Daily and hourly sourcing of metallic and mineral dust in urban air contaminated by traffic and coal-burning emissions

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Abstract

A multi-analytical approach to chemical analysis of inhalable urban atmospheric particulate matter (PM), integrating particle induced X-ray emission, inductively coupled plasma mass spectrometry/atomic emission spectroscopy, chromatography and thermal-optical transmission methods, allows comparison between hourly (Streaker) and 24-hour (High volume sampler) data and consequently improved PM chemical characterization and source identification. In a traffic hot spot monitoring site in Madrid (Spain) the hourly data reveal metallic emissions (Zn, Cu, Cr, Fe) and resuspended mineral dust (Ca, Al, Si) to be closely associated with traffic flow. These pollutants build up during the day, emphasizing evening rush hour peaks, but decrease (especially their coarser fraction PM_{2.5-10}) after nocturnal road washing. Positive matrix factorization (PMF) analysis of a large Streaker database additionally reveals two other mineral dust components (siliceous and sodic), marine aerosol, and minor, transient events which we attribute to biomass burning (K-rich) and industrial (incinerator?) Zn, Pb plumes. Chemical data on 24-hour filters allows the measurement of secondary inorganic compounds and carbon concentrations and offers PMF analysis based on a limited number of samples but using fuller range of trace elements which, in the case of Madrid, identifies the continuing minor presence of a coal combustion source traced by As, Se, Ge and Organic Carbon. This coal component is more evident in the city air after the change to the winter heating season in November. Trace element data also allow use of discrimination diagrams such as V/Rb vs. La/Ce and ternary plots to illustrate variations in atmospheric chemistry (such as the effect of Ce-emissions from catalytic converters), with Madrid being an example of a city with little industrial pollution, recently reduced coal emissions, but serious atmospheric contamination by traffic emissions.

Keywords: Atmospheric metal, mineral dust, Madrid, Cerium, Arsenic, PMF.

1. Introduction

There is considerable spatial and temporal variation in the chemistry of urban air within our towns and cities. The particular cocktail of gases and particles inhaled by a given citizen will depend on their proximity to anthropogenic pollution sources combined with the natural background of “geological” mineral particles. The greatest anthropogenic threats to urban air quality come from transport, industrial and domestic emissions, although not all cities face the same challenges. In many world cities, with London offering perhaps the most infamous example (Logan 1953; Bell and Davis 2001), a legacy of severe 20thC atmospheric pollution by domestic coal combustion and poorly controlled industrial contamination has been replaced in more recent years by concerns over deteriorating air quality due to traffic emissions (e.g. Jaecker-Voirol and Pelt, 2000; Querol et al., 2001a; Abu-Allaban et al., 2003; Artíñano et al., 2004; Kousoulidou et al. 2008; Amato et al., 2009a). In many other modern cities, however, and notably as a consequence of accelerating 21stC economic development in Asia, continued high levels of coal combustion emissions combine with rapidly growing road congestion simultaneously to inflict a double insult to ambient air quality (EC 2000; Xie et al., 2006; Vassilakos et al., 2007; Junninen et al., 2009; Fang et al., 2011; Kang et al., 2012).

The chemical character of urban anthropogenic emissions from traffic, coal, heavy fuel oil and industry is typically metalliferous, and many research papers have identified a range of metallic tracer elements that can be linked to specific air pollution sources and thus potentially used in pollution control strategies (e.g. Pakkanen et al., 2001; Harrison et al., 2003; Lin et al., 2005; Birmili et al., 2006; Ledoux et al., 2006; Querol et al., 2007; Bukowiecki, et al., 2009; Gietl et al., 2010). In this context examples of our own investigations of specific tracer elements have included La from oil refineries, Ce from the ceramic industry, V from heavy fuel oil and petcoke, As from coal, Mn from the ferromanganese industry, Sb from non-exhaust traffic, and Sr from fireworks (Amato et al., 2009a, Minguillón et al., 2009; Moreno et al., 2007, 2010, 2011; Querol et al., 2007; Pandolfi et al., 2011; Sánchez de la Campa et al., 2011). As a further contribution to the study of tracer elements useful to the chemical sourcing of contaminants, this paper examines a dataset from a traffic hot spot in the Spanish capital Madrid. The data were collected with the specific intention of sampling inhalable particles in the city centre during the change to cold month heating arrangements, which focus domestic and institutional coal burning into the period from 1st November to 31st March (Salvador et al., 2011). In recent years coal combustion within the city has been actively discouraged by the local government, promoting and financially supporting replacement of the old existing heating boilers. Given that a limited number of coal-fed installations still remain in operation, we were interested to know if a coal-related chemical signature could still

be detected in traffic-contaminated air. To pursue this objective, and to examine the main sources of air pollution in Madrid at the beginning of the cold season, we designed a study which combines standard measurements of gas concentrations and particulate matter (PM) mass variations with daily (24 hour filter, ICP-AES and ICP-MS analysis) and hourly (Streaker, PIXE analysis) chemical data.

2. Methodology

The monitoring site selected for this study is Escuelas Aguirre (03°40'52"W, 40°25'32"N), a well-documented Madrid traffic hotspot where two major roads merge alongside a large park in the city centre (Fig. 1; Artíñano et al., 2004; Salvador et al., 2012). For this campaign, which took place from 24th October to 18th November 2010, the Escuelas Aguirre site was equipped with a high volume sampler (30 m³/h) MCVPM1025 to collect 24h PM₁₀ samples (with daily sampling starting at 12:00 pm). Quartz microfiber filters (Pallflex) were conditioned (30-40% relative humidity during 48h) and weighed before and after sampling to determine PM₁₀ concentrations by standard gravimetric procedures. Once the gravimetric determination was performed the filters were treated and analysed for the determination of the chemical composition of PM₁₀.

One quarter of each filter was acid digested (HF:HNO₃:HClO₄, with a mixture of 2.5:1.25:1.25 ml, kept at 90°C in a Teflon reactor during 6h, driven to dryness and re-dissolved with 1.25 ml HNO₃ to make up a volume of 25 ml with water) for the chemical analysis using ICP-AES and ICP-MS (Querol et al., 2001a). Another ¼ of each filter was water leached (6h at 60°C, preceded by incubation in an ultrasound bath for 10 minutes, in 50 ml sealed PVC bottles) for the determination of soluble ion concentrations by ion chromatography (sulphate, nitrate and chloride) and ion selective electrode (ammonium), allowing an average detection limit for the analysed components of 25-30 ng/m³. A (1.5 cm²) portion of the remaining half of each filter was also used for the determination of organic and elemental carbon (OC and EC, respectively) by a thermal-optical transmission technique (Birch and Cary 1996) using a Sunset Laboratory OCEC Analyser with the EUSAAR-2 standard temperature programme. The accuracy of the equipment is 5% for both OC and EC. The sum OC+EC is C_{total}. The OM+EC (organic matter plus elemental carbon) value was obtained after applying a 1.6 factor to the OC concentrations (Turpin et al., 2000). SiO₂ and CO₃²⁻ were indirectly determined on the basis of empirical factors ($Al \cdot 1.89 = Al_2O_3$, $3 \cdot Al_2O_3 = SiO_2$ and $1.5 \cdot Ca = CO_3^{2-}$, see Querol et al., 2001a). Blank field filters were used for every stock purchased for sampling and analysed in the same batches of their respective filter samples. The corresponding blank concentrations were subtracted from each sample. To assure the quality of the analytical procedure a small amount (5 mg) of the NIST-1633b (fly ash) reference material loaded on a ¼ quartz micro-fibre filter was also analysed. Detection limit and accuracy of the techniques were estimated as 0.18 ng/m³ and 1-3% respectively for ICP-AES, and 0.007 ng/m³ and 0-7% respectively for ICP-MS. The detection limits for Zr and Hf are higher (0.05 ng/m³).

In addition to analysing the daily chemistry of PM₁₀ using 24-hour filter samples, an elemental characterization of PM was performed by a Streaker sampler collecting hourly aerosol samples in two size ranges (0.1-2.5µm and 2.5-10µm) at an air flow rate of 1 l/min that were then analyzed by Particle Induced X-Ray Emission (PIXE, see Lucarelli et al., 2011 for details) at the LABEC-INFN facility in Florence (based on a 3 MV Tandetron accelerator), where an external beam set-up is fully dedicated to atmospheric aerosol studies.

Individual estimates of the concentration errors were calculated following the methodology described by Amato et al. (2009a). The uncertainty estimate provides a basis to separate species which retain a significant signal from the ones dominated by noise. This principle is based on the signal-to-noise S/N ratio described by Paatero and Hopke (2003). However, due to the sensibility of S/N to sporadic values much higher than the level of noise, the percentage of data above detection limit (ADL) was used as complementary criterion. The combination of both principles allowed us to select 21 strong and 2 weak (uncertainty increased by a factor of 3) species out of 63 to perform the source apportionment study in the case of daily samples, and 13 strong species out of 26 in the case of the hourly samples.

A Positive Matrix Factorization (PMF, Paatero and Tapper, 1994) was performed on the two data matrices of concentrations and uncertainties for both daily and hourly samples (over 550 (1h) data points for each of the two size fractions obtained with the Streaker but only 25 (24h) high volume samples), applying the Multilinear Engine (ME-2, Paatero, 1999) in the case of the daily samples, a flexible computer program implementing a scripting language able to solve multivariate receptor models such as PMF and Chemical Mass Balance, among others. This constrained model differs from the customary PMF problem in several constraints which were introduced with the aim of driving the solution towards one which fulfills some a priori information about possible sources and the mass conservation principle. In addition to the traditional equations of PMF, several so-called auxiliary equations and upper-lower limits for species concentrations in source profiles were added.

3. Results

Our data confirm that Escuelas Aguirre provides a classical example of a city centre traffic-polluted site, dominated by the daily double peak of PM, NO_x, and CO associated with morning and evening journeys across the city (Fig. 1). Figure 2 focuses on the October-to-November time period in which we are specifically interested and demonstrates the typical weekday increase in traffic-related pollution which reaches a peak on Thursday evening then declines to a weekend low point (Fig. 2a). This pattern was reinforced in this case both by the arrival of a rainy cold front on Friday 29th October, and by the fact that in 2010 the bank-holiday of November 1st fell on a Monday. Thus the weekdays before and after 1st November were separated by a prominent

advective cleansing event which removed the contaminated late October weekday air mass from the city and provided an opportunity to observe any chemical differences present during the following week.

The Streaker hourly data allow us to add variations in PM chemistry and demonstrate that most major element concentrations, represented on Fig. 2b by Al and Ca (but also shown by other major elements such as K and Mg), follow the same daily traffic-related pattern. It is clear from this pattern that the concentration of inhalable mineral dust PM in Madrid air is strongly influenced by traffic resuspension. With regard to trace elements, the Streaker data similarly provide an elegant example of the correlation between many metal concentrations and traffic emissions (Fig. 2c), with levels of Zn, Cu, Cr (and Fe) rising and falling in harmony with the daily traffic peaks. The obvious exception to this pervasive influence of traffic emissions on air quality is provided by NaCl marine aerosols which record the bank holiday weekend arrival of the cold front which swept across Spain from the NW Atlantic coast (Fig. 2d).

The PMF analysis of the Streaker coarse fraction ($PM_{2.5-10}$) data allows us to detect 5 main source factors (Fig. 3) as follows: 1. **Ca, Al, Si-rich mineral dust** with major elements Ca, Al, Si, Mg, Fe and a range of trace elements that includes many metals (Ti, Mn, Cu, Cr, Zr); 2. **Metallic traffic emissions** which account for >50% of the Fe, Cu, Cr, Zr, and Mn in the analyses as well as significant amounts of Zn; 3. **Si-rich mineral dust** which accounts for 50% of the Si and lesser amounts of Al, K, Ti, Sr, Ca, Mg, and S; 4. **Marine aerosol** Na, Cl; 5. **Sodium-sulphur-bearing aerosol** which is an unusual factor dominated by Na, Mg and S which may include aged and chemically transformed (acidified) sea salt. We suggest however that another, more geological, explanation for this coarse sodic PM fraction may relate more to the highly unusual soil bedrock in the Madrid area, comprising Miocene sediments containing anhydrite, halite, clays, carbonates and abundant sodium-rich sulphate deposits (thenardite and glauberite: Alonso-Zarza et al., 2002). In addition to the 5 main coarse PM sources listed above it is possible to distinguish a very minor coarse PM factor characterized by high Zn, Pb, Mn (2%).

With regard to the fine aerosol fraction ($PM_{0.1-2.5}$) once again 5 main source factors can be detected, although with some differences from those of the coarser fraction: 1. **Metallic traffic emissions** again dominated by Fe and Cu, with Mn, Ti and Zn; 2. **Ca-rich Si-poor mineral dust** with major elements Ca, Al, Fe, Mg and trace metals Ti, Mn, and Cu; 3. **Marine aerosol** Na, Cl; 4. **Potassium-sulphur-bearing aerosol** responsible for the majority of the measured K due to a prominent spike on 29th October which we attribute to a biomass burning episode; 5. **Zn, Pb, Mn aerosol** similar to, but more pronounced than, the 6th factor in the coarser fraction and attributable to the occasional transient passage of an industrial (incineration?) plume of fine metalliferous condensates (Moffet et al., 2008). There is again a minor 6th factor in the fine fraction, although in this case this is a fine Sulphur-bearing aerosol (2%) of uncertain origin (Fig. 3).

The PM₁₀ mass data and ICP chemical data for the late October-early November period are summarized in Table 1. PM₁₀ 24-hour average mass levels ranged dramatically from 92 µg/m³ (Thursday-Friday 28-29th October) down to 15 µg/m³ (Sunday-Monday 31st October- 1st November). The two dominant components present in the PM₁₀ at such sites are typically mineral dust (MD = CO₃²⁻+SiO₂+Al₂O₃+Ca+K+Mg) and Organic + Elemental Carbon (OC + EC), although relative proportions of these can vary, as demonstrated by our data which show a clear difference between Weeks 1 and 2. During the Tuesday-Friday period of Week 1 MD>(OC+EC), whereas the reverse is true during the same period of Week 2 when Carbon is the main component (Table 1). This difference is due to variations in the amount of MD, which declines from an average of 26 µg/m³ in Week 1 to just 11 µg/m³ in Week 2 whereas (OC+EC) stays constant at 22 µg/m³ over both Tuesday-Thursday periods (Table 1).

The application of PMF methodology to this limited database, even given the low sample number (as compared to the Streaker data), nevertheless produces estimated factor profiles (Fig. 3c) comparable with previous studies on Spanish urban sites based on higher numbers of 24-hour samples (Amato et al., 2009b; Pandolfi et al., 2009; Ozturk et al., 2012). In order of abundance (with estimated mass and % of total) these contributing source factors are: 1. **Traffic** (11.02 µg/m³ = 30%) with OC, EC, Sn, Sb, Fe and lesser contributions from Al, Ca, Ti, and EC; 2. **Mineral dust** (9.35 µg/m³ = 25%) with Al, Ca, Ti, Rb and traces of V; 3. **Secondary inorganic compounds** (SIC: 8.55 µg/m³ = 23%) with NO₃⁻, NH₄⁺, and traces of Sn, Sb, Zn, V, and Fe; 4. **Marine** (4.25 µg/m³ = 11%) with Na and Cl and traces of SO₄²⁻ indicating aged, chemically reacted aerosols; 5. **Coal combustion** (3.10 µg/m³ = 8%) based mainly on anomalies in As, Se, Ge and OC and previously also recognized in receptor modeling analysis of Madrid air by Salvador et al. (2011); 6. **Lead-rich factor** (1.15 µg/m³ = 3%) dominated by Pb but with traces of Zn, Cd, SIC and carbon (Fig 3c).

Comparison between the Streaker and ICP data is hindered by the fact that the PIXE results do not show ammonium salts measurements and include only a limited number of trace elements, whereas the ICP cannot directly measure Si (due to the use of quartz fibre filters, unlike the Streaker which uses nuclepore). Thus the Streaker PMF cannot detect the SIC and coal factors recognised by PMF analysis of the ICP data, although it has the great advantage of being based on a much larger and statistically robust dataset (hourly rather than daily). Overviewing all results, the high-time resolved Streaker measurements show the advantage of capturing intra-daily variations, while daily PM characterization permits a more comprehensive chemical characterization. Thus, high-time resolved measurements such as provided by the Streaker data have the advantage of capturing intra-daily variations, while daily PM characterization permit a more comprehensive chemical characterization and mass closure. The hourly PMF-Streaker profile concentrations (elemental ratios) on coarse and fine PM size fractions are statistically much more robust, the daily-PMF profiles nevertheless provide useful information on the chemical source components of the PM₁₀

sample as a whole (including major species such as OC, EC and water soluble ions, which cannot be measured by PIXE).

Even given the limitations of comparing data obtained by different techniques and with different sample numbers, however, what is most clear from both datasets is that traffic emissions, both primary exhaust and those associated with dust resuspension, provide by far the dominant source of inhalable aerosols at Escuelas Aguirre. This is emphasised in Fig. 2 which shows the familiar weekday traffic peaks recorded by PM₁₀ and NO₂ data (Fig. 2a) also reflected in the Streaker data both for mineral dust and metallic sources (Fig. 2a, b, c). One result of the Streaker PMF analysis is that the coarser silicate mineral dust (MD) fraction can be split into two contrasting chemical types. The more common of these two is calcareous, more aluminous and more metalliferous (CaAlSi MD) whereas the other is more siliceous (Si MD). The difference between these two fractions must primarily reflect their “geological” rock-forming mineral content which will be dominated by silicates (quartz, feldspars and phyllosilicates) and carbonates. The CaAlSi MD chemistry is consistent with the presence of abundant calcite and aluminous, Fe-bearing phyllosilicates such as illite, whereas the Si-rich fraction is presumably richer in quartz (although no XRD analyses were performed due to the low mass of sample).

The presence of calcium enriched minerals (especially calcite) dominates the mineral dust pool in Madrid city under local and regional scenarios, which strongly contrasts with the major presence of phyllosilicates and much lower Ca/Si ratios during long range transports from North African regions (Coz et al., 2009; 2010). A likely reason for this is an increased presence of more calcareous mineral dust originating from construction-demolition site works active in the city during the day (cement typically contains >80% calcium minerals, the rest being mainly phyllosilicate-bearing argillaceous material). In addition, a recent study of soil resuspension in Retiro Park suggest there might be high load emissions of both calcium enriched particles and silicates associated with pedestrian activities (walking, running, biking, etc.) on non-paved roads and paths (Álvarez-Menchaca, 2012). Curiously, the CaAlSi MD PM_{2.5-10} is more emphasised during evening rather than morning rush hour periods (see coarse Ca distribution in Fig. 2b) which supports a daytime construction activity source. The quartz-rich dust component of the coarse PM fraction shows less direct correspondence with traffic rush hour patterns and so is likely to include a significant component of wind-blown soil particles derived from the nearby Retiro Park, especially given the typical pattern of daytime winds which typically rotate clockwise from more northerly to southerly directions during the day (Fig. 1 and Plaza et al., 1997).

Another interesting finding is the major presence of a calcium rich group of particles in the fine range, **Ca-rich Si-poor mineral dust**, which contrast with the coarser size of crustal calcite. This group of particles generally fall into the accumulation range with size distribution peaks below 1 µm and that have been recently associated to traffic resuspension/emission in Escuelas Aguirre

(Álvarez-Menchaca, 2012). This is especially relevant in this size range in terms of atmospheric processing, since calcium carbonate is known to react with both SO₂ and HNO₃ in the atmosphere becoming highly hygroscopic and thus, affecting both their optical properties and cloud microphysics in climate change (Laskin et al., 2005).

The prominent loss of ambient mineral dust from Weeks 1 to 2 is highlighted by the ICP-daily database, which also demonstrates how it was the CaAlSi MD component that was removed by the weekend cleansing advection event (Table 1). Concentrations of “crustal” elements Al, Ca, K, Mg, Ti, Rb and the lanthanoid “rare earth” series (La, Ce, etc.) are correspondingly higher during Week 1, reaching a peak on 28/10/10 (Table 1). In contrast, levels of Si MD show little difference between the two weeks, and transient peaks of metalliferous traffic emissions actually become more accentuated in Week 2 (Table 1). Another chemical contrast across the October-November divide is that the data from the first four days in November show mass-normalised (to PM) highs in both OC as well as a range of metals and metalloids which include As, Ge, Cd, Sn, Sb and Tl (Table S1 in supplementary material). Arsenic in particular shows its three highest mass-normalised values on 1st-3rd November (Table S1) and its highest measured mass value (2.85 ng/m³) on 3rd November (Table 1). This difference is well illustrated by mass-normalising the data as shown by Fig. 4a and is attributed to increased coal combustion from the 1st week of November. The need for domestic heating following a cold, rainy weekend (when maximum daily temperature had dropped suddenly from 21°C to 11°C) diminished during Week 2 as daytime temperatures rebounded to reach 24°C by 4th November. The heightened influence of coal emissions immediately after 31st October is also indicated by the PMF analysis of ICP data which shows the coal combustion factor to be most clearly present during early November.

4. Discussion and Conclusions

Madrid is an example of a European capital where industrially-sourced aerosols are minor but where the effects of dense traffic combine with a dry, continental climate, arrivals of intrusions of African dust (Díaz et al., 2012), and an unfavorable topography to create significant city-wide air pollution, especially during anticyclonic stagnation episodes (Artiñano et al., 1994, 2003, 2004; Monzón et al., 1999; Pujadas et al., 2000; Salvador et al., 2004, 2011; Coz et al., 2010; Jiménez et al., 2010; Maté et al., 2010; Gómez-Moreno et al., 2011; Karanasiou et al., 2011, 2012). The trace element chemistry of PM from Escuelas Aguirre reflects the particular high traffic/low industry character of Madrid air, with low V/Rb (1.1) and La/Ce (0.35) confirming the lack of influence from heavy hydrocarbon combustion and FCC refinery emissions, unlike in several more industrially contaminated cities we have investigated (Fig. 4b, c). Furthermore, the La/Ce is low enough to indicate Ce-enrichment relative to normal crustal values, as demonstrated by the ternary Ce-La-Sm plot (Fig. 4d). Given the lack of a ceramic industry in Madrid, we attribute this

enrichment to the release of Ce from catalytic converters (CC). Cerium oxide and aluminium coatings, combined with a layer of finely dispersed platinum group elements (PGE), are now ubiquitously used in modern road vehicle CC, and anomalously high levels of ambient PGE PM have already been reported in the city (Gómez et al., 2001). Our data provide a clear demonstration of the fact that traffic-contaminated urban air contains measurable anomalies in inhalable CePM, and it illustrates how this lanthanoid group element (given an absence of industrial Ce sources) is a useful marker for traffic emissions.

In contrast to the failure to control traffic emissions in Madrid, considerable effort has been placed into reducing coal combustion pollutants within the city. Residential heating systems utilising coal were cut by half over the period from 1999 to 2008 (from 2097 to 1021: Ayuntamiento de Madrid, 2010; Salvador et al., 2012), showing annual average concentrations of atmospheric inhalable As at Escuelas Aguirre of just 2.2 ng/m³ by 2009 (Ayuntamiento de Madrid, 2010). Such a level lies far below the EC target annual level of 6 ng/m³ proposed for 2013 (EC Directive 107/2004), although the value of annual averages is somewhat compromised by the fact that domestic coal burning inevitably focuses the problem of As contamination into the winter period. In this context daily As concentrations (and therefore transient inhalation doses) in 2007-2008 could still exceed 7 ng/m³ (Salvador et al., 2011). Since then levels of As have continued to fall markedly at Escuelas Aguirre, with average annual concentrations registering only 1.3 ng/m³ in 2010 (Ayuntamiento de Madrid, 2010), the same average value observed in our much shorter campaign (1.3 ng/m³: Table 1). We do not have information on the maximum levels of this contaminant reached in 2010, but our own more limited 2010 database shows a maximum As concentration of just 2.9 ng/m³ (on 3rd November). Given the strongly downward trend, and with average As concentrations currently low enough to lie within the national average for Spanish cities (Querol et al., 2007), one can conclude that the problem of coal emissions in Madrid has been greatly reduced.

Even given these currently much-reduced concentrations of atmospheric As in Madrid, they nevertheless remain high enough to allow us to use this metalloid as a tracer element to demonstrate the continued presence of coal combustion-related atmospheric pollutants. This can be illustrated using a As-Ce-La ternary diagram we previously introduced to show transboundary atmospheric emissions from coal contamination present in Japan but originating from China (Moreno et al., 2012). Plotting the weekday late October - early November Madrid data on this diagram reveals an As-enrichment trend from more crustal compositions typical of Week 1 to more coal-contaminated samples in Week 2, with 1st November demonstrating the highest relative amounts of As (Fig. 5). The build-up of weekday inhalable mineral dust from Monday to Friday in Week 1 produces the opposite effect, namely a trend towards lanthanoid enrichment, as the ratio of mineral dust to (OC+EC) progressively increases from 0.9 to 1.5 (Table 1). The slight bias towards Ce-enrichment,

with all Madrid data falling within a $\text{Ce}_{70}\text{Ce}_{50}\text{As}_{100}$ sub-triangle, is also apparent in this diagram (Fig. 5).

Overviewing our chemical database, it is useful to compare the pros and cons of hourly Streaker data with those produced by full chemical analysis on 24-hour filter samples. The Streaker, based on around 550 hourly measurements, allows us to identify different types of mineral dust in the coarser ($\text{PM}_{2.5-10}$) inhalable fraction (calcareous, siliceous, and sodic). The commonest of these is the calcareous type which is also aluminous and metalliferous, comprises >50% of the coarse (and most of the fine) mineral dust loading, and is directly linked to traffic flow, especially to evening rush hour peaks, suggesting a road dust resuspension origin. The chemical composition of this PM component suggests the mineralogy is mostly calcite and clay minerals sourced in large part from construction sites and roadworks active in the city. It increases in abundance during the day, until nocturnal road washing (which takes place at Escuelas Aguirre every night) reduces the amount of dust available for resuspension the following morning (Karanasiou et al., 2011, 2012). During 2010 the problem of air pollution related to urban construction in central Madrid was especially acute, with a major programme of roadworks and reconstruction taking place in the nearly highly congested central arterial route of Serrano Street (400 m from Escuelas Aguirre and with traffic flow directly connecting the two). The consequent damage to city centre air quality over the year is illustrated by data from Escuelas Aguirre where in 2010 annual average PM_{10} concentrations were $54 \mu\text{g}/\text{m}^3$ and there were 33 exceedences of NO_2 hourly values $>200 \mu\text{g}/\text{m}^3$ (the legal limit is 18 exceedences), the worst result in over 10 years of monitoring (Ayuntamiento de Madrid, 2010; Salvador et al., 2012).

The Streaker data also demonstrate with graphical clarity the direct link between traffic flow and concentrations of inhalable metalliferous PM, with peaks in Zn, Cu, Cr and Fe coinciding with rush hour patterns (Fig. 2c). While the analytical limitations of the Streaker only allow us to measure a relatively small number of metallic trace elements, source apportionment analysis of the trace element ICP-MS data further reveals not only a factor with high correlation between Zn and Cu and other toxic metals such as Sn and Sb (which can therefore also be linked to traffic emissions) but also the presence of new factors, notably that related to coal combustion, despite the heavy dominance of traffic emissions. It is the marriage of the contrasting datasets reported in this paper, combining Streaker hourly measurements with daily filter data on SIC, (OM+EC) and a full range of inorganic elements, that offers a deeper insight into the complex mixture of anthropogenic metals and mineral dust inhaled by urban residents.

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Figure and Table captions

Figure 1. Location maps of monitoring site at Escuelas Aguirre, central Madrid, with its classical daily double-peak pattern of traffic pollutants NO_2 , PM_{10} and $\text{PM}_{2.5}$ and their inverse relation to O_3 during the studied period.

Figure 2. Thirteen-day experimental period 24/10/10-6/11/10 showing two weekday traffic events separated by a 3-day rainy bank holiday weekend. The rush hour peaks displayed by NO_2 and PM_{10} (Fig. 2a) are repeated by Streaker chemical data on major elements (represented by Al and Ca on Fig. 2b) and trace metals (represented by Cu, Zn and Cr on Fig. 2c). In contrast, the passage of an Atlantic cold front over the weekend is recorded by NaCl peaks (Fig. 2d).

Figure 3. Positive Matrix Factorisation results for Streaker (a, b) and 24-hour filter (c) data showing the factor profiles. Bars correspond to mass fraction and diamonds to explained variation.

Figure 4. a) Comparison between As and Tl normalised (to PM) values between weekdays before (first week) and after (second week) the implementation of coal burning regulation on 1 November 2010. b) V/Rb vs. La/Ce discrimination plot for contrasting patterns of La, Ce and V contamination (see Moreno et al., 2010 for details) showing traffic-related atmospheric Ce-enrichment in Madrid (Weeks 1 & 2 data plotted as in Fig. 5). c) Ternary Ce-La-V plot comparing same Madrid samples with V-contaminated ambient PM_{10} samples from Mexico City (see Moreno et al., 2008). d) Ternary Ce-La-Sm plot showing Ce-enrichment of same Madrid samples compared to FCC refinery La-enriched PM and natural compositions of uncontaminated mineral dust (see Moreno et al., 2010). UCC = upper continental crust (Taylor and McLennan, 1995); MUQ = standard for unconsolidated argillaceous sedimentary rocks (Kamber et al., 2005).

Figure 5. Ternary AsLaCe diagram introduced by Moreno et al. (2012) illustrating the mixing line between uncontaminated crustal composition and urban PM highly contaminated by coal combustion and industrial emissions in the city of Wuhan, China (data from Querol et al., 2006). Week 1 sample compositions dominated by mineral dust (28-29th October) plot closest to upper continental crustal compositions and the clean tropospheric PM_{10} (from Izaña in the Canary Islands: Alastuey et al., 2005), whereas the most coal contaminated samples (1st-3rd November) plot closest to Wuhan compositions (see text for details). Also plotted are analyses of coal, and both light and heavy density fractions extracted from coal (Querol et al., 2001b), with the heavy density fraction (DF) containing toxic volatile elements such as As (numbers in black circles are only for legend).

For comparison we include data from PM₁₀ contaminated by Fluid Catalytic Converter (FCC) oil refineries (La-rich) and the ceramic industry (Ce-rich) (Moreno et al., 2010).

Table 1: Chemical analyses for 24-filter samples collected from Escuelas Aguirre from 24/10/10 to 18/11/10.

Supplementary material

Table S1. Mass-normalised values for the chemical data presented in Table 1.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Date	SUN 24/10/10	MON 25/10/10	TUE 26/10/10	WED 27/10/10	THU 28/10/10	FRI 29/10/10	SAT 30/10/10	SUN 31/10/10	MON 01/11/10	TUE 02/11/10	WED 03/11/10	THU 04/11/10	FRI 05/11/10	SAT 06/11/10	SUN 07/11/10	MON 08/11/10	TUE 09/11/10	WED 10/11/10	THU 13/11/10	FRI 14/11/10	SAT 15/11/10	SUN 16/11/10	MON 17/11/10	TUE 18/11/10	Average	MAX	Sdev
µg/m³																											
PM ₁₀	20.71	28.01	54.66	70.64	92.16	37.63	18.06	15.08	19.51	42.59	42.45	54.75	49.33	39.22	23.70	16.61	14.53	64.79	24.74	15.88	36.44	20.16	23.14	49.75	37.48	92.16	20.66
Ctotal	6.12	8.52	14.09	18.13	20.61	6.32	3.63	4.29	5.96	13.96	13.52	17.42	12.62	8.47	4.35	4.27	4.72	18.26	7.77	6.25	9.25	8.25	9.51	12.69	10.19	20.61	5.13
Cnm	5.8	7.9	12.9	16.5	18.7	5.7	3.6	4.2	5.8	13.5	13.0	16.7	12.0	8.1	4.1	4.0	4.6	17.8	7.6	6.1	9.0	8.1	9.3	12.3	9.69	18.67	4.77
OM+EC	9.3	12.7	20.7	26.4	29.9	9.2	5.7	6.7	9.3	21.7	20.9	26.8	19.3	13.0	6.6	6.5	7.3	28.5	12.2	9.8	14.4	12.9	14.8	19.7	15.51	29.88	7.64
OC	3.93	5.16	9.40	11.83	12.50	3.99	1.96	2.53	3.60	9.89	10.05	12.32	9.32	6.44	3.09	2.53	3.07	15.08	5.03	4.30	6.39	5.02	5.06	10.27	7.01	15.08	3.90
EC	2.18	3.36	4.69	6.29	8.11	2.33	1.67	1.77	2.36	4.08	3.47	5.09	3.29	2.03	1.26	1.73	1.65	3.18	2.75	1.95	2.86	3.23	4.45	2.42	3.18	8.11	1.59
CO ₂	1.6	2.9	5.9	8.0	9.7	3.0	0.3	0.6	0.7	2.1	2.4	3.4	2.8	1.8	1.2	1.1	0.7	2.3	0.9	0.5	1.2	1.0	1.2	2.0	2.47	9.68	2.34
SiO ₂	1.9	3.2	6.4	8.8	11.2	4.7	0.2	0.7	0.7	2.0	2.5	4.2	3.0	2.0	1.4	1.5	0.9	2.4	0.9	0.4	1.1	1.0	1.4	2.1	2.81	11.22	2.71
Al ₂ O ₃	0.64	1.05	2.14	2.94	3.74	1.58	0.08	0.23	0.22	0.67	0.84	1.41	1.00	0.67	0.45	0.49	0.30	0.81	0.31	0.13	0.37	0.33	0.46	0.71	0.94	3.74	0.90
Ca	1.04	1.95	3.93	5.34	6.46	2.02	0.21	0.40	0.46	1.43	1.62	2.26	1.89	1.19	0.81	0.74	0.47	1.55	0.59	0.35	0.80	0.65	0.80	1.31	1.65	6.46	1.56
Fe	0.93	1.50	2.69	3.76	4.59	1.39	0.78	0.78	0.90	2.25	2.42	3.27	2.32	1.00	0.70	0.71	0.79	3.17	1.78	1.00	1.66	1.61	1.65	2.51	1.88	4.59	1.06
K	0.23	0.28	0.55	0.73	1.26	0.49	0.08	0.10	0.10	0.24	0.27	0.44	0.40	0.36	0.17	0.16	0.13	0.38	0.25	0.11	0.12	0.14	0.17	0.25	0.32	1.26	0.27
Na	0.16	0.43	0.40	0.31	0.40	0.50	0.45	0.19	0.29	0.26	0.15	0.16	0.18	0.15	0.14	0.48	0.79	0.41	0.29	0.31	0.43	0.27	0.79	0.42	0.35	0.79	0.18
Mg	0.08	0.15	0.27	0.41	0.50	0.26	0.07	0.05	0.06	0.13	0.12	0.19	0.15	0.08	0.06	0.10	0.12	0.18	0.08	0.06	0.11	0.08	0.15	0.15	0.15	0.05	0.11
SO ₂	1.00	1.22	1.34	1.56	1.94	0.89	0.86	0.27	0.73	1.50	1.35	1.18	2.08	1.94	1.03	0.62	1.98	3.07	1.44	0.95	0.94	0.64	0.94	1.28	1.32	3.07	0.63
NO ₂	0.34	1.32	1.09	2.12	4.17	1.04	0.42	0.18	0.80	1.93	1.13	1.34	4.42	3.41	0.63	0.42	0.46	6.16	2.64	1.25	1.21	1.31	0.77	2.54	1.83	6.16	1.58
Cl ⁻	0.17	0.41	0.61	0.38	0.43	0.84	0.79	0.30	0.44	0.72	0.53	0.60	0.68	0.65	0.55	1.08	1.77	1.17	0.73	0.84	1.19	0.39	1.37	0.67	0.71	1.77	0.37
NH ₄ ⁺	0.18	0.30	--	0.38	0.64	0.16	0.18	0.02	0.13	0.40	0.21	0.21	1.06	0.19	0.30	0.04	0.03	2.45	0.76	0.38	0.24	0.19	0.12	0.55	0.44	2.45	0.51
Mineral	6.4	11.0	21.9	30.0	37.4	13.5	1.8	2.8	3.1	8.9	10.2	15.2	11.6	7.1	4.8	4.8	3.4	10.8	4.9	2.6	5.4	4.8	5.8	9.0	10.22	37.45	8.76
OM+EC	9.3	12.7	20.7	26.4	29.9	9.2	5.7	6.7	9.3	21.7	20.9	26.8	19.3	13.0	6.6	6.5	7.3	28.5	12.2	9.8	14.4	12.9	14.8	19.7	15.51	29.88	7.64
SIC	1.5	2.8	3.2	4.1	6.7	2.1	1.5	0.5	1.7	3.8	2.7	7.6	5.5	2.0	1.1	2.5	11.7	4.8	2.6	2.4	2.1	1.8	4.4	3.59	11.68	2.60	
Marine	0.3	0.8	1.0	0.7	0.8	1.3	1.2	0.5	0.7	1.0	0.7	0.8	0.9	0.8	0.7	1.6	2.6	1.6	1.0	1.2	1.6	0.7	2.2	1.1	1.06	2.56	0.51
Trace metals	0.4	0.6	1.0	1.0	1.1	0.3	0.2	0.2	0.3	0.6	0.6	0.7	0.7	0.3	0.2	0.2	0.6	0.8	0.4	0.3	0.3	0.3	0.3	0.5	0.52	1.09	0.30
ng/m³																											
Li	0.35	0.86	1.18	1.98	3.61	1.03	0.11	0.12	0.17	1.77	0.81	1.26	--	0.41	0.24	0.22	0.21	2.20	0.52	0.37	0.66	0.47	0.30	0.55	--	3.61	0.83
Sc	0.15	0.17	0.22	0.28	0.31	0.20	0.07	0.11	0.09	0.11	0.10	0.13	0.12	0.12	0.11	0.09	0.16	0.11	0.06	0.07	0.05	0.04	0.08	0.10	0.13	0.31	0.07
Ti	18.40	29.66	58.26	81.68	101.21	45.44	5.03	11.50	9.63	30.34	31.33	45.02	41.33	20.62	13.55	13.54	12.90	37.31	12.35	7.28	18.08	16.70	16.98	27.96	30.30	101.21	23.63
V	0.86	0.95	1.53	2.65	3.51	2.30	0.30	0.23	0.42	1.14	0.93	1.24	2.38	1.55	0.64	0.36	0.28	1.96	1.45	0.62	0.58	0.70	0.66	1.38	1.28	3.51	0.94
Cr	8.50	9.38	15.43	20.04	20.97	5.31	2.47	3.41	3.92	11.40	12.44	17.32	12.16	4.19	2.92	2.45	44.74	14.49	8.09	4.76	7.89	7.97	8.08	13.40	11.14	44.74	8.93
Mn	10.11	17.27	31.09	42.03	56.50	17.99	7.21	6.62	7.02	25.83	22.80	30.62	30.60	10.96	6.49	6.30	7.21	39.02	20.01	16.25	14.22	16.04	14.88	32.31	20.84	56.50	13.18
Co	0.15	0.22	0.44	0.57	0.67	0.26	0.08	0.05	0.07	0.26	0.31	0.37	0.34	0.12	0.06	0.05	0.09	0.36	0.22	0.14	0.20	0.24	0.22	0.37	0.25	0.67	0.16
Ni	1.46	2.38	4.27	4.12	4.46	1.88	0.78	0.29	0.39	1.88	2.19	2.54	2.67	1.06	0.77	0.35	1.00	2.76	1.77	0.96	1.32	1.52	1.41	2.51	1.93	4.46	1.21
Cu	210.29	366.88	578.74	487.92	359.28	111.96	86.10	94.36	100.65	244.89	241.75	285.61	241.66	116.45	81.05	83.88	283.75	178.47	102.04	61.17	94.92	92.40	92.61	144.47	215.34	642.31	162.30
Zn	47.32	58.96	94.74	126.47	231.64	52.66	34.80	32.17	37.19	104.28	89.61	120.75	129.92	53.89	30.82	32.04	67.21	229.82	119.74	110.46	47.70	46.31	42.17	119.41	86.46	231.64	55.43
Ga	0.15	0.31	0.45	0.59	0.72	0.29	0.06	0.10	0.22	0.41	0.36	0.41	0.29	0.20	0.15	0.10	0.12	0.30	0.12	0.15	0.16	0.14	0.16	0.32	0.27	0.72	0.16
Ge	0.31	0.59	0.66	0.71	0.65	0.54	0.43	0.51	0.51	0.76	0.66	0.66	0.81	0.41	0.17	0.51	0.88	0.67	0.06	0.08	0.03	0.08	0.08	0.08	0.46	0.88	0.28
As	0.71	1.38	1.73	1.88	1.79	0.73	0.41	0.51	1.62	2.57	2.85	2.49	1.70	1.22	0.64	0.38	0.43	1.62	0.92	1.04	1.08	0.85	0.83	2.24	1.32	2.85	0.72
Se	0.21	0.22	0.55	0.65	0.51	0.23	0.14	0.07	0.17	0.44	0.35	0.29	0.38	0.26	0.13	0.08	0.12	0.46	0.30	0.18	0.13	0.11	0.11	0.38	0.28	0.65	0.17
Rb	0.82	1.20	2.55	3.60	4.60	1.88	0.15	0.28	0.27	0.83	0.96	1.58	1.25	0.96	0.67	0.55	0.37	1.07	0.55	0.31	0.46	0.48	0.53	0.98	1.17	4.60	1.09
Sr	2.40	4.16	7.36	10.33	14.30	5.57	0.99	1.36	1.30	3.88	4.37	6.00	4.83	2.51	1.76	1.80	1.90	4.39	1.78	1.23	2.35	1.91	2.55	3.93	3.98	14.30	3.13
Y	0.15	0.20	0.41	0.62	0.62	0.32	0.05	0.21	0.05	0.25	0.18	0.29	0.37	0.17	0.13	0.14	0.25	0.23	0.03	0.02	0.03	0.07	0.07	0.17	0.22	0.62	0.17
Zr	5.74	10.41	12.62	16.13	17.14	6.41	1.01	0.96	6.90	13.23	12.64	14.29	14.05	9.34	8.07	4.38	--	13.62	10.32	8.73	10.23	10.51	10.46	12.13	9.72	17.14	4.65
Nb	0.13	0.22	0.46	0.68	0.83	0.28	0.05	0.08	0.11	0.34	0.33	0.50	0.37	0.17	0.12	0.11	0.08	0.44	0.19	0.11	0.21	0.19	0.20	0.33	0.28	0.83	0.20
Cd	0.09	0.26	0.29	0.35	0.91	0.09	0.06	0.04	1.00	0.25	0.27	0.25	0.24	0.13	0.05	0.04	0.40	0.84	0.25	0.21	0.10	0.11	0.12	0.22	0.27	1.00	0.26
Sn	8.34	13.83	25.85	38.86	45.43	10.12	6.20	6.50	8.98	24.70	26.77	35.98	24.65	7.97	5.73	5.50	7.14	31.34	17.19	10.22	15.92	15.76	15.43	26.92	18.45	45.43	11.52
Sb	6.01	8.72	18.58	27.55	30.53	7.84	4.74	4.76	5.78	17.19	17.65	25.81	17.61	6.58	4.16	4.12	4.53	25.05	13.30	7.20	11.81	10.78	10.74	18.67	13.19	30.53	8.16
Cs	0.05	0.08	0.16	0.23	0.29	0.12	--	--																			

Date	SUN 24/10/10	MON 25/10/10	TUE 26/10/10	WED 27/10/10	THU 28/10/10	FRI 29/10/10	SAT 30/10/10	SUN 31/10/10	MON 01/11/10	TUE 02/11/10	WED 03/11/10	THU 04/11/10	FRI 05/11/10	SAT 06/11/10	SUN 07/11/10	MON 08/11/10	TUE 09/11/10	WED 10/11/10	THU 13/11/10	FRI 14/11/10	SAT 15/11/10	SUN 16/11/10	MON 17/11/10	TUE 18/11/10	Average	MAX	Sdev
Ctotal	29.54	30.16	25.78	25.66	22.36	16.81	20.09	28.48	30.56	32.78	31.85	31.81	25.58	21.58	18.35	25.69	32.48	28.19	31.43	39.35	25.39	40.93	41.10	25.50	28.39	41.10	6.43
Cnm	28.03	28.09	23.62	23.39	20.26	15.20	19.75	27.69	29.85	31.78	30.71	30.57	24.43	20.68	17.32	24.35	31.51	27.47	30.71	38.69	24.73	39.96	40.05	24.71	27.23	40.05	6.55
OM+EC	44.85	44.95	37.79	37.43	32.42	24.32	31.60	44.31	47.76	50.84	49.13	48.92	39.08	33.08	27.71	38.96	50.41	43.95	49.13	61.91	39.56	63.94	64.09	39.54	43.57	64.09	10.49
OC	19.00	18.26	17.19	16.75	13.56	10.62	10.87	16.75	18.46	23.21	23.68	22.51	18.90	16.41	13.05	15.26	21.11	23.28	20.33	27.08	17.54	24.89	21.88	20.63	18.80	27.08	4.30
EC	10.54	11.90	8.59	8.91	8.80	6.19	9.22	11.73	12.10	9.57	8.17	9.30	6.68	5.18	5.30	10.42	11.37	4.91	11.10	12.28	7.85	16.04	19.22	4.87	9.59	19.22	3.45
CO ₂ ⁺	7.56	10.33	10.79	11.34	10.51	8.04	1.72	3.95	3.55	5.02	5.71	6.19	5.75	4.54	5.15	6.68	4.87	3.60	3.61	3.32	3.30	4.83	5.21	3.95	5.81	11.34	2.66
SiO ₂	9.34	11.20	11.77	12.48	12.17	12.62	1.28	4.49	3.37	4.73	5.95	7.73	6.06	5.13	5.70	8.91	6.27	3.73	3.81	2.53	3.03	4.96	5.91	4.31	6.56	12.62	3.41
Al ₂ O ₃	3.11	3.73	3.92	4.16	4.06	4.21	0.43	1.50	1.12	1.58	1.98	2.58	2.02	1.71	1.90	2.97	2.09	1.24	1.27	0.84	1.01	1.65	1.97	1.44	2.19	4.21	1.14
Ca	5.04	6.89	7.20	7.56	7.00	5.36	1.15	2.63	2.37	3.35	3.81	4.13	3.83	3.03	3.43	4.45	3.25	2.40	2.40	2.21	2.20	3.22	3.48	2.63	3.88	7.56	1.77
Fe	4.50	5.30	4.93	5.32	4.99	3.71	4.33	5.18	4.63	5.27	5.70	5.96	4.70	2.56	2.97	4.28	5.47	4.90	7.19	6.28	4.56	7.98	7.13	5.05	5.12	7.98	1.23
K	1.09	0.99	1.01	1.04	1.36	1.29	0.43	0.70	0.51	0.56	0.63	0.80	0.80	0.92	0.72	0.97	0.90	0.59	1.01	0.71	0.33	0.68	0.72	0.51	0.80	1.36	0.26
Na	0.79	1.52	0.72	0.44	0.44	1.32	2.51	1.29	1.51	0.62	0.36	0.29	0.36	0.39	0.61	2.86	5.46	0.63	1.17	1.97	1.18	1.34	3.42	0.84	1.33	5.46	1.21
Mg	0.40	0.54	0.50	0.57	0.55	0.68	0.39	0.34	0.33	0.30	0.29	0.34	0.29	0.20	0.24	0.58	0.86	0.29	0.32	0.38	0.31	0.42	0.64	0.31	0.42	0.86	0.16
SO ₄ ⁺	4.85	4.31	2.46	2.21	2.10	2.37	4.75	1.79	3.74	3.51	3.18	2.16	4.21	4.96	4.35	3.71	13.59	4.74	5.81	6.01	2.58	3.19	4.07	2.57	4.05	13.59	2.36
NO ₃ ⁺	1.65	4.68	2.00	3.00	4.52	2.77	2.32	1.20	4.09	4.52	2.66	2.44	8.95	8.69	2.66	2.50	3.15	9.50	10.69	7.90	3.33	6.50	3.32	5.11	4.51	10.69	2.73
Cl ⁻	0.82	1.46	1.11	0.53	0.47	2.22	4.38	2.00	2.25	1.70	1.25	1.10	1.39	1.66	2.30	6.48	12.15	1.80	2.93	5.28	3.27	1.91	5.91	1.34	2.74	12.15	2.59
NH ₄ ⁺	0.88	1.06	1.42	0.54	0.69	0.42	0.98	0.15	0.69	0.93	0.45	0.38	2.15	0.47	1.28	0.27	0.22	3.78	3.08	2.37	0.66	0.94	0.51	1.10	1.06	3.78	0.92
Li	1.71	3.03	2.16	2.81	3.92	2.74	0.63	0.80	0.87	4.17	1.92	2.31	2.51	1.06	1.01	1.35	1.44	3.40	2.11	2.35	1.80	2.35	1.28	1.10	2.03	4.17	0.98
Sc	0.70	0.60	0.41	0.39	0.33	0.52	0.41	0.71	0.47	0.25	0.23	0.24	0.24	0.30	0.46	0.56	1.09	0.16	0.24	0.45	0.12	0.20	0.33	0.19	0.40	1.09	0.22
Ti	88.86	104.99	106.60	115.64	109.82	120.78	27.82	76.28	49.32	71.24	73.90	82.22	83.79	52.58	57.19	81.52	88.77	57.58	49.94	45.82	49.62	82.87	73.37	56.20	75.28	120.78	24.65
V	4.16	3.35	2.79	3.76	3.80	6.12	1.64	1.53	2.14	2.69	2.20	2.27	4.83	3.95	2.72	2.19	1.94	3.02	5.85	3.93	1.59	3.48	2.84	2.78	3.15	6.12	1.24
Cr	41.05	33.23	28.23	28.37	22.75	14.12	13.69	22.60	20.06	26.75	29.31	31.62	24.65	10.67	12.31	14.74	307.83	22.37	32.72	30.00	21.65	39.55	34.90	26.93	37.09	307.83	58.26
Mn	48.81	61.14	56.88	59.50	61.30	47.56	39.92	43.88	35.99	60.64	53.72	55.93	62.05	27.96	27.37	37.93	49.60	60.22	80.88	102.33	39.03	79.59	64.27	64.94	55.06	102.33	17.18
Co	0.71	0.79	0.81	0.81	0.72	0.69	0.43	0.34	0.34	0.61	0.73	0.68	0.68	0.31	0.25	0.32	0.59	0.56	0.90	0.91	0.55	1.18	0.96	0.74	0.65	1.18	0.23
Ni	7.03	8.41	7.81	5.84	4.84	5.01	4.31	1.92	2.00	4.41	5.15	4.64	5.42	2.71	3.24	2.12	6.88	4.26	7.14	6.08	3.64	7.52	6.07	5.05	5.06	8.41	1.86
Cu	1015.46	1298.91	1058.88	690.75	389.85	297.56	476.72	625.85	515.79	574.96	569.48	521.64	489.93	296.90	342.03	504.94	1952.53	275.44	412.53	385.24	260.50	458.40	400.14	290.39	587.70	1952.53	390.61
Zn	228.50	208.74	173.34	179.04	251.35	139.97	192.67	213.36	190.58	244.83	211.08	220.53	263.38	137.40	130.06	192.89	462.49	354.70	484.07	695.64	130.91	229.73	182.20	240.02	248.23	695.64	131.04
Ga	0.73	1.11	0.83	0.84	0.78	0.76	0.32	0.63	1.13	0.95	0.84	0.75	0.60	0.52	0.63	0.58	0.80	0.46	0.48	0.98	0.44	0.72	0.68	0.63	0.72	1.13	0.20
Ge	1.48	2.10	1.22	1.01	0.71	1.45	2.37	3.38	2.60	1.78	1.55	1.21	1.64	1.05	0.73	3.04	6.08	1.03	0.24	0.52	0.08	0.37	0.33	0.16	1.51	6.08	1.33
As	3.45	4.89	3.17	2.67	1.94	1.93	2.28	3.39	8.29	6.03	6.70	4.56	3.45	3.10	2.68	2.27	2.95	2.50	3.71	6.53	2.96	4.21	3.60	4.50	3.82	8.29	1.64
Se	1.03	0.79	1.01	0.92	0.55	0.61	0.80	0.49	0.89	1.04	0.83	0.53	0.77	0.67	0.53	0.46	0.81	0.71	1.20	1.11	0.37	0.56	0.47	0.77	0.75	1.20	0.23
Rb	3.96	4.23	4.66	5.09	4.99	4.98	0.83	1.83	1.40	1.96	2.26	2.89	2.54	2.46	2.81	3.30	2.57	1.65	2.24	1.96	1.27	2.38	2.27	1.97	2.77	5.09	1.25
Sr	11.61	14.73	13.47	14.63	15.52	14.81	5.48	8.99	6.68	9.12	10.30	10.96	9.80	6.41	7.43	10.82	13.06	6.78	7.21	7.76	6.45	9.49	11.04	7.90	10.02	15.52	3.07
Y	0.71	0.70	0.75	0.87	0.67	0.84	0.27	1.42	0.23	0.60	0.42	0.54	0.75	0.44	0.54	0.85	1.71	0.36	0.11	0.14	0.08	0.32	0.32	0.35	0.58	1.71	0.39
Zr	27.70	36.87	23.09	22.83	18.60	17.03	5.58	6.37	35.35	31.06	29.78	26.09	28.48	23.80	34.07	26.37	--	21.02	41.72	54.95	28.09	52.14	45.20	24.38	27.52	54.95	13.31
Nb	0.64	0.79	0.84	0.96	0.90	0.74	0.26	0.52	0.57	0.80	0.79	0.91	0.76	0.44	0.52	0.65	0.54	0.67	0.76	0.72	0.57	0.96	0.88	0.65	0.70	0.96	0.17
Cd	0.45	0.92	0.54	0.50	0.99	0.23	0.33	0.28	5.13	0.60	0.64	0.46	0.49	0.33	0.23	0.23	2.77	1.30	1.02	1.29	0.27	0.55	0.50	0.45	0.85	5.13	1.06
Sn	40.28	48.96	47.30	55.01	49.30	26.90	34.32	43.14	46.04	57.99	63.07	65.72	49.98	20.32	24.19	33.14	49.12	48.37	69.49	64.34	43.70	78.18	66.68	54.12	49.15	78.18	14.72
Sb	29.04	30.86	33.99	39.01	33.13	20.85	26.24	31.58	29.62	40.37	41.57	47.14	35.70	16.78	17.54	24.81	31.14	38.66	53.76	45.36	32.42	53.48	46.41	37.52	34.87	53.76	10.05
Cs	0.26	0.30	0.29	0.32	0.31	0.32	--	--	--	0.15	0.17	0.20	0.18	0.16	0.18	0.21	--	0.12	0.13	--	0.09	0.15	0.14	0.14	0.16	0.32	0.11
Ba	279.01	261.95	217.88	189.12	158.17	180.65	308.55	497.88	294.46	236.70	234.41	223.43	225.52	179.10	254.36	387.54	637.42	250.96	173.57	151.96	125.10	197.40	182.77	131.53	249.14	637.42	116.83
La	0.78	0.89	0.84	0.95	0.93	1.04	0.27	0.71	0.43	0.70	0.61	0.72	0.79	0.72	0.63	0.67	0.69	0.55	0.41	0.57	0.31	0.56	0.51	0.44	0.65	1.04	0.20
Ce	2.23	2.61	2.40	2.82	2.51	2.49	0.84	2.23	1.32	2.33	2.12	2.28	2.04	1.81	1.64	1.97	2.14	1.79	1.40	1.68	1.13	2.05	1.87	1.49	1.97	2.82	0.49
Pr	0.14	0.16	0.17	0.20	0.18	0.20	0.04	0.13	0.05	0.11	0.10	0.13	0.12	0.09	0.10	0.14	0.11	0.07	0.06	0.05	0.05	0.09	0.08	0.07	0.11	0.20	0.05
Nd	0.65	0.75	0.76	0.90	0.82	0.92	0.22	0.60	0.22	0.52	0.44	0.58	0.53	0.40	0.40	0.64	0.56	0.31	0.28	0.22							