euro IV	V13	8.9 vs 9.5	V3	19.4 vs 2.6
Euro V vs HD	V13	6.8 vs 5.8	H4	4.9 vs 4.2
Euro V vs CNG	V3	4.5 vs 5.7	V3	4.1 vs 6.9
Euro V vs Electric	34	4.9 vs 7.2	-	-
Euro IV vs HD	47	3.5 vs 8.9	19	3.8 vs 2.9
Euro IV vs CNG	V17 vs V11	6.3 vs 3.8	V3	3.9 vs 4.7
Euro IV vs Electric	-	-	60	9.6 vs 4.9
HD vs CNG	H12	3.8 vs 3.1	H12	6.4 vs 6.4
HD vs Electric	34	3.1 vs 4.7	34	1.0 vs 0.3
CNG vs HCNG	39	3.8 vs 5.3	39	2.0 vs 4.2
CNG vs Electric	H16	2.7 vs 2.4	H16	2.7 vs 3.2
Tourist Inside vs outside	Blue	3.6 vs 6.1	Blue	2.4 vs 2.5
Tourist Inside vs outside	Red	3.8 vs 5.5	Red	1.9 vs 2.3

Table 3

Aromatics										Alkanes					
Route	Engine	25	Median	75	Wilcoxon Signed Rank Test		Spearman's Correlation		25	Median	75	Wilcoxon signed rank test		Spearman's correlation	
					Z	p-Value	r _s	p-Value				Z	p-Value	r _s	p-Value
H4	Hybrid Diesel	0.43	2.77	3.42	-2.856	0.004	0.996	0.000	0.95	2.04	5.18	-1.362	0.173	0.983	0.000
	Euro V Diesel	0.38	1.63	3.16					0.85	2.07	5.33				
V3	Compressed Natural Gas	0.22	1.38	2.54	-0.282	0.778	0.952	0.000	0.59	1.18	4.42	-0.533	0.594	0.917	0.001
	Euro V Diesel	0.24	1.31	2.82					0.66	1.25	4.13				
39	Hybrid Compressed Natural Gas	0.38	1.77	3.29	-1.961	0.050	0.974	0.000	0.91	1.72	5.72	-1.12	0.263	0.983	0.000
	Compressed Natural Gas	0.38	1.98	3.42					0.86	1.70	6.08				
V3	Euro IV Diesel	0.24	1.31	2.57	-2.919	0.004	1.000	.	0.81	1.45	3.96	-2.666	0.008	0.950	0.000
	Euro V Diesel	0.26	1.40	2.79					0.85	2.52	5.67				
BT	Outside	0.19	2.36	4.90	-2.856	0.004	0.991	0.000	1.13	2.76	9.16	-2.666	0.008	0.983	0.000
	Inside	0.20	2.53	6.20					1.22	2.96	10.94				
RT	Outside	0.16	1.66	4.25	-2.040	0.041	0.988	0.000	0.83	1.40	6.37	-1.244	0.214	0.939	0.000
	Inside	0.13	1.54	3.72					0.72	1.32	6.37				
H16	Electric	0.40	2.06	4.34	-0.943	0.345	0.996	0.000	0.93	1.92	7.18	-2.666	0.008	0.988	0.000
	Compressed Natural Gas	0.46	2.39	4.12					1.15	2.69	10.44				
H12	Compressed Natural Gas	0.31	2.30	3.97	-3.180	0.001	0.991	0.000	1.29	4.32	11.23	-2.666	0.008	0.77	0.009
	Hybrid Diesel	0.17	1.68	2.75					0.67	1.29	5.26				
34	Hybrid Diesel	0.27	1.64	3.32	-3.296	0.001	0.855	0.000	0.75	1.46	6.04	-2.666	0.008	0.491	0.150
	Electric	2.68	5.86	55.27					10.05	19.24	74.41				

Table 4

Figure 1

a)

b)

c)

Figure 2

Figure 3

Figure 4

Figure 5

not for summer average			SUMMER																				not for summer average		
ENGINE ROUTE DATE	EIV (V13) 10/05/17	EV (V13)	EV (V13) 16/05/17	HD (V13) 16/05/17	Elect. (34) 23/05/17	HD (34) 23/05/17	CNG (V3) 30/05/17	EV (V3) 30/05/17	CNG (H16) 08/06/17	Elect. (H16) 08/06/17	HCNG (39)	CNG (39) 13/06/17	EIV (TB out) 20/06/17	EIV (TB in) 20/06/17	EIV (TR out) 26/06/17	EIV (TR in) 26/06/17	EIV (47) 10/07/17	HD (47) 10/07/17	HD (H12) 18/07/17	CNG (H12) 18/07/17	Elect. (34) 14/09/17	EV (34) 14/09/17	CNG (V11) 20/09/17	EIV (V11) 20/09/17	
µg/m³																									
PM _{2.5}	177.13	230.60	129.58	117.58	118.32	111.81	119.64	130.22	75.52	70.18	104.96	99.05	127.25	176.07	90.44	99.51	146.14	114.79	80.85	95.91	131.40	143.51	138.92	158.76	
OC	41.1	22.3	15.1	13.8	13.1	12.9	12.9	15.5	9.7	8.9	15.1	16.1	13.9	16.5	10.1	10.9	31.5	17.0	15.2	8.2	15.8	14.6	13.9	17.0	
EC	8.9	9.5	6.8	5.8	4.7	3.1	5.7	4.5	2.7	2.4	5.3	3.8	6.1	3.6	5.5	3.8	3.5	8.9	3.8	3.1	7.2	4.9	3.8	6.3	
CO ₂ ²⁻	5.6	0.2	0.3	2.6	1.4	0.2	1.3	1.8	1.1	0.8	0.7	0.8	0.6	1.3	<0.1	0.4	1.0	1.9	0.4	0.6	3.9	4.0	4.2	4.1	
SiO ₂	0.3	<0.1	<0.1	0.1	0.9	<0.1	1.4	0.6	0.5	0.4	0.3	0.8	0.6	0.8	0.8	0.9	1.4	1.2	0.3	<0.1	<0.1	0.3	0.2	0.2	
Al ₂ O ₃	0.1	<0.1	<0.1	<0.1	0.3	<0.1	0.5	0.2	0.2	0.1	0.1	0.3	0.2	0.3	0.3	0.3	0.5	0.4	0.1	<0.1	<0.1	0.1	0.1	0.1	
Ca	3.7	0.1	0.2	1.7	0.9	0.1	0.9	1.2	0.7	0.5	0.5	0.6	0.4	0.9	<0.1	0.3	0.6	1.3	0.3	0.4	2.6	2.7	2.8	2.8	
Fe	1.2	1.0	0.5	0.8	0.6	0.2	1.9	0.9	0.4	0.2	0.6	0.5	0.6	0.6	0.5	0.5	0.4	0.5	0.6	0.3	5.5	5.5	5.3	5.4	
K	0.1	<0.1	<0.1	0.2	0.1	0.1	0.2	0.4	0.1	0.2	<0.1	0.1	0.2	0.2	0.2	0.2	<0.1	<0.1	<0.1	0.3	3.7	4.3	5.2	5.9	
Na	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	
Mg	0.7	<0.1	<0.1	0.1	0.1	<0.1	0.1	0.3	0.2	0.1	0.1	0.1	0.1	0.3	0.1	0.1	0.1	0.3	0.1	0.1	2.3	4.9	2.5	2.2	
P	0.2	0.1	0.1	0.1	0.1	<0.1	0.1	0.1	0.1	0.1	0.2	<0.1	<0.1	0.1	<0.1	0.1	<0.1	0.3	0.1	0.1	4.6	19.2	2.8	3.7	
SO ₄ ²⁻	5.2	1.5	1.8	1.5	2.2	1.6	2.5	3.3	2.4	2.1	3.1	1.7	2.7	3.5	2.6	2.5	2.5	3.4	3.3	2.5	2.9	3.7	<0.1	<0.1	
Mineral OC+EC	5.1	0.2	0.3	2.2	2.4	<0.1	3.0	2.8	1.7	1.4	1.2	1.8	1.5	2.5	1.4	1.9	2.6	3.5	0.8	1.0	13.3	31.4	13.5	14.9	
	50.0	31.8	22.0	19.6	17.8	16.0	18.5	20.0	12.5	11.2	20.4	19.9	20.0	20.1	15.6	14.7	35.0	25.9	19.0	11.2	23.0	19.5	17.7	23.3	
ng/m³																									
Ti	50.97	17.30	4.31	6.25	13.90	12.50	22.16	16.94	5.37	4.92	176.64	11.86	5.51	9.56	12.04	8.13	35.21	20.17	5.38	2.86	6.58	12.04	6.35	5.64	
V	4.72	<0.10	15.65	7.95	6.55	0.94	2.66	0.25	8.99	5.94	31.20	21.91	10.92	1.89	2.65	9.58	9.90	2.54	10.34	3.41	21.13	3.59	6.03	23.88	
Cr	10.25	24.67	2.83	5.27	6.35	<0.10	9.00	3.86	6.37	0.96	0.50	15.00	8.93	8.41	15.86	11.63	25.81	18.81	7.48	2.52	8.71	<0.10	6.34	12.40	
Mn	16.23	13.91	5.26	3.76	7.91	5.17	18.95	11.28	5.82	2.30	11.41	7.78	8.42	9.50	7.17	6.29	3.59	6.20	5.35	3.26	7.45	4.99	6.70	9.44	
Ni	10.12	32.05	3.38	13.14	13.87	0.15	12.43	25.36	6.44	7.82	2.25	19.64	13.00	18.92	17.36	13.94	10.12	4.17	3.12	1.53	6.14	<0.10	1.47	<0.10	
Cu	111.64	46.34	39.12	138.18	32.06	208.34	178.28	119.84	15.00	5.84	129.23	159.80	46.22	25.99	37.62	20.67	50.83	97.72	118.67	25.75	25.21	6.89	13.63	89.89	
Zn	228.26	58.04	42.42	138.89	51.97	35.52	100.25	69.55	37.04	49.48	33.93	57.39	91.58	60.67	28.43	29.48	14.96	25.87	19.76	21.77	16.98	44.69	154.16	159.22	
As	0.91	<0.10	4.27	1.21	0.27	<0.10	<0.10	<0.10	2.02	0.66	6.17	4.75	2.89	<0.10	<0.10	2.26	2.06	<0.10	2.37	<0.10	7.40	<0.10	2.35	6.29	
Sr	12.51	1.77	<0.10	1.41	1.02	0.33	1.80	6.49	4.14	0.83	1.77	1.17	2.32	4.47	0.51	1.66	2.16	9.96	2.04	1.86	0.58	5.06	1.87	3.83	
Zr	63.67	53.01	<0.10	33.66	35.57	<0.10	41.84	33.93	7.57	<0.10	21.58	26.29	31.98	18.45	29.62	5.25	34.40	<0.10	4.94	<0.10	39.85	48.97	64.86	53.23	
Nb	<0.10	3.17	<0.10	<0.10	1.49	<0.10	<0.10	<0.10	<0.10	0.93	<0.10	<0.10	1.58	<0.10	<0.10	<0.10	1.60	<0.10	<0.10	<0.10	2.14	<0.10	<0.10	<0.10	
Cd	<0.10	<0.10	1.75	<0.10	<0.10	<0.10	1.43	<0.10	0.93	<0.10	<0.10	1.40	<0.10	2.61	1.23	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.74	0.68	<0.10	
Sn	6.93	4.96	2.19	2.37	6.43	3.76	7.80	15.18	1.55	1.48	3.67	3.10	4.09	4.08	3.66	2.79	4.05	3.64	2.13	2.47	4.97	3.65	3.36	5.25	
Sb	9.91	12.97	5.40	2.14	6.19	1.83	23.66	14.94	3.13	1.03	10.56	6.35	3.96	3.52	3.17	2.75	2.43	4.72	2.92	3.24	6.26	5.11	6.50	8.59	
Ba	62.16	39.92	8.77	9.99	29.21	7.62	51.12	33.26	60.17	10.38	13.30	21.40	52.92	25.99	19.10	12.54	9.91	41.05	60.59	12.73	10.48	10.63	15.46	11.83	
La	0.46	0.20	0.16	0.19	0.27	0.10	0.34	0.12	0.14	0.16	0.91	0.23	0.42	0.23	0.13	0.25	0.15	0.17	<0.10	<0.10	<0.10	<0.10	0.24	0.17	
Ce	0.91	0.61	0.28	0.35	0.52	<0.10	0.56	0.17	0.35	0.24	0.79	0.62	0.83	0.60	0.57	0.52	0.35	0.44	0.13	<0.10	<0.10	<0.10	0.38	0.98	
Nd	0.19	0.50	0.29	0.49	0.49	0.14	0.22	0.37	0.23	0.18	0.10	0.14	0.53	0.56	0.42	0.42	0.47	0.36	<0.10	<0.10	<0.10	<0.10	0.14	<0.10	
Gd	0.34	0.21	0.11	0.20	0.14	<0.10	0.12	0.05	0.05	<0.10	<0.10	<0.10	<0.10	0.34	0.12	<0.10	0.21	0.24	<0.10	<0.10	<0.10	<0.10	0.25	<0.10	
Dy	0.41	0.29	0.23	0.22	0.38	<0.10	0.38	0.26	0.17	0.18	<0.10	0.25	0.43	0.45	0.42	0.41	0.18	0.22	0.15	0.16	<0.10	<0.10	<0.10	0.25	
Hf	3.20	3.07	<0.10	1.73	1.50	<0.10	1.65	1.61	0.34	<0.10	0.84	1.18	1.61	0.57	1.39	0.24	1.67	<0.10	0.25	<0.10	2.22	2.39	3.33	3.02	
Pb	4.96	6.23	3.22	3.28	4.04	2.40	3.72	2.85	1.91	1.66	3.20	2.76	2.63	4.26	2.23	2.36	5.81	5.36	1.78	1.50	1.30	2.38	1.46	2.39	
Bi	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	
U	<0.10	0.76	0.41	0.63	0.65	0.13	0.47	0.55	0.25	0.34	<0.10	<0.10	0.46	0.63	0.54	0.59	0.43	0.38	<0.10	0.12	<0.10	<0.10	0.10	0.15	

WINTER																		not for winter average					
EV (H4)	HD (H4)	EIV (V3)	CNG (V3)	CNG (V3)	EV (V3)	HD (19)	EIV (19)	CNG (39)	HCNG (39)	EV (V3)	EIV (V3)	EIV (TB											

	Route H4		Route V3		Route 39		Route V3		Route Blue Tourist		Route Red Tourist		Route H16		Route H12		Route 34	
	14-16/11/17		1 st , 12-13/12/17		10-12/01/18		16-18/01/18		23-25/01/18		30/01-1/02/18		21/01/18	31/01/18	26/02 & 1/03/18		27-28/03/18	
	Hybrid Diesel	Euro V Diesel	CNG	Euro V Diesel	Hybrid CNG	CNG	Euro IV Diesel	Euro V Diesel	Outside	Inside	Outside	Inside	Electric	CNG	CNG	Hybrid Diesel	Electric	Hybrid Diesel
Aromatics:																		
Benzene	2.8	2.6	2.5	1.9	3.2	3.2	2.3	2.3	3.7	3.9	2.8	2.8	3.1	3.8	3.9	2.6	2.4	4.5
Toluene	21	15	18	17	16	20	9.7	15	26	29	11	12	27	22	17	16	14	43
Ethylbenzene	3.1	2.6	2.3	2.2	2.9	3.2	2.1	2.2	4.9	6.6	4.1	3.7	4.0	3.9	3.4	2.7	2.7	95
o-Xylene	3.8	3.4	2.8	2.8	3.7	4.0	2.6	2.8	5.0	6.0	4.6	3.8	5.3	4.8	4.1	3.0	3.5	160
m-Xylene	8.7	6.8	6.0	6.1	7.3	8.4	5.5	6.0	14	17	11	9	11	10	9.5	7.3	7.5	43
p-Xylene	2.9	2.4	2.2	2.2	2.7	3.0	2.0	2.1	4.1	4.9	3.7	3.1	3.4	3.8	3.2	2.5	2.6	91
1,2,4-Trimethylbenzene	3.3	3.1	2.2	2.8	3.0	2.9	2.6	2.9	3.9	4.2	3.4	2.4	3.9	3.8	3.4	2.4	3.3	39
1,3,5-Trimethylbenzene	0.82	0.76	0.57	0.71	0.80	0.80	0.66	0.72	1.0	1.1	0.54	0.69	1.0	1.0	0.93	0.66	0.86	4.8
n-Propylbenzene	0.54	0.50	0.30	0.48	0.45	0.45	0.42	0.46	0.60	0.65	0.54	0.40	0.51	0.58	0.53	0.40	0.46	3.0
Isopropylbenzene	0.17	0.15	0.11	0.14	0.17	0.17	0.13	0.13	0.19	0.21	0.17	0.14	0.20	0.21	0.18	0.14	0.15	3.0
n-Butylbenzene	0.22	0.23	0.08	0.24	ND	<LOD	0.24	0.27	0.14	0.01	0.13	0.07	0.28	0.22	0.20	0.14	0.16	1.7
p-Cymene	0.50	0.43	0.26	0.23	0.53	0.50	0.23	0.23	0.17	0.18	0.15	0.11	0.44	0.54	0.34	0.17	0.31	1.4
sec-Butylbenzene	<LOD	0.10	<LOD	0.10	<LOD	<LOD	<LOD	0.09	0.06	0.07	0.05	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.3
Styrene	2.7	0.85	0.49	0.37	0.77	1.0	0.38	0.35	0.54	0.55	0.56	0.48	0.88	0.70	1.40	0.93	0.50	6.9
Branched alkanes:																		
2-Methylbutane	22	19	15	14	26	27	17	18	33	36	25	25	26	35	32	21	26	92
2,3-Dimethylpentane	0.81	0.71	0.51	0.49	0.85	0.79	0.50	0.63	1.1	1.2	0.79	0.78	0.90	1.0	1.3	0.62	0.69	9.9
Isooctane	0.51	0.41	0.45	0.14	<LOD	<LOD	1.1	2.6	0.61	0.65	0.50	0.48	0.58	0.98	0.43	ND	ND	0.57
Cycloalkanes:																		
Cyclohexane	1.1	0.99	0.69	0.82	1.7	1.7	0.62	0.64	1.4	1.4	1.3	1.3	1.7	1.7	7.6	0.80	1.0	86
n-Alkanes:																		
n-Pentane	8.1	7.3	5.7	5.2	9.0	9.3	5.6	6.1	12	13	8.6	8.8	9.9	13	15	7.1	9.3	29
n-Hexane	2.0	2.1	3.1	1.2	0.99	1.3	2.3	5.2	6.7	7.1	4.1	3.9	4.5	7.5	4.3	3.4	2.8	19
n-Octane	1.3	1.4	0.7	1.1	0.97	0.94	1.0	1.1	1.2	1.3	0.86	0.66	0.96	1.27	1.31	0.71	0.80	12
n-Heptane	2.3	2.1	1.4	1.7	2.4	2.3	1.5	1.8	2.8	3.0	2.0	1.95	2.26	2.69	3.05	1.79	1.91	10
n-Decane	2.2	3.4	1.2	3.0	2.0	2.9	1.9	2.5	3.4	9.0	1.40	1.05	1.92	6.32	4.87	1.29	1.46	63
Monoterpenes:																		
d-Limonene	2.7	11	4.2	3.6	30	65	2.0	3.1	1.6	3.2	0.94	0.49	6.4	8.6	12	1.1	2.7	5.8
alpha-Pinene	1.6	0.78	0.52	0.32	0.68	0.90	0.40	0.56	0.65	0.80	0.61	0.46	0.66	0.81	0.92	0.56	0.43	0.55
beta-Ocimene	0.20	0.26	0.24	0.12	0.27	0.36	0.13	0.23	0.03	ND	ND	ND	0.35	0.64	0.43	0.05	0.24	0.38
alpha-Ocimene	0.10	0.12	0.11	0.05	ND	ND	ND	0.10	ND	ND	ND	ND	0.18	0.30	0.20	ND	0.10	0.21
Alkenes:																		
Isoprene	2.3	6.3	5.3	1.8	6.8	8.2	2.8	1.1	1.3	0.95	0.78	0.80	8.7	10	5.9	1.2	3.4	5.6
trans-2-Pentene	1.2	1.0	0.85	0.76	1.6	1.6	0.94	1.0	2.0	2.2	1.4	1.4	1.5	1.9	1.6	1.0	0.94	3.0
1-Pentene	0.40	0.39	0.35	0.25	0.61	0.59	0.41	0.35	0.67	0.67	0.50	0.48	0.60	0.69	0.60	0.42	0.40	1.1
cis-Pentene	0.41	0.35	0.29	0.25	0.53	0.54	0.33	0.35	0.68	0.74	0.47	0.47	0.52	0.63	0.57	0.35	0.35	1.1
Oxygenated compounds:																		
Ethyl methacrylate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.3
Tetrahydrofuran	0.32	0.54	0.40	0.11	0.16	0.21	0.17	<LOD	0.23	0.25	0.27	0.27	0.43	0.76	0.26	0.19	0.19	3.2
Methyl methacrylate	0.15	0.64	0.28	0.13	<LOD	0.15	ND	<LOD	0.12	0.07	0.19	0.30	0.39	0.62	0.89	0.54	0.27	2.4
Isobutanol	0.07	0.33	0.24	0.19	0.14	<LOD	0.11	<LOD	0.11	<LOD	0.12	0.18	0.39	0.30	0.34	0.30	1.3	1.1
Diethyl ether	0.10	0.12	0.38	0.12	<LOD	<LOD	0.12	0.30	0.36	ND	0.27	0.20	0.16	0.60	0.21	0.15	0.36	0.21
Halocarbons:																		
Tetrachloroethylene	1.1	1.4	0.74	0.55	0.64	0.70	0.45	0.41	1.2	1.2	1.3	1.3	1.4	1.5	1.2	1.6	1.7	1.7
1,2,2-Trichlorotrifluoroethane	0.79	0.76	0.78	0.54	0.75	0.80	0.83	0.77	0.71	0.73	0.71	0.73	0.93	1.0	0.75	0.39	0.75	0.71
1,1,2-Trichloroethane	<LOD	ND	ND	ND	0.00	0.00	ND	ND	ND	ND	ND	ND	0.00	0.32	ND	ND	ND	0.66
Carbon Tetrachloride	0.32	0.48	0.62	0.44	0.34	0.38	0.46	0.41	0.43	0.35	0.43	0.46	0.67	0.82	0.60	0.31	0.59	0.43
1,2-Dichloroethane	0.09	0.15	0.14	0.10	0.00	0.00	0.14	0.12	0.18	0.10	0.27	0.26	0.65	0.54	0.28	0.24	0.33	0.33
Chloroform	0.14	0.60	0.51	0.05	0.06	0.00	0.19	0.91	0.14	0.03	0.03	0.03	0.09	0.24	0.09	0.07	0.95	0.23
Trichloroethylene	0.18	0.14	<LOD	<LOD	0.00	0.00	<LOD	0.10	0.27	0.27	0.43	0.47	0.26	<LOD	0.70	0.56	0.18	0.21
Nitriles:																		
Propionitrile	<LOD	0.07	<LOD	ND	0.00	0.16	<LOD	ND	<LOD	<LOD	0.06	<LOD	<LOD	<LOD	<LOD	<LOD	ND	0.11

Table S2