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Chemical characterization of filterable PM_{2.5} emissions generated from regulated stationary sources in the Metropolitan Area of Costa Rica



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ABSTRACT

Filterable PM_{2.5} concentrations and their chemical characterizations were analyzed for 67 boilers and 25 indirect furnaces located in the Metropolitan Area of Costa Rica from February 2014 to November 2015. The PM_{2.5} samples were characterized by their composition, focusing on trace elements, inorganic ions and organic and elemental carbon. The results of PM_{2.5} concentrations ranged from 72 to 735 mgm⁻³, with the highest concentrations found for sources using biomass fuel, particularly Type B boilers, and the lowest values for diesel boilers. Further speciation of fine particulate matter (PM) showed significant levels of vanadium and nickel for boilers that use heavy fuel oil (bunker); 4886 and 1942 μgm⁻³, respectively. Copper and manganese were the most relevant metals for biomass burning sources, due to plant absorption from the soil. As for ion concentration, sulfate presented the highest concentrations for biomass boilers and furnaces, whereas chloride only presented the highest concentrations for furnaces. To complete the balance, organic and elemental carbon (OC and EC) analyses were made, in which biomass burning sources presented values five times higher than oil fuels. A Spearman's correlation analysis was made for the data set, revealing significant relationships between heavy metals, sulfate, and fine PM with respect to heavy fuel oil. For the biomass sources, the correlations pointed to K, Na, Mn and, in some cases, oxygen.

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1. Introduction

Particulate matter (PM) present in the atmosphere could be defined as a collection of substances in solid and liquid states found in suspension, or that tend to be deposited as sediment at a velocity that is directly dependent on size. From an epidemiological perspective, PM with a diameter of less than 10 μm (PM₁₀) represent an inhalable size, which can be further divided into heavy (diameters between 2.5 and 10 μm), fine (diameters less than 2.5 μm, PM_{2.5}) and ultrafine (less than 1 μm) (González et al., 2011). Atmospheric PM can be directly emitted from both natural and

anthropogenic sources, and/or formed from the conversion of gases into secondary particles via chemical reactions (Im et al., 2012).

Combustion processes produce significant fine PM emissions with a morphology and chemical composition that is very heterogeneous and directly dependent on the type of fuel used. The fine PM generated is comprised of inorganic elements that are released from the fuel particles as gases during pyrolysis and combustion. Once freed, high supersaturations at decreasing temperatures and a more oxidative environment lead to the homogeneous nucleation of the species. Further growth of the nuclei takes place through condensation and agglomeration. Alkaline sulfates play an important role in the formation of submicron particles, which can also contain varying amounts of metals (Sippula et al., 2009). Soot and organic material are the result of incomplete combustion. The organic material in fine PM comes from organic gases that escape the furnace and later condense in the particulate phase (Yatkin and Bayram, 2008).

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Processes that use petroleum derivatives typically produce fine PM with an elemental carbon nucleus, typically covered by a layer of organic material (Hays et al., 2008). However, they may also contain soot and sulfuric acid, depending on the quality of fuel used. Lower grade fuels (such as oil), contain high concentrations of sulfur and various ash-forming metals, which largely contribute to particulate emissions. In this case, various authors suggest that the formation of fine ash particles is initiated by the nucleation of metal oxides, such as NiO, which act as condensation seeds for other condensable gases (Linak et al., 2000). Additionally, biomass fuel sources typically emit fine particles that are mainly comprised of alkaline metals, but also contain various amounts of organic soot (elemental carbon, or EC) and metals such as zinc (Sippula et al., 2007; Tissari et al., 2008).

Various epidemiological studies have established a link between exposure to PM and adverse health effects (Brauer et al., 2012; Dadvand et al., 2013; Fann et al., 2012). PM_{2.5}, specifically, can easily enter and be deposited in the lungs, causing various acute and chronic health problems. Furthermore, for boilers and furnaces used for energy production, the corrosive properties of the PM limit the equipment's efficiency. PM emissions also effect climate, as atmospheric aerosols can absorb, reflect, refract and diffract sunlight (Zhang et al., 2012). In this context, it is extremely important to not only monitor PM concentrations, but to also determine the chemical makeup or speciation of the PM and link these characterizations to specific source categories. Costa Rica regulates air pollutants emitted from boiler and indirect furnaces (Decree No. 36551-S-MINAE-MTSS, April 2011). This decree covers some existing stationary sources in urban environments, including typical pollutants such as sulfur dioxide, nitrogen oxides and total suspended particles. However, point source emissions from combustion processes can generate several other pollutants, such as heavy metals and organic compounds (Yoo, 2002).

The purpose of this paper is to develop speciation profiles for PM_{2.5} emitted from boilers and indirect furnaces in the metropolitan area of Costa Rica. These profiles are expected to strengthen air quality management by expanding existing emissions inventories to include chemical speciation. The expanded inventories should then be used in routine air quality modeling.

2. Experiment

2.1. Study area

Within Costa Rica's urban system, the Metropolitan Area ranks highest in emissions, accounting for 75% of the vehicle fleet (approximately 734,200 units), 65% of the domestic industry and 60% of the country's population (2,580,000), per data from the latest census, conducted in 2010 (INEC, 2012). The heavy concentration of commercial and industrial activities in such a small geographical area has resulted in significant deterioration of air quality, exposing its inhabitants to average PM_{2.5} concentrations of 21–28 $\mu\text{g m}^{-3}$ annually (UNA, 2016). This was the main reason to focus the research in the Metropolitan Area. Fig. 1 shows the spatial distribution of the sampled point sources in the area of interest, during the 2014–2015 campaign.

2.2. Sample selection

A list of boilers and furnaces authorized to operate legally in the metropolitan area was provided by the Ministry of Labor and Social Security (MTSS) and the Costa Rican Ministry of Health (MS). The list was the basis for defining the number of point sources to be sampled. The boilers and furnaces were classified by their geographical location (Metropolitan Area), capacity or category

(per the Boiler Regulation), and type of fuel used. Stratified random statistical sampling criteria were then applied per fuel type and category to achieve a sampling error of less than 10%. A total of 92 point sources were selected, 67 of which were boilers and 25 of which were indirect furnaces. Table 1 outlines the number of samples collected per source and fuel type, compared with the information obtained from the MTSS database. The boilers are classified based on steam generation capacity: Type A for >7500 kg h^{-1} , Type B for 2000–7500 kg h^{-1} , Type C for 70–2000 kg h^{-1} and Type D < 70 kg h^{-1} . Sampling was carried out from February 2014 to November 2015. LP gas fired Type C and diesel fueled Type D boilers were not included, because they did not generate significant concentrations of PM according to the MS historic emission measures data base.

2.3. Sampling methodology

Sampling of PM emissions was carried out using Method 201A of Federal Code of Regulations No. 40, Part 60, of the United States Environmental Protection Agency (U.S. EPA).

Following this methodology, dual cyclonic separators were used. The method yielded three nominal aerodynamic equivalent diameter size fractions: greater than PM₁₀, between PM₁₀ and PM_{2.5}, and less than PM_{2.5}. To achieve this separation, the system (APEX) had two cyclones connected in series. In the first, fractions smaller than 10 μm passed through, and the remainder was retained in a reservoir in the bottom of the cyclone. The second retained PM sizes between 2.5 and 10 μm , and allowed the passage of the finest fraction (<PM_{2.5}) to be collected on a quartz fiber filter. This methodology was used to determine filterable PM. Condensable PM was not determined for this study, as it was expected that the contribution of condensable PM to total PM would be minor compared to the contribution of filterable PM for the sources evaluated (Pei et al., 2016). Method 201A was preferred over others, such as the dilution method, as Method 201A minimizes the loss of PM and secondary/condensation reactions (Chang and England, 2004). It is also a more rapid and practical method in the field, since it requires little space and modifications at the sampling site, allowing a greater number of samples to be gathered.

In each selected stack, a 10 cm long port with an inner diameter of 15 cm was installed in the sampling port. U.S. EPA Method 1 was used to properly size and position the sampling port within the exhaust duct, thus ensuring acceptable laminar flow conditions. Proper port placement was verified using U.S. EPA Method 2 to check for cyclonic flow. If cyclonic flow was found, the sampling port was moved or a new stack extension was added to achieve acceptable laminar flow.

All thermocouples, manometers and chronometers were properly calibrated by an external metrological laboratory as a quality control mechanism (Table 2). U.S. EPA Methods 2, 3, and 4 were used to determine temperature (ambient and stack), air velocity in the stack, volumetric flow rate, moisture content of the stack gas, and molecular weight of the gases. An analysis of combustion gases (NO, NO₂, NO_x, SO₂, O₂, CO, CO₂) was also carried out in the field using an automatic analyzer with Testo Model 350XL electrochemical cells, properly calibrated with Air Liquid gas cylinders at certified concentrations, following the U.S. EPA Method CTM-34.

2.4. Laboratory analysis

To collect the PM_{2.5} fraction, quartz filters were previously heated for at least five hours in a muffle furnace at a temperature of 900 °C to remove trace organic substances and other impurities. The sample filters were stabilized in a temperature and humidity controlled incubator before and after collection. Quartz filters were

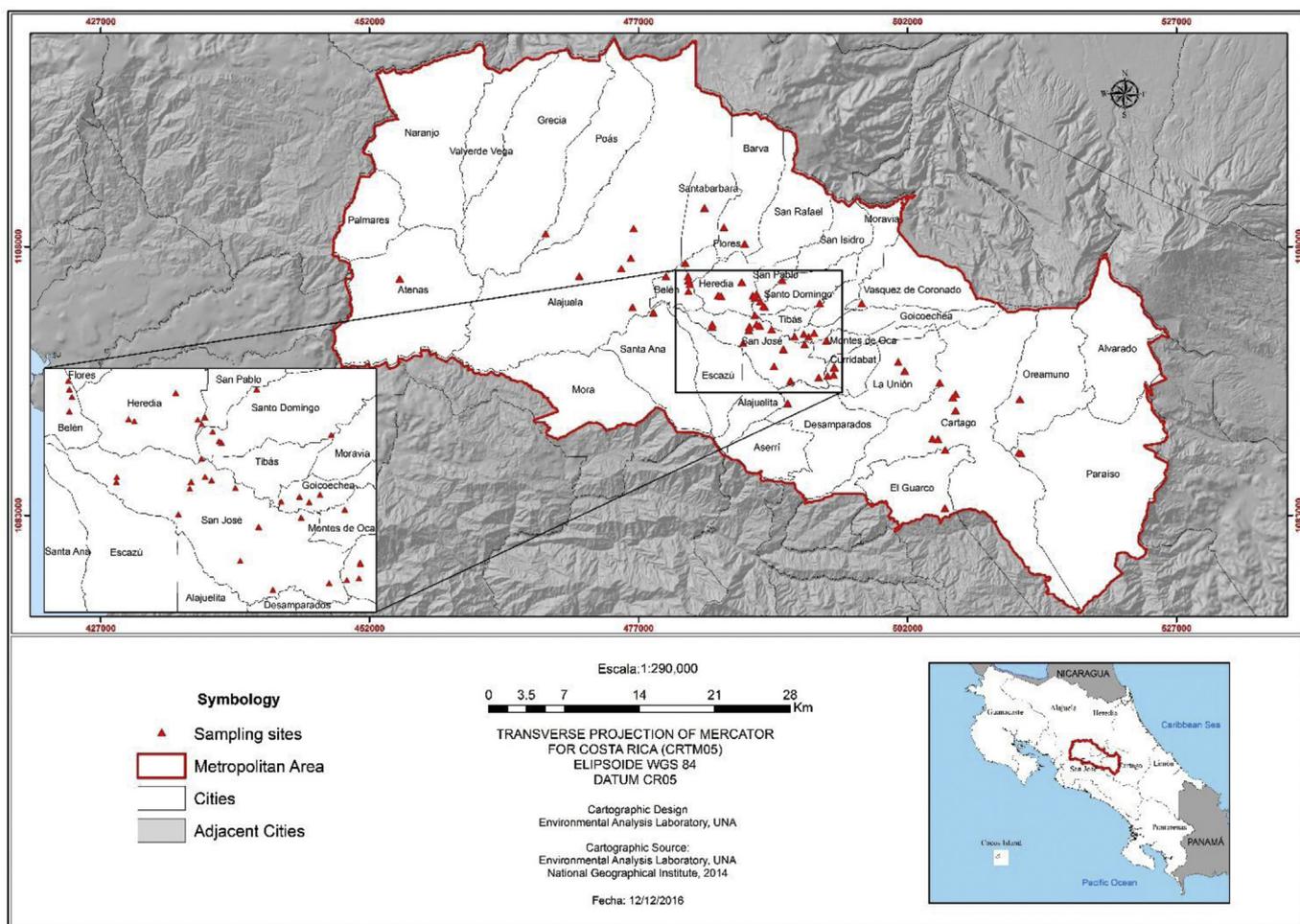


Fig. 1. Distribution of point sources sampled in the Metropolitan Area of Costa Rica, 2014–2015.

Table 1
Composition of the fixed sources sample population by source category and fuel type.

Source/Classification by steam production capacity	Diesel		Bunker		Biomass		Gasoil		LP Gas	
	S	A	S	A	S	A	S	A	S	A
Boilers Type A >7500 kgh ⁻¹	0	0	8	40	12	20	2	2	0	0
Boilers Type B 2000 to 7500 kgh ⁻¹	0	14	11	97	2	6	1	1	0	0
Boilers Type C 70 to 2000 kgh ⁻¹	24	205	6	66	1	10	0	0	0	42
Boilers Type D <70 kgh ⁻¹	0	2	0	0	0	0	0	0	0	0
Furnaces	0	NR	0	NR	22	NR	0	NR	3	NR

NR=No official records; S = Sampled; A = Available according to MTSS database.

gravimetrically measured for particle mass concentrations using a semi-microbalance (Mettler MT5) with a sensitivity level of ±1 µg. The samples collected in the filter were transported to the laboratory in a sealed bag protected from light and at a temperature of less than 4 °C.

The filter was later divided into equal parts for the analysis of ions, metals, and organic and elemental carbon. Each of the analysis methods was validated in the laboratory per the EURACHEM International Guide. At least, parameters such as detection limit (LOD), quantification limit (LOQ), linearity, working range, homoscedasticity and accuracy (as a recovery test) were evaluated.

results obtained for the performance parameters of the methods used are shown in Table 3.

For analysis quality control, clean filters were prepared for both the laboratory and the field, as blanks. They were subjected to the same chain of custody and treatment as the samples, and were analyzed in the assessment of background levels and cross-contamination, this represented the first quality control. Additional portions were cut from these same filters, similar to those used in the analyses, and each part was enriched to an intermediate level of concentration and evaluated as a second quality control, with a recovery percentage between 80 and 120%.

Table 2
Quality control of sampling equipment.

Equipment	Type of quality control	Standard	Traceability
Sampling nozzles	Verification of inside diameter	Vernier	SCM-Fox Valley-NIST
Dry Gas Meter	Determination of correction factor for sampled volume	Critical Orifice Set	Apex Instruments-NIST
Sampling timer	Comparison with certified standard	Chronometer	SCM-Control Company-NIST
Pressure gauges	Comparison with certified standard	Pressure module	SCM-Furness-UKAS
Type S Pitot tube	Verification of dimensions	Coordinate-measuring machine	SCM-Fluke-NIST/PTB/LNE
Thermocouples	Comparison with certified standard	Dry bath block	SCM-Quality Vision/Precision - NIST
		Process calibrator	SCM-Fluke-NIST
		RTD	SCM – Fluke/Agilent Tech.-LMVE/NIST/NRC/NPL/PTB/BNM
		Type K thermocouple	SCM-Fluke-NIST
			SCM-Fluke-NIST-LMVE

Table 3
Performance parameters of validated analytical methods for the identification of metals, ions, organic and elemental carbon.

Parameter	$\mu\text{g l}^{-1}$						$\mu\text{g l}^{-1}$			$\mu\text{g cm}^{-2}$	
	Cr	Cu	Pb	Mn	V	Ni	Cl	NO ₃	SO ₄	CO	CE
Detection limit	2.7	0.7	2.2	1.9	2.7	0.9	0.16	0.9	0.29	0.05	0.05
Quantification limit	3.9	0.9	4.1	2.2	3.5	1.5	0.18	0.13	0.30	0.05	0.05
Coefficient of variation of repeatability (CV_r)	1.6	1.5	1.5	0.6	2.0	2.8	1.9	3.6	1.9	2	2
Coefficient of variation of reproducibility (CV_R)	2.6	2.0	3.7	0.7	3.7	3.6	2.5	7.7	2.2	3	3
Recovery Percentage	96	98	94	99	98	97	101	99	99	99	99
Linear Working Range	0 to 70	0 to 70	0 to 100	0 to 60	0 to 100	0 to 100	0 to 35	0 to 35	0 to 35	0 to 600	0 to 600
Type of linear regression	Homoscedastic						Homoscedastic			N.A.	

N.A.: Not applicable.

2.4.1. Determination of anion content

An eluant extraction technique, described by Brown and Edwards, 2009, was used for the analysis of the anions content in the fine particulate matter fraction. A portion of the filter was taken, to which 7 ml of mobile phase was added (4.5 mmol/l Na₂CO₃, 1.4 mmol/l NaHCO₃) in a 10 ml glass tube provided with a teflon screw cap. The tubes were placed in an ultrasonic bath at room temperature and sonicated for 20 min, after which a portion of the residual liquid was filtered using a 0.45 μm membrane filter for subsequent analysis through ion chromatography with auto suppression. For this purpose a Dionex ICS-3000, equipped with a quaternary pump, autosampler, 25 μl injection loop, conductivity detector and a IonPac AS22 column (with a precolumn), was used. Ionic species were identified and quantified by interpolation in a calibration curve of seven standard solutions covering a working range of 0.25–10 mg l^{-1} using stock solutions prepared from Merck Suprapur certified salts. A fresh calibration curve was prepared for every 20 samples, together with a quality control standard of 5 mg l^{-1} prepared from a certified Dionex synthetic sample. The above steps were done to monitor the response and reproducibility of the peak shape and retention times.

2.4.2. Determination of heavy metal content

A portion of the filter was placed in a 200-ml beaker, and 20 ml of deionized water (ASTM Type I) and 3 ml of ultrapure concentrated nitric acid (HNO₃) were added and heated on a hot plate until nearly dry, and a quantitative transfer was made to a 25 ml volumetric flask. Another 20 ml of deionized water and one drop of perchloric acid was added to the same filter in the beaker and was again heated until nearly dry, and finally transferred to the same volumetric flask, using deionized water to bring the final volume up to the capacity mark. This was then transferred to a high-density polyethylene vial with a screw cap. Analysis of metals was made using atomic absorption spectrometry in a Perkin Elmer Analyst 700 equipped with graphite furnace and an autosampler. Metal species were identified and quantified by interpolation in a calibration curve of five standard solutions covering a working range of

5–50 $\mu\text{g l}^{-1}$ for V, Cu, Cr, Ni, Pb, Fe and Al, and 5–30 $\mu\text{g l}^{-1}$ for Mn; prepared from 1000 mg l^{-1} certified Perkin Elmer commercial dis-solutions with traceability to NIST.

2.4.3. Determination of organic, inorganic and elemental carbon content

The carbon speciation analysis of the collected particulate fine fraction was carried out using a thermal/optical Sunset Laboratory analyzer, following the analytical protocol established in the NIOSH 5040 method. A standard portion of the quartz fiber filter containing the sampled PM was cut for analysis, and placed in the quartz chamber that is part of the Sunset Laboratory equipment. The chamber was then purged with helium, and its temperature was gradually increased to 890 °C. The detached carbon was passed through a catalyzer, which converted it to CO₂, thermally reabsorbing the organic components and products of pyrolysis in an oxidation chamber containing manganese dioxide (MnO₂). The CO₂ was then purged from the oxidation chamber using a stream of helium mixed with ultra-high purity nitrogen. This mixture was passed through a heated nickel catalyst, where the CO₂ was quantitatively reduced to methane. The amount of methane produced was measured using a flame ionization detector (FID). Once the initial ramp of temperature for the measuring chamber was completed, it was cooled to 500 °C and the composition of the carrier gas was changed to a mixture of 2% oxygen in helium. Finally, a second temperature ramp for the oxidation of elemental carbon was initiated.

A thermogram was obtained for each sample and, by integrating peaks, the ratio of organic, inorganic (in the form of carbonates) and elemental carbon present in the PM (deposited on the area of the section cut for analysis) was calculated. Results were extrapolated for the entire effective particle collection area of the filter. For the OC and EC determination, the analyzer was calibrated using various aliquots (0, 3, 5, 7, 10, 12, 15, 20 and 25 μl) of a standard sucrose solution (4260 mg l^{-1}) over a filter blank (preheated quartz filter punch).

3. Results and discussion

Table 4 shows a profile of the species present in the finest PM fraction (<PM_{2.5}) for the emissions of sampled boilers and furnaces. The results were organized by source, category, and fuel type, then the coefficients of divergence (COD) for each analyzed parameter were calculated to determine the presence or absence of significant differences in how they were grouped (Table 5). These coefficients measure the degree of variability between different data sets, with values close to 0 representing uniformity between pairs of samples, and values close to 1 indicating complete divergence or heterogeneity. Previous studies have established a boundary value of 0.2 between 0 and 1 to determine the degree of distribution (Wang et al., 2011). CODs were calculated according to Equation (1), yielding average source category values below 0.2, indicating homogeneity between boilers A, B and C. In the case of distribution by source and fuel type, COD averages were above 0.2, so these classifications were used for comparison.

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left[\frac{(X_{ij} - X_{ik})}{(X_{ij} + X_{ik})} \right]^2} \quad (1)$$

After determining how to group the data, a normality test was applied to determine if the data distribution was normal. This helped establish which type of statistical test (parametric or non-parametric) must be applied for further analysis in this work or for other future purposes (e.g., presenting the results to local authorities). The data was divided by source (boilers and indirect fire furnaces) and fuel type, and subsequently grouped by parameter (PM_{2.5}, ions, metals, etc.) to run a Kolmogorov-Smirnov statistical test. It was found that most of the parameters (over 95%) followed a no-normal distribution, regardless of how they were grouped (p < 0.010, α = 0.05), so non-parametric statistical tests were used in subsequent analyses.

3.1. Filterable PM_{2.5} concentrations

The average PM_{2.5} concentrations ranged from 18 to 735 mgm⁻³. Sources that burned biomass exhibited concentrations that ranged from 183 to 735 mgm⁻³. There were no significant PM_{2.5} concentration differences between boilers and furnaces that burned biomass. The majority of the sources that burned biomass exceeded the allowable Costa Rican regulations for PM.

When comparing sources (boilers and indirect furnaces) by fuel type, the highest PM_{2.5} concentrations were observed for biomass

Table 5
Coefficients of divergence (DC) for comparison of boiler capacity.

Parameter	A-B	A-C	B-C
PM _{2.5}	0,11	0,17	0,05
Chloride	0,11	0,06	0,18
Nitrate	0,08	0,11	0,10
Sulfate	0,17	0,14	0,11
Copper	0,15	0,06	0,12
Chromium	0,16	0,09	0,20
Vanadium	0,11	0,07	0,12
Lead	0,01	0,02	0,02
Nickel	0,05	0,11	0,11
Manganese	0,07	0,19	0,10

boilers, while the lowest concentrations were found for those using diesel fuel, corresponding to Type C boilers. In the case of biomass boilers, Type B had the highest average concentrations. This can be explained by the fact that the heterogeneity of the fuel—as is the case for biomass boilers—promotes the generation of PM in coarser fractions compared to fossil fuels. This was also observed by statistically contrasting biomass and fossil fuels using the Mann-Whitney test, revealing a significant difference in particle emissions (p < 0.0001, α = 0.05).

In the case of biomass fuels, the same statistical test showed a significant difference (p = 0.0206, α = 0.05) between boilers and furnaces. This can be explained by the nature of the two sources, since boilers are pressurized and require well-sieved biomass to maintain relatively high temperatures (>100 °C). Indirect furnaces operate at lower temperatures and at atmospheric pressure, so do not require finely divided biomass; although this would likely improve their efficiency. The preparation of biomass, however, requires a greater financial investment (equipment, human resources, drying, energy, etc.) so companies typically choose the most convenient and practical option for operation, and use biomass in the condition that it is received. Thus, “particle size” plays a key role in combustion efficiency, which is directly related to the amount of fine PM produced.

3.2. Heavy metals

Boilers had higher concentrations of heavy metals in particle emissions with respect to indirect furnaces, regardless of fuel type (Table 4). Similar concentrations were found for manganese and lead, while chromium in boilers was higher than in furnaces. However, the average value of copper in furnaces was twice that

Table 4
PM_{2.5} particle concentration and its chemical composition emitted in sampled boilers and furnaces, by capacity and type of fuel (particulate values are corrected by oxygen).

	Boilers								Furnaces			
	Diesel		Bunker		Biomass		Gasoil		Biomass	LPG		
	C	A	B	C	A	B	C	A			B	
N	24	8	11	6	12	2	1	2	1	22	3	
PM _{2.5} (mg/m ³)	18 (27)	131 (84)	141 (64)	178 (84)	183 (117)	358 (83)	735 (0)	72 (48)	119 (0)	328 (175)	77 (74)	
Chloride (µg/m ³)	347 (332)	484 (433)	520 (443)	284 (55)	3298 (4737)	7554 (6070)	14 823 (0)	228 (129)	547 (0)	10226 (8320)	918 (1134)	
Nitrate (µg/m ³)	66 (21)	95 (53)	93 (54)	64 (10)	88 (77)	377 (119)	499 (0)	48 (10)	68 (0)	333 (171)	59 (2)	
Sulfate (µg/m ³)	339 (753)	17547 (12628)	10990 (7800)	17433 (9354)	6536 (11701)	16625 (9872)	34 224 (0)	3549 (3258)	12121 (0)	28566 (21280)	494 (482)	
Copper (µg/m ³)	2 (1)	6 (6)	15 (19)	6 (3)	11 (6)	5 (3)	17 (0)	3 (3)	5 (0)	19 (20)	2 (1)	
Chromium (µg/m ³)	5 (4)	27 (20)	22 (13)	7 (5)	20 (18)	6 (5)	2 (0)	12 (4)	29 (0)	6 (7)	2 (1)	
Vanadium (µg/m ³)	1 (1)	717 (836)	8887 (12295)	1334 (1537)	7 (15)	21 (26)	2 (0)	1415 (1874)	522 (0)	4 (11)	0.3 (0.3)	
Lead (µg/m ³)	2 (1)	5 (3)	13 (15)	4 (2)	2 (1)	2 (2)	9 (0)	5 (3)	4 (0)	3 (7)	1 (1)	
Nickel (µg/m ³)	2 (4)	563 (341)	3289 (4572)	678 (618)	7 (9)	7 (8)	9 (0)	291 (345)	427 (0)	4 (5)	3 (2)	
Manganese (µg/m ³)	4 (2)	12 (14)	16 (15)	7 (2)	47 (31)	18 (18)	9 (0)	4 (1)	6 (0)	23 (15)	4 (1)	
OC (mg/m ³)	6 (1)	21 (30)	57 (16)	62 (42)	42 (32)	118 (55)	337 (121)	5 (10)	8 (9)	60 (37)	NA	
EC (mg/m ³)	7 (7)	47 (66)	28 (4)	56 (37)	56 (38)	66 (27)	103 (84)	48 (4)	83 (15)	51 (44)	NA	

found in boilers. These furnaces use biomass and are primarily used in the coffee sector, meaning that a portion of the waste from coffee processing and plant cutting (husks and wood) is normally used to feed the furnaces. These residues may contain significant amounts of copper that was absorbed from the soil during the crop's plant growth and fruit production (Senkondo et al., 2014). The presence of this metal in the soil is due to the application of copper compounds such as copper oxide, copper hydroxide and copper oxychloride in doses of 1–2 kg per hectare. These compounds act as fungicides for diseases such as "Roya," which is very common in Latin American coffee plantations. In Costa Rica, copper compounds are currently used as a protective fungicide, the application of which is recommended to prevent the disease from attacking the plants (Barquero, 2013). It is also a common practice to uproot diseased coffee trees and use them to fuel furnaces, which releases any metal absorbed by the plant.

Vanadium and nickel were found in the highest concentrations, particularly in boilers because they use fuels that are richer in heavy metals than biomass fuels. Fossil fuels generally have much higher levels of heavy metals than biomass fuels (Vaisman and Lacerda, 2003). Analyzing the boilers by fuel type showed that diesel has lower levels of these metals, while bunker fuel had the highest concentrations of metals, apart from manganese, which was highest for biomass (Fig. 2). With respect to fossil fuels, it is expected that heavier fuels such as bunker contain higher levels of heavy metals compared to lighter fuels such as diesel (Streibel et al., 2016). Of all the metals analyzed, vanadium and nickel, which are markers of heavy fuels, had the highest levels of particle emissions from boilers that used bunker (Streibel et al., 2016).

The fact that the highest concentration of manganese emissions came from stationary sources that use biomass fuels may be attributed to the presence of manganese in fertilizers, which is absorbed by plants once it has been liberated in the soil. Manganese is a micronutrient that is essential for plant development; it plays a

key role in photosynthesis and is part of a vital antioxidant structure that protects plant cell tissue from attacks by free radicals, so its application often increases crop quality and yields (Mousavi et al., 2011). When biomass is burned, the manganese present in the plant structure is released in the particles.

When observing the distribution of metal emissions in PM per boiler type, it was found that Type A and Type B (high capacity) boilers had the highest emissions, including chromium and manganese for Type A, and copper, lead, nickel and vanadium for Type B (Fig. 1). Type C boilers had the lowest emissions of heavy metals, since most Type C boilers operate with diesel fuel, which contains a smaller amount of heavy metals. Nickel and vanadium dominate in Type B boilers, since most of them use heavy fuel oil. As previously explained, this fuel contains large amounts of these heavy metals.

3.3. Ions

On average, indirect furnaces produced higher levels of chloride, nitrate and sulfate than boilers, likely because the furnaces sampled used biomass fuels, which absorb various mineral components from the soil, which were subsequently released during the combustion process. Sulfate was the anion found at the highest levels. In the case of boilers, it is very likely that this comes from the sulfur present in heavy fuels. For furnaces that primarily use wood and coffee husks, sulfur is a macronutrient present in the coffee plants, particularly in the fruit (Sadeghian et al., 2013). The results obtained do not allow us to determine how much of the sulfate was due to the oxidation of SO₂ present in the fuel gases, and how much was due to sulfate present as an ionic species in the fuel.

Nitrate was found at relatively low levels compared to other ions, and its origin is partly due to the oxidation of nitrogen oxides (NO_x) and the nitrate present in the fuel in the form of free ions. Chloride is an ion not normally present in fuels, unless there are significant amounts of chlorinated compounds (solid waste

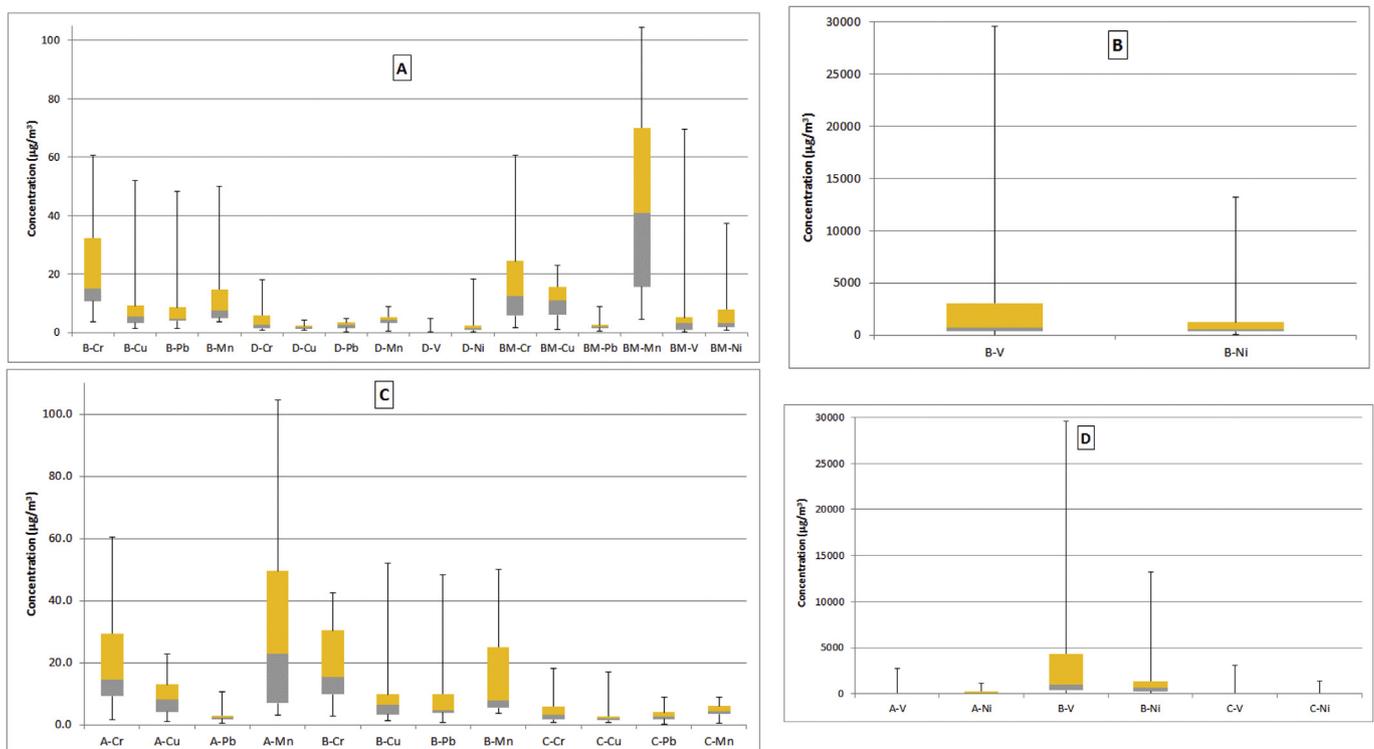


Fig. 2. Levels of heavy metals in filterable PM_{2.5} emissions by fuel (A and B) and boiler type (C and D). B:Bunker, D:Diesel, BM:Biomass.

combustion). Biomass used in indirect furnaces, however, may contain chloride absorbed from the soil during plant growth, or as part of the soil that is carried along with the biomass. It is not common to clean the biomass prior to combustion, during which the chloride absorbed from the soil is released directly as a particle or as hydrochloric acid or chlorine gas (depending on the nature of the combustion), and the fuel may continue to react and form new chloride. This creates severe corrosion problems, which are common in biomass boilers operating at high temperatures (Nunes et al., 2016).

When analyzing the distribution of ions by fuel type (Fig. 3), it was observed that sources that use bunker (largely boilers) had the highest levels of sulfate emissions due to the high sulfur content of this fuel, the specification of which is roughly 3% (m/m) according to the 2014–2015 RECOPE Product Manual. During combustion, sulfur is converted to sulfur dioxide; however, in the presence of vanadium oxides (present in the fuel) it catalyzes the transformation of sulfur dioxide to sulfur trioxide at high temperatures (Montero and Galetz, 2016). The latter forms sulfuric acid in the presence of water, which may explain the high concentration of sulfate. This implies that these boilers suffer accelerated corrosion of their internal components, which can be reflected in their emissions. In the case of biomass, sulfate emissions may be due to the presence of sulfur in the plant structure, as well as in the soil that is carried along with the biomass, as explained above.

The presence of chloride in PM emitted by sources that burn fossil fuels may come from impurities. For biomass combustion, chloride was the most relevant emission from both boilers and furnaces. The high content of ions in the PM is related to corrosion processes in the structures caused by deposits that promote oxidation reactions (Fern et al., 2006).

3.4. Organic carbon (OC) and elemental carbon (EC)

One of the most significant results observed in each of the sampled categories (A, B, C and furnaces), is that biomass fuels have the highest concentration levels of organic carbon—five times higher than fossil fuels, where Type B boilers had the highest

average among the different source types. This behavior is expected for biomass fuels as compared to fossil fuels, given the significant differences that occur during the combustion process (Chow et al., 2016). Factors such as humidity, particle size and excess air generate differences in the concentrations of OC and EC by affecting combustion. Biomass fuels have much higher moisture levels than fossil fuels, reducing combustion efficiency by requiring additional energy to vaporize excess moisture, which in turn results in higher emissions of volatile and semi-volatile organic compounds as biomass is incompletely burned (Shen et al., 2013). A similar pattern was observed for elemental carbon (EC) in the case of biomass fuels, which can be explained by reasons like those for OC. On average, OC emissions were higher than EC emissions, regardless of the type of boiler, which suggests that the combustion conditions are not ideal, resulting in the incomplete burning of organic by-products. This was not the case for furnaces, which had an OC/EC value of less than 1, suggesting different (but not necessarily better) combustion conditions, which may be related to the source type and its control of excess air. When furnaces operate at ambient pressure with large volumes of highly moist biomass fuel comprised of large particle sizes, they require large amounts of excess air. This involves a higher concentration of oxygen, which favors the formation of various forms of elemental carbon due to greater lift of the combustion flame (Li et al., 2009).

Boilers using fossil fuels had lower OC/EC relationships (1.5 on average) than those using biomass, partly because the use of liquid fuel and less excess air represent better combustion conditions. Among these boilers, those that used diesel fuel had the lowest OC/EC ratio because their combustion is more generous than that of boilers that use bunker fuel, ensuring that most of the OC is burned.

3.5. Statistical correlation analysis

To determine dependence between emissions and other complementary parameters (flow, temperature, combustion gases, etc.), a Spearman correlation analysis was used, as most of the data was abnormally distributed. This statistical analysis was applied to biomass furnaces, and to bunker, diesel and biomass boilers

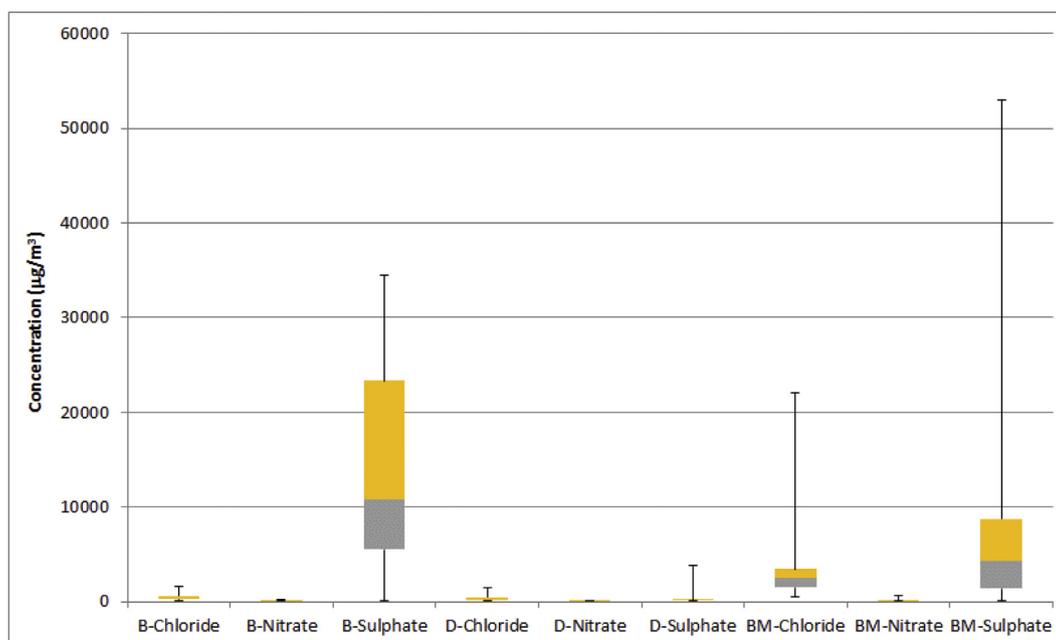


Fig. 3. Anion speciation for filterable PM_{2.5} emissions from boilers by fuel type (B:Bunker, D:Diesel, BM:Biomass).

Table 6

Spearman correlation matrix for all parameters in furnaces and boiler by fuel type; the lower value corresponds to the statistical index p.

Biomass Furnaces	Diesel Boilers	Biomass Boilers	Bunker Boilers
PM _{2.5} vrs % O ₂ 0.450 (0.027)	SO ₂ vrs %O ₂ 0.822 (0.000)	PM _{2.5} vrs %O ₂ 0.564 (0.007)	SO ₂ vrs %O ₂ 0.574 (0.005)
%O ₂ vrs CO 0.564 (0.004)	Cl ⁻ vrs % Moist 0.721 (0.011)	SO ₂ vrs %O ₂ 0.453 (0.014)	Cl ⁻ vrs NO ₃ ⁻ 0.552 (0.008)
SO ₂ vrs CO 0.510 (0.011)	Cl ⁻ vrs NO ₃ ⁻ 0.607 (0.012)	NO ₃ ⁻ vrs PM _{2.5} 0.451 (0.008)	Cr vrs Cl ⁻ 0.519 (0.013)
SO ₂ vrs %O ₂ 0.788 (0.000)	Cr vrs Cl ⁻ 0.632 (0.010)	NO ₃ ⁻ vrs CO 0.552 (0.021)	Pb vrs Cu 0.937 (0.000)
NO _x vrs PM _{2.5} 0.404 (0.050)	Ni vrs Pb 0.799 (0.010)	Cl ⁻ vrs NO ₃ ⁻ 0.764 (0.001)	Mn vrs Cu 0.618 (0.002)
Cl ⁻ vrs % Moist 0.484 (0.019)	Ni vrs PM _{2.5} 0.568 (0.017)	SO ₄ ²⁻ vrs PM _{2.5} 0.584 (0.008)	Mn vrs Pb 0.666 (0.001)
Cl ⁻ vrs SO ₂ -0.449 (0.032)	Mn vrs Cu 0.731 (0.002)	SO ₄ ²⁻ vrs NO ₃ ⁻ 0.545 (0.021)	V vrs PM _{2.5} 0.516 (0.014)
NO ₃ ⁻ vrs PM _{2.5} 0.541 (0.008)	Mn vrs Pb 0.772 (0.001)	Cl ⁻ vrs SO ₄ ²⁻ 0.700 (0.032)	V vrs Cu 0.566 (0.006)
SO ₄ ²⁻ vrs PM _{2.5} 0.669 (0.000)	Pb vrs Cu 0.733 (0.000)	Mn vrs Cr 0.530 (0.009)	V vrs Pb 0.580 (0.005)
SO ₄ ²⁻ vrs SO ₂ 0.466 (0.025)	Cu vrs SO ₄ ²⁻ 0.546 (0.008)	Mn vrs Cu 0.536 (0.017)	V vrs Mn 0.607 (0.003)
SO ₄ ²⁻ vrs Cl ⁻ 0.542 (0.007)	Cr vrs SO ₄ ²⁻ 0.538 (0.009)	Ni vrs V 0.681 (0.033)	Ni vrs PM _{2.5} 0.574 (0.005)
SO ₄ ²⁻ vrs NO ₃ ⁻ 0.584 (0.003)			Ni vrs Cu 0.710 (0.008)
Cu vrs NO _x 0.448 (0.028)			Ni vrs Pb 0.765 (0.014)
Cu vrs SO ₄ ²⁻ 0.745 (0.000)			Ni vrs Mn 0.688 (0.022)
Pb vrs SO ₂ 0.422 (0.040)			Ni vrs V 0.892 (0.005)
Mn vrs Cl ⁻ 0.455 (0.029)			
Mn vrs NO ₃ ⁻ 0.522 (0.011)			
Mn vrs SO ₄ ²⁻ 0.545 (0.007)			
Mn vrs Cr 0.443 (0.030)			
Ni vrs V 0.762 (0.000)			

separately. It was not subdivided by boiler category, because no significant differences were found between boiler types for the parameters analyzed.

Biomass furnaces (Table 6) were grouped into one category and correlations between PM with oxides of nitrogen, nitrate and sulfate were determined. The latter two oxides contribute to the formation of PM because of their relatively high concentrations. Both chloride and nitrate were correlated with sulfate and manganese, which are primarily micro and macronutrients.

In the case of biomass boilers (Table 6), a correlation between the level of PM and the presence of oxygen and sulfate was observed. The percentage of oxygen can determine the amount of PM because it is related to the efficiency of the combustion process, of which sulfate is a major component. There is also a correlation between nitrate and sulfate, which suggests that both partly originate from the oxidation of combustion gases. Other important relationships were observed for heavy metals, most of which are micronutrients trapped in biomass. Finally, the strongest correlation was found between chloride and nitrate, which suggests that they may have a common source.

For boilers using diesel fuel (Table 6), no significant correlations were found except for manganese, copper and lead, which are heavy metals commonly found in fossil fuels. The largest number of correlations were found in the case of bunker boilers (Table 6), principally between copper, lead, manganese and vanadium, which are present in significant concentrations in heavy fuels such as

bunker. Particle concentrations were most strongly correlated with sulfate, vanadium and nickel, suggesting they may play a key role in the formation of PM during the combustion process. Chloride was significantly correlated with chromium and nitrate, but there was no correlation between the latter two substances, indicating that they participate in separate processes that favor the emission of chloride. A negative correlation was observed between oxygen and sulfur dioxide, chromium, manganese, vanadium and nickel, probably due to a dilution effect.

4. Conclusions

The nature of each fuel type significantly influences fine PM emissions and related speciation. Additionally, the combustion conditions of each source represent a key difference in the magnitude and distribution of the analyzed species.

Biomass emission sources are the most significant emitters of fine PM (PM_{2.5}), mainly from Type C boilers, followed by Type B boilers and furnaces. Chloride and sulfate ions were the most frequently found ions in the PM analyzed. Sulfate ions had the highest concentration in emissions from boilers using bunker fuel, due to its high sulfur content and the presence of vanadium. Chloride showed the highest levels in biomass emissions, indicating oxidizing reactions within the combustion source that can cause severe wear on metal surfaces.

Diesel fuel in boilers had atmospheric emissions with the lowest

levels of heavy metals, while bunker fuel had the highest levels of heavy metals. Heavy metals such as copper and manganese were found in significant concentrations in emissions from the burning of biomass, due to their presence in soil and their later absorption into plants used as fuel. Vanadium and nickel are the most important metals in boiler emissions, and are associated with the use of bunker fuel.

The conditions of the combustion processes are critical in determining the concentration of fine PM and its relationship to elemental carbon/organic carbon. Biomass fuels contain the highest concentration of unburned organic species, due to poor combustion conditions.

No significant correlations were found for boilers using diesel. In the case of biomass, some correlations were found for several metals that are micronutrients and ions that are part of the biomass. In the case of bunker fuel, the influence of sulfate, vanadium and nickel dominated particle formation. In the latter case, better quality fuel could decrease the concentration of particles emitted.

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